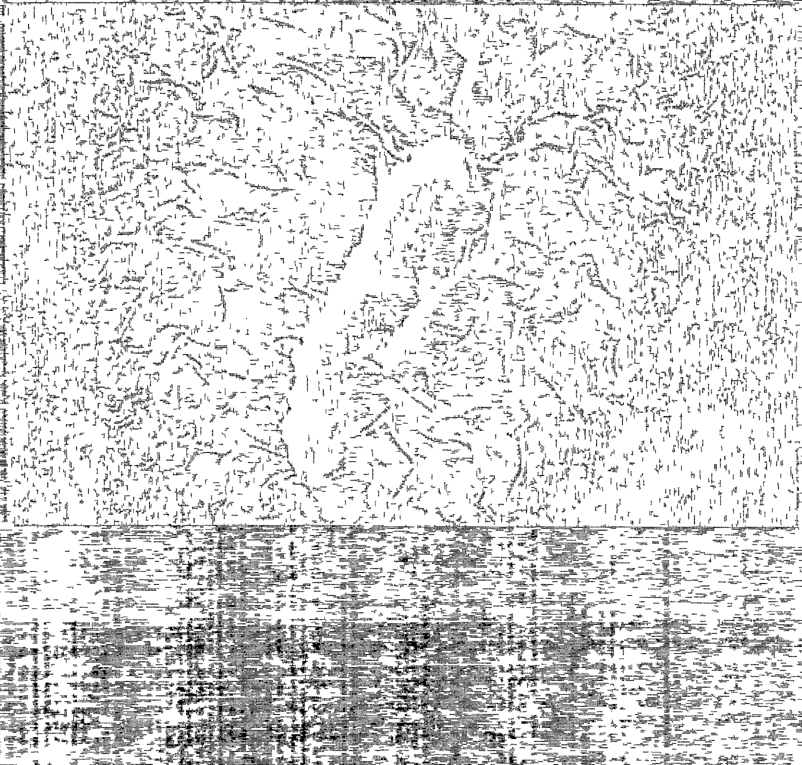
Stabilization of supported liquid membranes



Antoine Kemperman

35

STABILIZATION
OF
SUPPORTED LIQUID MEMBRANES

PROEFSCHRIFT

ter verkrijging van
de graad van doctor aan de Universiteit Twente,
op gezag van de rector magnificus,
prof. dr. Th.J.A. Popma,
volgens het besluit van het College voor Promoties
in het openbaar te verdedigen
op vrijdag 20 oktober 1995 te 15.00 uur.

door

ANTONIUS JOSEPHUS BERNARDUS KEMPERMAN

geboren op 27 april 1968
te Arnhem

Dit proefschrift is goedgekeurd door de promotor prof. dr. ing. H. Strathmann en de assistent-promotoren dr. D. Bargeman en dr. Th. van den Boomgaard.

Cover: the gentle art of making membranes.

CIP-DATA KONINKLIJKE BIBLIOTHEEK, DEN HAAG

Kemperman, Antonius Josephus Bernardus

Stabilization of supported liquid membranes/
Antonius Josephus Bernardus Kemperman-[S.l. : s.n.]. - Ill.
Thesis Enschede. - With Ref. - With Summary in Dutch.
ISBN 90-9008507-6
Subject Headings: supported liquid membranes / stabilization / interfacial polymerization / gels

Printed in the Netherlands by Ponsen & Looijen B.V., Wageningen.

This thesis is printed on 100% recycled paper.

VOORWOORD

Samen met de stellingen is het voorwoord van een proefschrift, zeker voor kollega's en bekenden van de promovendus, het eerste dat men leest. Dit heeft te maken met het feit dat een voorwoord meestal bestaat uit bedankjes, en mensen nu eenmaal graag hun naam daar gedrukt zien staan. Ook bij mijn proefschrift ben ik dank verschuldigd aan een hele lading mensen, die allemaal op de een of andere manier hebben bijgedragen aan de totstandkoming van dit boekje.

Op de eerste plaats is daar de vakgroep Membraantechnologie, waar ik 4 jaar met heel veel plezier heb mogen vertoeven. Heiner, bedankt voor het doornemen van het concept en de diskussies met je over mijn werk. Dick, ik heb zeer genoten van je kritische begeleiding in het eerste gedeelte van mijn onderzoek en na je pensioen. Maar ik zal je vooral herinneren vanwege je onvergetelijke anekdotes. Je wist de verhalen over vroeger altijd met een zeer prettige komische noot te brengen! Thonie, de diskussies met jou waren vaak een stuk serieuzer. Ik heb veel van je geleerd, niet alleen op wetenschappelijk gebied maar ook organisatorisch o.a. door samen met jou het PMST '94 kongres te organiseren.

De enorme hoeveelheid experimentele data heb ik niet alleen vergaard. Op de eerste plaats ben ik heel veel dank verschuldigd aan Erik Rolevink. Ik had me geen betere experimentele duizendpoot als technisch assistent kunnen wensen. Ook je visies op mens en milieu hebben me altijd aan het denken gezet. Jeannette, Marc, Ben, Bert en Maarten: dank je wel voor jullie inzet en amusante gezelschap als afstudeerder of stagaire.

In een vakgroep hoeft niet altijd alles er even serieus aan toe te gaan, zeker niet wat mij betreft. Middels zaalvoetbal, volleybal, klootschieten, fietstochten, zeilen en het KSKR toernooi hebben we onze konditie aardig op peil weten te houden. Een konditie trouwens die het door de vele borrels, BBQ's, (promotie)feesten en gezamelijk cafébezoek weer aardig te verduren had.

Een aantal mensen uit de groep wil ik nog even extra bedanken. Christel, je werkte net als ik op het soms heel frusterende gebied van de vloeistofmembranen. Bedankt voor de diskussies op vak- en menselijk gebied. John, bedankt voor het altijd vlekkeloos bestellen van chemicaliën en apparatuur. Johnny, je was niet alleen kollega: buiten werktijd heb ik me ook prima vermaakt bij voetbalwedstrijden en, natuurlijk, in de kroeg. Kamergenoten heb ik voldoende gehad. Monique, Arnold, Wei, Christel, Ljubo, Jianjun, Elena, Franca en Meifang: ik heb het prima naar mijn zin gehad bij jullie. Greet en Bartie, jullie zijn dijken van secretaressen! De rest van mijn (ex) kollega's zal ik ook nooit vergeten: bedankt voor de fijne tijd en de serieuze en minder serieuze gesprekken.

Een vakgroep kan niet alles alleen doen. Richard Egberink, bedankt voor de hulp bij de synthese van de membraanvloeistof. De glasblazers worden bedankt voor het maken van de vele meetcelletjes. De portiers van CT, jullie hebben op je eigen manier allemaal wel (indirekt) een steentje bijgedragen aan mijn boekje. I also would like to thank the people and my friends at the Dalian Institute of Chemical Physics in P.R. China. Thanks for all you have done for me during my stay in Dalian!

Met het werk alleen kom je er niet. Minstens net zo belangrijk is de hele wereld buiten de vakgroep om van tijd tot tijd de zorgen te vergeten en de batterij weer op te laden. Zonder iemand te willen vergeten, zou ik mijn vrienden en vriendinnen, de (ex) uitleners van de Stichting Discotheek Drienerlo, de recreanten van Harambee en iedereen van Loesje Enschede willen bedanken voor de broodnodige afleiding. Zonder jullie was het boekje er niet geweest!

Tot slot wil ik mijn familie bedanken voor alle interesse en vertrouwen die ze gedurende mijn 9 jaar in Twente hebben gehad. Het is niet voor niets geweest.

Antoine

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INTRODUCTION

SUMMARY

In this chapter, a brief introduction will be given on membranes. Furthermore, liquid membranes will be described. Finally the structure of this thesis will be presented.

1.1 Membranes: an introduction

In the chemical, pharmaceutical and many other industries, the purification of products and raw materials and the cleaning of waste streams is a necessary separation step. Such separation processes are usually based on differences in physical or chemical properties of the species to be treated. In general, separation processes should fulfill two criteria [1]: the separation should be feasible technically, and the separation process must be feasible economically. In order to minimize the energy consumption of the separation process and to minimize the waste, new separation techniques have been developed in the last 25 years. One of the techniques fulfilling these requirements is membrane technology.

It is not easy to give an exact definition of a membrane. According to the nomenclature of the European Society of Membrane Science and Technology (ESMST), a membrane is 'an intervening structure separating two phases and/or acting as an active or passive barrier to the transport of matter between the phases adjacent to it' [2]. When we take a look at the definition of the term *permselective membrane*, we find the following definition: a permselective membrane is 'a membrane which separates components of a fluid by differences in one or more properties of the components, such as size and shape, electrical charge, solubility and diffusion rate' [2]. This is the definition of a membrane most applicable to their use in separation processes. When in this thesis the word membrane is used, we refer in fact to a permselective membrane.

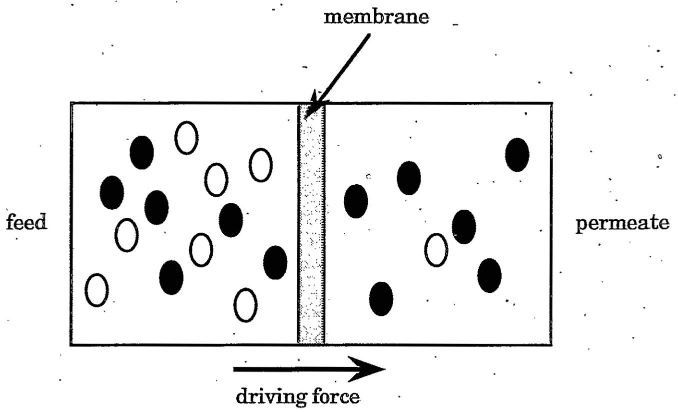

Figure 1.1. *Schematic illustration of a membrane separation process.*

The most central part in every membrane separation process is the membrane, as illustrated in figure 1.1. At one side of the membrane there is the feed or upstream phase, while at the other side we have the permeate or downstream phase. For a mass transport across the membrane, a driving force is necessary. The driving force can be a pressure difference, a concentration (activity) difference, a temperature difference or an electrical potential difference [1]. Due to the permselectivity of the membrane, one component is more readily transported than other components in the feed. In figure 1.1 the black species are transported at a higher rate than the white ones. In this way, a separation can be achieved. Excellent reviews on developments in membrane science and technology have been presented by Lonsdale *et al.* [3] and Matson *et al.* [4].

1.2 Liquid membranes

An overview of all different types of membrane processes possible was given by Mulder [1]. In this thesis, research is carried out only on liquid membranes. For these membranes, the general definition for a permselective membrane given in section 1.1 still holds. Liquid membranes are media consisting of liquid films through which selective mass transfers of gases, ions and molecules occur via permeation and transport processes [5]. The transport through liquid membranes can be either passive or facilitated by the presence of a carrier. Such a carrier molecule should posses a high affinity for one of the solutes in the feed and it should accelerate in this way the transport of this specific component across the liquid membrane. In this thesis, only facilitated transport is discussed. When more than one component is transported simultaneously, the term coupled transport is used.

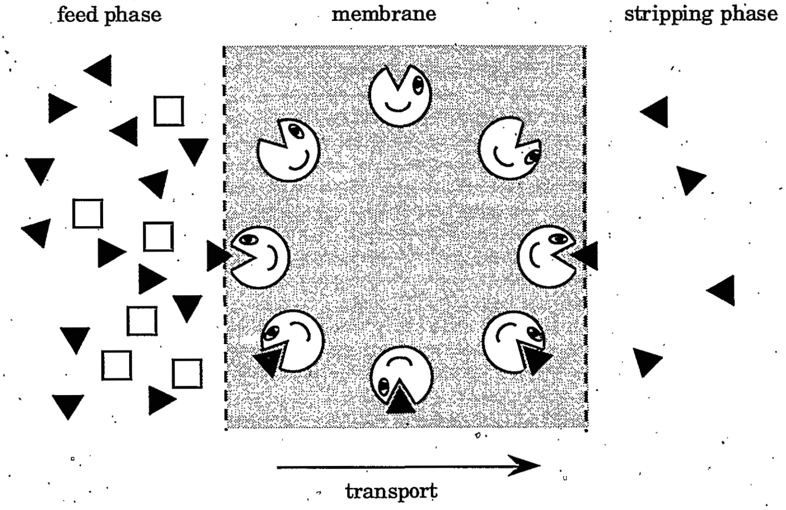

Figure 1.2. *Facilitated transport in a membrane by means of selective carriers.*

The separation mechanism of facilitated transport by a carrier is shown in figure 1.2 for the uncoupled case. The carrier binds selectively with one of the components in the feed (the black triangles) and transports it from the feed phase to the *receiving* or *stripping* phase due to a electro-chemical potential difference of the component on both sides of the membrane. By using a carrier in liquid membranes, both selectivity and permeability are increased compared to diffusive transport in the absence of a carrier. For other membrane processes, the selectivity and permeability are usually inversely related.

Figure 1.2 showed a typical example of simple carrier mediated (or facilitated) transport. In liquid membranes, several other transport mechanisms are possible. Most important is coupled transport, where the carrier couples the flows of two components. It is then even possible to transport one of the two species against its concentration (chemical potential) gradient ('uphill transport') when the driving force for the counter-transport is high enough. Coupled transport can be either co-coupled or counter-coupled. In the first case, both components move in the same direction. In counter-coupled transport processes, the components move in opposite directions. Both coupled transport types are illustrated in figure 1.3. A review on coupled transport membranes is given by Baker and Blume [6].

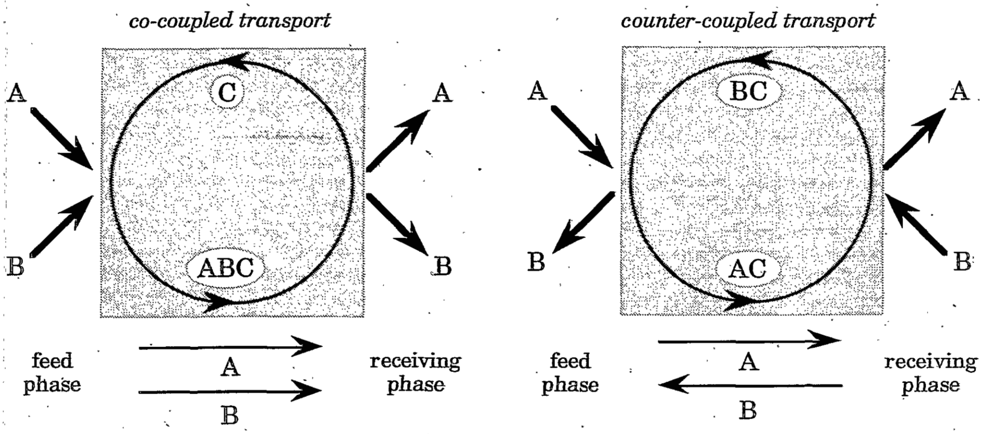

Figure 1.3. *Schematic drawing illustrating the principle of co- and counter-current facilitated transport. A: component to be transported. B: coupled species. C: carrier species.*

Basically, there are two types of liquid membranes for practical use: the emulsified liquid membrane (ELM) and the immobilized or supported liquid membrane (SLM) [1]. Both types are schematically shown in figure 1.4. In an ELM (figure 1.4a), the receiving phase (inner phase) is emulsified in the liquid membrane phase which may contain a carrier. The emulsion is dispersed in a third phase, the continuous outer phase, which is usually miscible with the inner phase. This method firstly was described by Li at the end of the sixties [7]. Separation takes place by transport of the species from the continuous outer phase through the liquid membrane phase to the inner phase. The transport is stopped when the inner phase is saturated. Subsequently, the continuous outer phase and the emulsion phase are separated and the emulsion is broken in a coalescing unit after which the inner phase with the product is recuperated or discarded. This batch process can be improved considerably in a different set-up where a fixed macroporous support is used in which the liquid membrane phase is immobilized by capillary forces: a supported liquid membrane (figure 1.4b). As macroporous support, several geometries can be applied [8]. A flat geometry is useful for laboratory purposes, but for industrial applications spiral wound and hollow fiber modules are preferred due to their high surface to volume ratio. The work described in this thesis is focussed on SLMs.

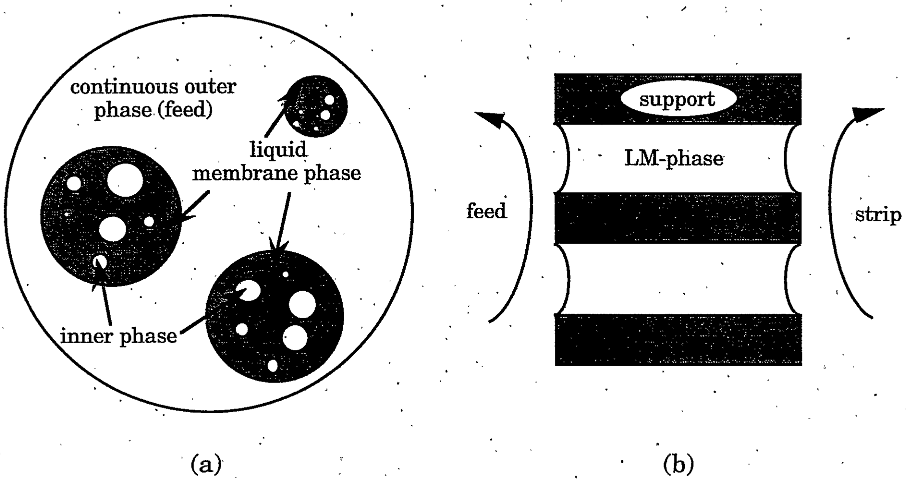

Figure 1.4. *Schematic drawing of (a) an emulsion-type of liquid membrane (ELM) and (b) a supported liquid membrane (SLM).*

The intrinsic advantages of SLMs compared to other (membrane) separation techniques are summarized below [8-11].

- High fluxes are possible. For not too small species, diffusion coefficients in liquids are usually higher than in solid materials. This, combined with the presence of a carrier, results in larger fluxes than can be obtained in polymer membranes.
- High selectivities can be achieved when the right carrier is chosen and added to the LM-phase. The selective nature of the carrier provides much better separations than those based solely on relative differences in solubility and diffusivity of various components in a polymer matrix.
- Species, especially ions, can be concentrated. By means of coupled transport,

ions can be pumped uphill, *i.e.* against their concentration gradient (chemical potential difference) due to the driving force of other species transported downhill.

- Expensive extractants can be used. Only a small quantity of carrier is necessary since the amount of solvent associated with the membrane is small.

Despite the advantages that SLMs have compared to other separation techniques, they are not widely used at an industrial scale nowadays. This is mainly due to their instability and subsequent short lifetime [6,9,11,12]. With a certain time, the membrane liquid (either the carrier, the membrane solvent or both) disappears from the pores of the support. In case only the carrier is lost, the flux will decline in time, but the flux might also increase in time when either the solvent or LM-phase is lost (due to a smaller diffusion path length) When the membrane breaks down due to a large loss of membrane liquid, a direct connecting channel in the membrane between feed and strip phase will lead to nonselective transport of the components. Furthermore, feed and strip phase are polluted with the membrane liquid. The reason for the instability is still a point of discussion, but it seems most likely to be a combination of several effects [11]. This discussion is one of the main issues of this thesis.

1.3 Structure of this thesis

The work described in this thesis is aimed at improving the lifetime of supported liquid membranes by applying a thin polymeric toplayer on the macroporous support. This toplayer should prevent loss of LM-phase. In the major part of the work described in this thesis, the toplayer is applied by means of an interfacial polymerization reaction. This technique is well known for the preparation of reverse osmosis and nanofiltration membranes, but its use to prepare stable SLMs is new.

Chapter 1 is an introduction to membrane technology and, in particular, to liquid membranes. The two main types of liquid membranes and their drawbacks are discussed in more detail

In *chapter 2*, a state-of-the-art literature review is given on the stability of supported liquid membranes. Firstly, several mechanisms responsible for the degradation of SLMs are discussed in detail. Then, several suggestions for improving the lifetime of SLMs described in literature are discussed. At the end of this chapter, several new liquid membrane configurations are described.

The theoretical backgrounds of interfacial polymerization and its use in membrane technology are discussed in *chapter 3*. From the literature, a series of monomers were selected which were known to have a low salt rejection, a necessity to stabilize SLMs without a large flux reduction. By means of an interfacial polymerization reaction, monomers were polymerized on top of microfiltration membranes. The coated membranes were used as support for SLMs to remove nitrate from water and they were tested for their stabilizing effect on SLMs and on the nitrate flux, respectively.

From the screening experiments two monomers were chosen whose toplayers showed the most promising results in increasing the stability of the SLMs without a reduction in their flux. *Chapter 4* describes a thorough investigation of these SLMs. A large number of reaction parameters was varied systematically to optimize the system. Several characterization techniques were applied to investigate the toplayer morphology and chemical composition of the membrane. In an appendix to this chapter, some peculiar results on double layered SLMs are described.

In all chapters, except *chapter* 5, flat sheet microfiltration membranes were used as support. In chapter 5, the use of hollow fibers as support is discussed. The fibers were coated by interfacial polymerization with the toplayers shown to increase the stability of flat sheet SLMs. Scanning Electron Microscopy (SEM) was used to check the uniformness of the applied toplayer. In two different setups, the hollow fiber SLMs were tested.

In *chapter 6*, the gelation of the liquid membrane phase, containing trioctylmethylammonium chloride (TOMA-Cl) as a carrier by means of PVC is described. SLMs with this carrier are usually very instable, and it is tried to improve their lifetime by homogeneous gelation of the LM-phase and by application of (chemically) crosslinked PVC toplayers on the support.

Finally, in *chapter 7* the mechanisms behind SLM degradation are critically reviewed. By a theoretical analysis, an attempt is made to calculate whether emulsion formation can take place in the SLMs as used throughout this thesis. Furthermore, it will be discussed which other mechanisms might be responsible for the degradation of SLMs

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2

THE STABILITY OF SUPPORTED LIQUID MEMBRANES

-State of art review

SUMMARY

This chapter presents a state of art literature review on the stability of supported liquid membranes. Firstly, an overview is presented dealing with the background of SLM instability phenomena. Several mechanisms that are proposed in literature will be treated in detail. Furthermore, suggestions for membrane lifetime improvement are discussed briefly.

It can be concluded that the stability of SLMs is still a severe problem. In literature there is no agreement on the mechanism that causes instability. Although new membrane configurations seem to be very promising due to their high stability, modification of the LM-phase or the support is simpler.

2.1 Introduction

Supported liquid membranes (SLMs) are a promising alternative to liquid–liquid extraction and other (membrane) separation techniques for the selective removal of ions or neutral molecules from solutions and gases. In most membrane processes like *e.g.* reverse osmosis, ultrafiltration or microfiltration, the solvent and various solute particles permeate through the membrane while other molecules or particles are rejected. To transport the permeate through the membrane a certain amount of energy has to be supplied. SLMs are different, since in this case only the component to be separated is transported. This fundamentally different approach for separation can be much more energy efficient.

SLMs usually consist of an organic solvent, immobilized in the pores of a hydrophobic microfiltration membrane. In general, the organic solvent contains a carrier, which binds very selectively one of the components in the feed solution. Furthermore, the organic phase might contain a modifier, which favors the extraction of a certain selected species in a synergistic fashion, and improves the selectivity of the SLM in this way [1]. Because the transport takes place in a liquid, for not too small molecules the fluxes are higher compared to 'solid' polymeric membranes since diffusion coefficients in liquids are in general orders of magnitude higher than in solid materials. Another advantage of SLMs is the high selectivity of the process, when a proper selective complexing agent is chosen as carrier. Furthermore, it is possible to separate and concentrate species at the same time, *i.e.* liquid membranes are capable of providing co-current and counter-coupled transport. Other advantages of SLMs are the modest capital and operating costs, the low energy consumption and the possibility of using expensive extractants [2,3].

Despite the above mentioned advantages, supported liquid membranes are not used at a large scale in industry nowadays. The major reason for this is the membrane stability or lifetime, which is in general far too low to assure good commercial application possibilities. The instability of SLMs is due to the loss of carrier and/or membrane solvent from the membrane phase which has an influence on both flux and selectivity of the membrane [2,4-6]. The effect of solvent and carrier loss on flux is schematically drawn in figure 2.1. In case 1, membrane solvent is lost to the adjacent phases. Due to the increase in carrier concentration and the decrease of the actual liquid membrane thickness, the flux increases in time until the membrane breaks down. When the carrier molecules are lost (case 2 in figure 2.1), the flux will gradually decrease in time until no components are transported anymore at the moment no carrier is left. Finally, the flux might be nearly constant when both carrier and solvent are lost to such a degree that the carrier concentration in the liquid membrane phase remains almost equal. When all LM-phase is lost, the membrane breaks down and a direct transport between the two phases adjacent to the liquid membrane takes place with a complete loss of selectivity. The time period after which instability phenomena are observed varies from less than one hour [5,7] to several months [3,8-10] depending on the system (carrier, solvent, and support used).

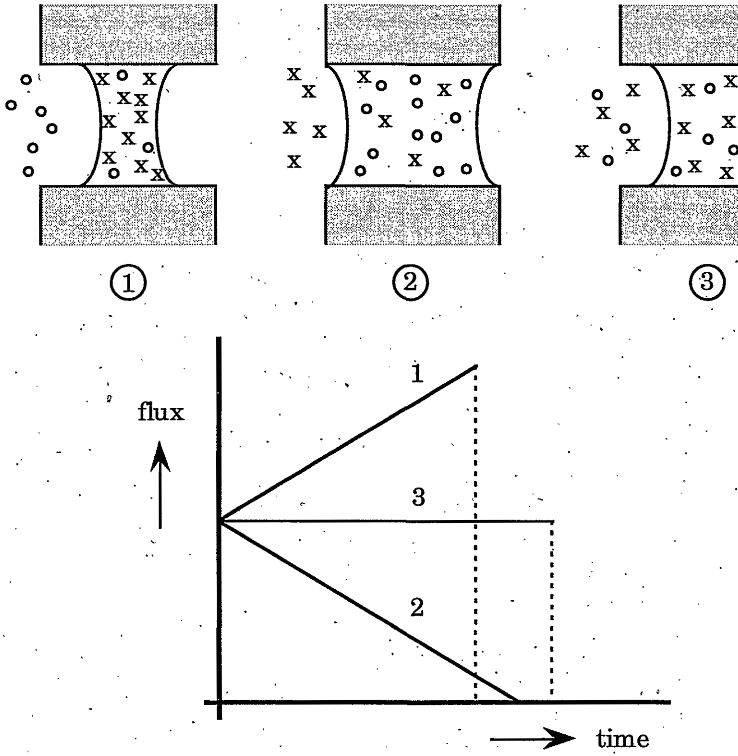


Figure 2.1. *Degradation of SLMs and its influence on component flux in time for three extreme cases. 1) Loss of solvent. 2) Loss of carrier. 3) Loss of both solvent and carrier. The dashed lines indicate membrane breakdown. The crosses represent the carrier molecules, the circles represent the solvent molecules.*

Throughout this thesis, a decrease in component flux is used to decide whether a membrane is stable or not. When the flux is decreased below a certain percentage of the initial flux of a newly prepared membrane at a certain moment (*e.g.* to 90 % of the initial flux), we will consider the liquid membrane to be instable. This definition implies however that we might observe an increase in 'flux' stability despite a leakage of membrane solvent as was shown in figure 2.1. The term 'stable membrane' is not used in its absolute meaning, but only used relative to other systems. This means that a certain liquid membrane can be more or less stable than another one for the same transport system, but it is not claimed that a 'stable' (in absolute terms) SLM is obtained.

In literature, it is not uniformly stated under what conditions a liquid membrane is considered to be (in)stable and in which way the (in)stability of a membrane is measured. Most of the authors consider a flux or permeability decrease of the transported species to be an indication for membrane instability [*e.g.* 4,6,9,18] as is used also throughout this thesis. However, several other authors claim their membranes to be stable, when a constant flux is obtained by replacing the removed liquid membrane phase continuously by fresh LM-solution [19-23] or simply state their system is reliable without any further details [24]. Sometimes, a significant decrease in selectivity is used to measure the instability of a membrane [25-27]. To determine the stability of liquid membranes, factors like a volume flux of water through the membrane [5,28-30], a rapid increase in pH [31] or interfacial properties such as the contact angle or a so called 'progressive wetting time' [32] are used. In most literature references, however, no attention at all is paid to the stability of the system.

This chapter will not present an overview of all the separations and enrichments possible with (supported) liquid membranes. For this, one is referred to several excellent review articles and books [6,11-17]. This thesis is mainly focussing on improving of the stability of SLMs. Therefore, in this chapter a state of the art-review will be given on the stability of SLMs. In the following section, the causes of SLM instability will be discussed. We restrict ourselves to the removal of components from liquids and do not treat the more specific instability problems for liquid membranes for gas separation or fixed-site carrier membranes. Then, several ways for improving the stability of SLMs, known from literature, are presented in section 2.3. Finally, various other configurations for liquid membranes, from which the authors claim that they are much more stable than conventional supported liquid membranes, are discussed in detail in section 2.4.

2.2 The mechanisms of SLM degradation

As mentioned before, the reason for a supported liquid membrane to become instable is the loss of LM-phase out of the pores of the support structure. According to previous work on SLM destabilization as described in literature, this loss of carrier and/or membrane solvent can be due to

1) the pressure difference over the membrane;
2) the solubility of carrier and membrane solvent in the adjacent feed and strip

solutions;
3) wetting of the support pores by the aqueous phases;
4) the blockage of the support pores by precipitation of the carrier or by water;
5) the presence of an osmotic pressure gradient over the membrane;
6) emulsion formation of the LM-phase in water induced by lateral shear forces.

These proposed mechanisms of SLM destabilization will be discussed in more detail in this section.

The pressure difference over the membrane

Due to pumping of the solutions, a pressure difference might exist over the membrane [3,5]. This pressure effect is of special importance when hollow fibers are used as support [25]. When the pressure difference exceeds a certain critical value, the liquid membrane phase is pushed out of the pores of the support. Zha *et al.* defined the critical displacement pressure P_c for an SLM as the minimum transmembrane pressure required to displace the impregnating phase out of the largest pore [6,33]. For a cylindrical capillary, P_c is given by the Laplace equation [34]:

$$P_c = \frac{2\gamma \cos\theta}{r}, \qquad (1)$$

where P_c is the critical displacement pressure ($N\ m^{-2}$), γ the interfacial tension between strip or feed solution and the liquid membrane phase ($N\ m^{-1}$), θ the contact angle between the membrane pore wall and the impregnating liquid and r the pore radius (m). Equation 1 is only valid for cylindrical capillaries. However, SLM supports usually are highly irregular in geometry. Zha *et al.* derived an equation for the estimation of the critical displacement pressure for SLMs in such cases. By establishing a so called 'neck model' for the membrane pores, their deviation from cylindrical capillaries was taken in consideration. Comparison of their experimental data with their calculated values showed a good agreement. Measured critical displacement pressures for Accurel supports (nominal pore size 0.2 μm) were in between 50 and 250 kPa, depending on the system. As long as the transmembrane pressure is smaller than the critical pressure, the liquid membrane phase will not be replaced by the aqueous feed or strip solutions. Pulsations of the feed and strip fluxes, in addition to transmembrane pressure gradients surely will affect membrane stability: due to the loss of carrier and solvent the flux will decrease. Pressure differences of 0.2 kPa across the membrane were shown to be high enough to cause water leakage in flat polytetrafluoroethylene (PTFE) supports (pore size 2.0 μm) filled with toluene as was experimentally determined by Takeuchi *et al.* [5]. To obtain a stable liquid membrane, transmembrane pressure differences including fluctuations should be minimized. When pressure differences are avoided, SLMs are still showing instability phenomena which indicates that pressure differences are not the main cause of SLMs degradation.

The solubility of carrier and membrane solvent

In case a chemical potential difference $\Delta\mu$ between the liquid membrane and the aqueous phases is present for carrier or organic solvent (*e.g.* when the phases are not saturated with the LM-phase), there is a driving force for the LM components to dissolve in the aqueous phases which is the case in many actual operation conditions. The solubility greatly influences membrane lifetime when the membrane solvent or carrier have a significant solubility in the adjacent aqueous phases. The higher the partition coefficient towards the aqueous phases, the shorter the membrane lifetime [3-5,20,26,30,31,35-37]. Danesi *et al.* found that the lifetime of SLMs containing acidic carriers like HDEHP, di-(2-ethylhexyl)phosphoric acid, decreased when one of the aqueous solutions had a high pH [3]. This is in agreement with the increased solubility of this type of carrier in water with increasing pH. Due to the high solubility of their membrane solvent, 2-ethylhexyl alcohol, in water (app. 0.1 wt%), Tanigaki *et al.* observed a rapid decrease in phenol flux [20]. Pre-saturation of the aqueous feed and strip phases with the organic phase improved membrane lifetime. However, a rather constant flux for longer time (9 days) could only be obtained when the support was continuously reimpregnated with LM-phase in the case the aqueous phases were not pre-saturated. The effect of membrane solvent solubility in water and volatility on membrane stability was investigated by Lamb *et al.* [35]. It was observed that the membrane stability increased as the boiling point of the solvent increased or water solubility decreased. The same was found by Deblay *et al.*: when the solubility of the organic solvent in water was higher than 30 ppm, the membrane was instable (lifetime lower than 10 hours) [26].

Also the solubility of the carrier in the adjacent aqueous phases is of importance, as was shown by Chiarizia [31]. Three different, commercially available, long chain aliphatic amines (a primary, secondary and tertiary one) were tested as carriers for the removal of several ions from synthetic groundwater. The stability decreased in the order tertiary>secondary>primary amine. The solubility of the carrier in water decreased in the order primary>secondary>tertiary amine, opposite to the stability order: the higher the carrier solubility, the lower membrane stability. Dozol *et al.* determined aqueous solubilities and SLM lifetimes for a large number of membrane solvents ('diluents') [30]. Membrane lifetimes over 200 hours could be obtained when solvents with a water solubility lower than 12 g l^{-1} were applied. Bloch *et al.* prepared solvent membranes using PVC as polymer, plasticized with phosphate esters which acted as carrier for metal ions [36]. Dissolution of the plasticizer in the adjacent aqueous solutions and subsequent impermeability of their solvent membranes was considered to be the cause of membrane failure [36].

Several authors claim an improvement of SLM lifetime when the aqueous phases are pre-saturated with the organic phase [10,20]. Others, however, claim the opposite. Takeuchi *et al.* did find no or only little effect on SLM lifetime when the aqueous phases were pre-saturated with the membrane solvent [5]. Neplenbroek *et al.* pre-saturated the aqueous phases with decanol, but the amount of LM-phase removed was independent of the saturation, in agreement with the results of Takeuchi *et al.* [5]. Both argue that the breakdown of an SLM is not caused by the solubility of the LM-phase components. However, in their system probably the solubility is not the most important mechanism, but in other systems the solubility certainly might be important.

The wetting of the support pores by the aqueous phases

This mechanism for SLM degradation was firstly proposed by Danesi *et al.* [3] and worked out in detail by Takeuchi *et al.* [5,32]. As a result of *e.g.* the formation of metal complexes, contamination of the interface between organic phase and aqueous phases or dissociation of the carrier, both the interfacial tension (between the aqueous phase and the organic phase) and the contact angle (between the aqueous phase and the porous membrane wall) might decrease in time. When the interfacial tension has decreased to below a certain level, the aqueous phases might enter the membrane pores and replace the organic LM-phase, according to Takeuchi *et al.* [32].

To investigate this wetting phenomenon, Takeuchi *et al.* [32] measured contact angles and interfacial tensions of aqueous drops (solutions of metal ions) lying on macroporous sheets, submerged in organic solutions containing a carrier (see figure 2.2). The contact angle θ as defined by Takeuchi (between aqueous solution and the membrane) is different from that in equation (1) where we defined it as the angle between the membrane pore wall and the impregnating liquid. However, the use of the change in time of the contact angle, in order to determine the critical interfacial tension at which penetration of the aqueous phase in the pores starts, is not allowed for (highly) porous materials as was pointed out by Franken *et al.* [38]. The results of Takeuchi *et al.* are therefore doubtful. Another objection against this mechanism is that it is not expressed clearly. Finally, when this wetting mechanism is valid, the LM-phase lost should have the same chemical composition as the remaining liquid in the pores. Neplenbroek *et al.* found by a careful analysis of the remaining LM-phase that this was not the case: carrier and solvent were lost to the aqueous phases in different ratios [4]. So, this mechanism for LM instability is not of major importance.

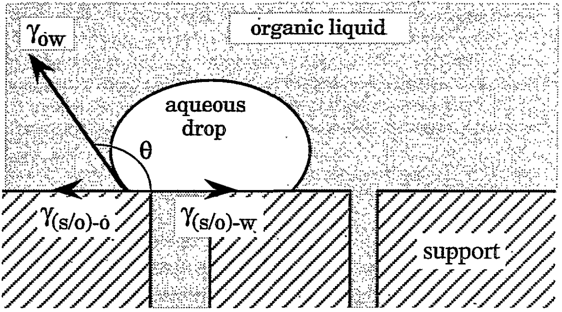


Figure 2.2. *Schematic drawing showing an aqueous drop on a horizontal porous sheet submerged in an organic solution. Adapted from Takeuchi et al. [32].* γ *= interfacial tension,* θ *= contact angle (aqueous phase / membrane phase), o = oil, w = aqueous solution, s = porous solid.*

The pore-blocking mechanism

'Fouling' and subsequent blocking of the support pores can occur in two ways *i.e.* by carrier precipitation and by water blockage. Precipitation of carrier molecules in the pores was observed by Belfer *et al.* for calcium-phosphinic acid complexes [39] and by Chiarizia for long chain aliphatic amines [31,40]. Nitrate-trilaurylamine salts were thought to precipitate locally in the membrane pores. The formation of solid or gelatinous precipitates in the pores, beyond the saturation limit in the liquid membrane phase, slows down the diffusion rate of the permeating species. On the other hand, according to Chiarizia, this precipitation might enhance SLM stability by preventing the formation of emulsions with the aqueous phase and by acting as a barrier against water bridging in semi-devoid pores [31]. Both water channeling and emulsion formation will be discussed later on in this section.

Babcock *et al.* observed a gradual copper flux decay in time and subscribed this flux decay to blockage of membrane pores by water [41,42]. This mechanism was also cited by Baker and Blume, who called it 'spontaneous emulsification' [15]. This term is however only applicable for the spontaneous formation of micro-emulsions which is impossible in SLMs due to the relatively high interfacial tension. For the spontaneous formation of emulsions without additional energy very small interfacial tensions (smaller than 0.01 $\mathrm{mN\ m^{-1}}$) are required [43,44], much lower than interfacial tensions usually encountered in LM-systems. This term is therefore used incorrectly. The process according to Baker *et al.* [15] is schematically drawn in figure 2.3. Beforehand, one remark is that the way the meniscus is drawn by Baker and Blume is wrong: the LM-phase will never enter the pores spontaneously if the meniscus has this shape since the contact angle between impregnating phase and membrane wall here is larger than 90°.

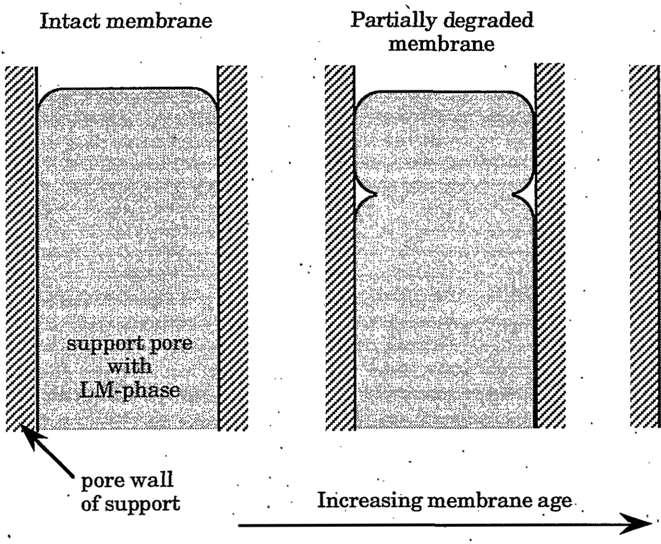


Figure 2.3. *Schematic drawing (from Baker et al. [15]) of SLM degradation by the formation of an interfacial emulsion.*

It was thought that water could enter the organic phase at the surface of the membrane and replace the organic phase. The formation of micelles by the carrier molecules, thereby solubilizing water, might result in the introduction of water in the organic phase. Zhu claimed this solubilization of water by micelles to be the reason for water uptake in their SLMs [45]. They give however no experimental proof at all for the existence of these micelles. Furthermore, such micelles are small in general, and it is therefore doubtful whether sufficiently large quantities of water can be introduced into the organic phase. In contradiction to the results of Zhu, no water droplets or micelles with solubilized water in decayed SLMs were detected by Zha by gas chromatography and he rejected therefore the pore-block mechanism for his system [6]. The intrusion of water into the organic phase is not clear for situations where the formation of micelles in the membrane is impossible. Babcock *et al.* suggested that the hydrophobic membrane pore wall could be wetted by the aqueous phase due to a change in the contact angle θ between organic phase and water, *e.g.* when the surface active carrier is lost to the aqueous phases by solubility effects [41,42]. When the micelles break up or when the organic phase pulls away from the pore walls, organic droplets are formed. Nevertheless, this is very doubtful. It is not explained how the micelles can break up spontaneously. Furthermore, there will always be a driving force to minimize the surface area, and without the supply of extra energy it is not likely that extra area is created to form small LM-phase droplets.

The 'fouling' was believed to propagate from the strip side of the membrane to the feed side, but again the driving force for this process is ambiguous. Furthermore, the term fouling is somewhat misleading, since usually fouling is associated with the (ir)reversible deposition of retained particles, macromolecules or salts on or in the membrane [46]. Due to the presence of organic droplets surrounded by the aqueous phase in the support pores, the transport of permeants is hindered. As a result, the flux decreases. Experiments with 5 pieces of membrane, laminated together, showed that the flux decay indeed was the largest near the aqueous strip side. Also the interfacial tensions between LM- and aqueous phases are so large, that spontaneous emulsion formation is not likely to occur [4,37]. Finally, another objection against this mechanism is that it does not explain why the ratio of carrier to organic solvent loss to the adjacent aqueous solutions was different from that in the initial membrane liquid as found in Babcock's experiments and by Neplenbroek *et al.* [4]. The correctness of the pore-blocking mechanism is therefore very doubtful.

The osmotic pressure effect

The osmotic pressure effect as a mechanism of SLM degradation was developed independently by Fabiani *et al.* [29] and Danesi *et al.* [18]. The effect was proposed also by several other authors as one of the causes of SLM instability [10,13,17,26,30,31,47]. Fabiani *et al.* measured water flows and salt fluxes through SLMs separating two LiCl solutions at different concentrations. There were no hydrostatic pressure gradients applied to the membrane [29]. When the osmotic pressure difference $\Delta\Pi$ increased, the water transport increased. According to the authors, as a consequence of the volume flux across the membrane, the organic phase is dragged out of the pores of the support and the SLM becomes instable.

An impressive piece of work dealing with the lifetime of several supported liquid membranes for metal ion transport, and in particular the influence of osmotic pressure gradients, was published by Danesi *et al.* [18]. The relation between membrane lifetime and several physical properties of the system was investigated. The stability of the membrane was measured by determining the salt permeation and water transport through the membrane as a function of time. The water transport was measured by means of horizontal, calibrated glass tubes attached to the membrane cell. An SLM was considered to be stable when it showed a constant flux in time and when there was no water transport. In case the liquid membrane phase could dissolve a significant amount of water and additionally an osmotic pressure difference $\Delta\Pi$ difference was present, water transport was observed and the SLMs were considered to be instable. A mechanism of membrane failure was proposed, in which the presence of an osmotic pressure gradient could lead to the displacement of the organic membrane phase from the support pores by the moving water. To maximize SLM lifetime, systems should be used which are characterized by high organic/water interfacial tensions, a low solubility of water in the LM-phase and a low tendency of the support to be wetted by the aqueous phases. These characteristics were however not quantified by Danesi *et al.* but are just qualitative guidelines for obtaining stable SLMs.

In literature, several objections against this osmotic pressure effect can be found. Neplenbroek *et al.* [4,37] state that only in case the LM-phase is removed from the support pores by another primary mechanism, an osmotic water flow might occur. According to Neplenbroek *et al.*, for an osmotic flow of water a continuous water path must be present in the LM-phase to create the osmotic pressure difference. However, this objection to the osmotic pressure effect is not correct. To obtain an osmotic pressure gradient, apart from a difference in ionic strength of both aqueous solutions it is only necessary that the water has a sufficiently high solubility in the LM-phase, while the ions have not. In that case the membrane is semi-permeable to water and an osmotic pressure difference might develop. Neplenbroek *et al.* state that a continuous water path has to be present, but in that case never an osmotic pressure gradient can develop since both water *and* ions can be transported. The membrane is no longer semi-permeable and transport of water and ions takes place according to the activity differences of both components between the two phases.

Nevertheless, Neplenbroek *et al.* showed clearly that in absence of an osmotic pressure difference by using equal salt concentrations in feed and strip, their SLMs still showed a considerable loss of carrier and solvent [4,37]. When an osmotic pressure difference across the membrane was created by an increase in salt concentration in the stripping phase, Neplenbroek *et al.* showed even an increase in stability of the SLM, which is in contradiction with the proposed theory of the osmotic pressure effect. Similar results were obtained by Zha for SLMs for phenol transport [6], who also draw the conclusion that the osmotic pressure mechanism was not the cause of SLM degradation in his system. Furthermore, the type of salt used in the aqueous phases had a remarkable influence on carrier removal [37]. Since the osmotic pressure is a colligative property and depends therefore upon the number of solute molecules rather than on their kind [34], the osmotic pressure model does not explain the differences. As a conclusion, it appears that an osmotic water flow might be an additional reason of SLM instability, but this depends on the solubility of water in the LM-phase. Not all effects can be explained when the osmotic pressure is the only cause of SLM instability.

Shear-induced emulsion formation

A hypothesis about the instability of supported liquid membranes was proposed by

Neplenbroek *et al.*: emulsion formation induced by lateral shear forces [2,37,48]. Zha *et al.* further developed and extended this hypothesis [6,49]. Neplenbroek *et al.* found a striking similarity between the instability of an SLM and the stability of emulsions formed by droplets of the identical LM-phase in the same aqueous environment with the carrier as the emulsifier. A relation was found between the removal of the LM-phase from the membrane pores as a function of the molecular structure of the carrier, the type of organic solvent and the formation of oil in water emulsions. A similar relation was found for the counterions: the stability of SLMs increased with an increase in the concentration of counterions while at the same time a decrease of emulsion stability was experimentally observed. In their system, Neplenbroek *et al.* used a 4 * 10^{-3} M $NaNO_3$ solution as the feed and a 4 M NaCl solution as the strip. According to their hypothesis, LM-phase should be lost only to the feed solution due to the low salt concentration of the feed. Indeed it was observed that no LM-phase was lost when on both sides of the membrane the salt concentration was high, while the loss increased when on both sides of the membrane the salt concentration was lowered. The stability of emulsions of LM-phase in the aqueous phases as determined by light transmission measurements showed that the emulsion droplets were more stable in the feed solution than in the strip solution. The same relationship was found for the molecular structure of the carrier. When trioctylmethylammonium chloride (TOMA) was used as carrier, the loss of LM-phase was much higher than when tetraoctylammonium bromide (TeOA) was applied under identical test conditions. TOMA is much more surface active than TeOA, and is therefore emulsified to a much larger extent as was revealed by light transmission measurements. So, the experimental results of Neplenbroek *et al.* confirmed their emulsion formation hypothesis although the emulsion droplets were never observed directly in the feed solution and no droplet size distributions were given.

From a thermodynamical point of view, a system will always aim at a surface area as small as possible. Emulsions are therefore per definition thermodynamically instable. Nevertheless, emulsions can be formed when a sufficiently high amount of energy is supplied to enlarge the surface area. The presence of surface active species subsequently can stabilize the newly formed surface creating an energy barrier again reducing the total surface area of the system. When the hypothesis of Neplenbroek *et al.* is correct, we have to take a closer look at the increase in energy of the liquid membrane system. The increase in energy might lead to an increase in surface area for instance by local deformations of the LM-meniscus. Neplenbroek *et al.* assumed that these local deformations of the LM-meniscus could finally lead to the splitting off of emulsion droplets [37]. This is schematically shown in figure 2.4. The local deformation of the LM-meniscus can have several origins according to Neplenbroek *et al.* [37]:

- Kelvin-Helmholtz instabilities: these instabilities occur when two phases move with different velocities parallel to the interface [50,51]. The formation of waves on the water surface due to blowing of the wind also results from Kelvin-Helmholtz instabilities;

- vibrations of the membrane: the repeatedly, small deformation of the SLM due to pulsations of the aqueous phases might result in the formation of ripples on the surface of the LM-phase [51].

Zha [6] and Gopal [52] also mentioned three other hydrodynamic instabilities:

- instabilities caused by the laminar-turbulent flow transition (Tollmien-Schichting instability);
- Rayleigh-Taylor instabilities which occur when the interface is accelerated perpendicular to its plane and directed from the lighter into the heavier phase;
- the Bernard instability which is due to density differences.

Most likely, Kelvin-Helmholtz instabilities and membrane vibrations are the main causes for deformations of the LM-meniscus.

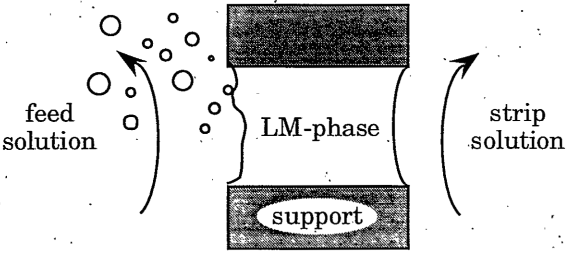


Figure 2.4. *Schematic drawing illustrating the local deformation of the LM-meniscus in the pores of the support resulting in the formation of emulsion droplets. High salt concentration at strip side, low salt concentration at feed side.*

Once the LM-meniscus is deformed and rippled, emulsion droplets have to be formed. One possible mechanism to explain this is based on the so called Marangoni effect [37]. Suppose the interface is locally curved in such a way that the concave side is the surfactant side as shown schematically in figure 2.5. This curved part contains less surfactant molecules per unit area compared to a flat interface, and will therefore have a higher interfacial tension. Surfactant molecules will diffuse towards the most strongly curved interface, together with a flow of liquid dragged along, to restore the low interfacial tension. Interfacial tension gradients are intrinsically instable [53]. Marangoni effects are important because they can have drastic consequences, despite the short time they operate. According to Neplenbroek *et al.*, this instable situation might cause droplet shedding and emulsion formation [37]. However, the exact mechanism and influence of the hydrodynamical interfacial effects on emulsion formation is a severe problem still not understood [51]. Nevertheless, Neplenbroek *et al.* consider the small size of emulsion droplets removed from their SLMs (in between 2 and 140 nm) comparable to emulsion droplet sizes in other, Marangoni-effect based systems. That Kelvin-Helmholtz instabilities and membrane vibrations playing a role in emulsion formation might be an explanation for the decreased SLM stability (higher carrier losses) when flow velocities are increased as was experimentally measured by Neplenbroek *et al.* [37]. The higher the flow velocity, the more meniscus instabilities and the more probable emulsion formation. Although emulsification of the LM-phase can explain all observed instability phenomena, it is doubtful whether enough energy can be supplied to the LM-interface to cause droplet shredding. This is worked out in more detail in chapter 7 in this thesis. Furthermore, the emulsion droplets are never observed directly in the aqueous feed phase.

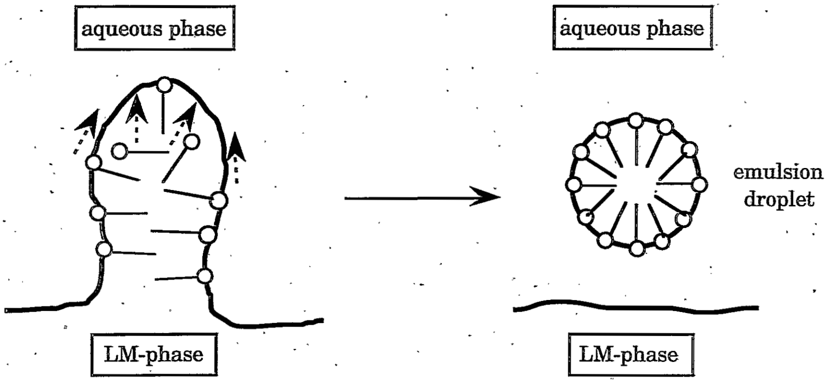


Figure 2.5. *Schematic drawing illustrating the influence of Marangoni effects on droplet shredding for an SLM.*

The emulsion formation hypothesis as main cause of SLM instability also was investigated by Zha *et al.* [6,49]. This impressive piece of work is very interesting for our study on the stabilization of SLMs and therefore it will be described extensively in this chapter. The influence of several parameters, which were shown by Neplenbroek *et al.* to influence membrane instability and emulsion stability [37], was investigated for a system for the removal of phenol. The factors included the effect of stirring speed, aqueous electrolyte concentration and the HLB (hydrophilic-lipophilic balance) of the membrane liquid. The HLB is an expression for the relative simultaneous attraction of an emulsifier for water and oil. An emulsifier with a high HLB value (8-18) will form a water in oil (W/O) emulsion, while emulsifiers with a low HLB (3-8) normally forms oil in water (O/W) emulsions [54]. It was found that a high stirring speed, low electrolyte concentration and high HLB values produce stable emulsions and instable SLMs. These results are identical to those of Neplenbroek *et al.* [37], but again it is doubtful whether a sufficiently high amount of energy can be supplied to the system to produce the emulsion droplets. By means of an autosizer the size and amount of emulsion droplets of LM-phase in several aqueous phases, prepared by an ultrasonic method and thus different from the actual situation in SLM processes, were determined. According to Zha, this method is a better way for determining the stability behaviour of emulsions than the turbidity measurements of Neplenbroek *et al.* [37]. It was found that the emulsion droplet size increased with increasing salt concentration in the aqueous phase and that the number of emulsion droplets per unit volume decreased at the same time. So, the higher the salt concentration, the lower the concentration of emulsion droplets, but of a larger size. Again the similarity between emulsion stability and SLM instability was striking. Attempts to detect the emulsion droplets in feed and strip during operation of SLMs failed due to the very small concentration of the droplets and the detection limit of the autosizer.

It is worthwhile to analyze the possibility of emulsion formation in SLMs from a thermodynamical and hydrodynamical point of view. Zha [6] derived an equation to calculate the free energy change ΔG between state I, where the membrane phase is impregnated in the membrane pores and in contact with the aqueous phase, and state II where the membrane phase is lost to the aqueous solution due to emulsion formation. The pressure was assumed to be constant and volume changes were neglected because of the small volume fraction of membrane phase to the aqueous phase. Furthermore, the interfacial area in state I of both aqueous and membrane phase is thought to be very small compared to state II. Since the total bulk energies in the two phases are constant during the process, equation (2) could be derived [6]

$$\Delta G = \gamma_{OW} A_O^{II} - \gamma_{OS} A_C^{I} - T S_O^{II}, \tag{2}$$

where γ_{OW} = oil/water interfacial tension [N m^{-1}]
A_O^{II} = emulsion droplet area [m^2]
γ_{OS} = oil/polymeric interfacial tension [N m^{-1}]
A_c^{I} = total area of capillaries holding the membrane phase [m^2]
T = absolute temperature [K]
S_O^{II} = configurational entropy of emulsion droplets formed [J K^{-1}].

After introducing the proper relations for the different terms in equation (2), it appeared that the first part of the equation is normally much larger than the last two terms in absolute values, unless γ_{OW} was extremely small. As a result, ΔG is large and positive: spontaneous emulsification does not take place and a minimum energy equal to ΔG has to be supplied to the system. The energy needed for emulsion formation, which must be at least equal to ΔG, is applied by the aqueous solutions (*e.g.* stirring) and results in hydrodynamic instabilities of the interfaces. Although several interfacial instabilities were mentioned (like Kelvin-Helmholtz instabilities, Rayleigh-Taylor instabilities and vibrations of the membrane), a combination of those mechanisms will be responsible for SLM instability.

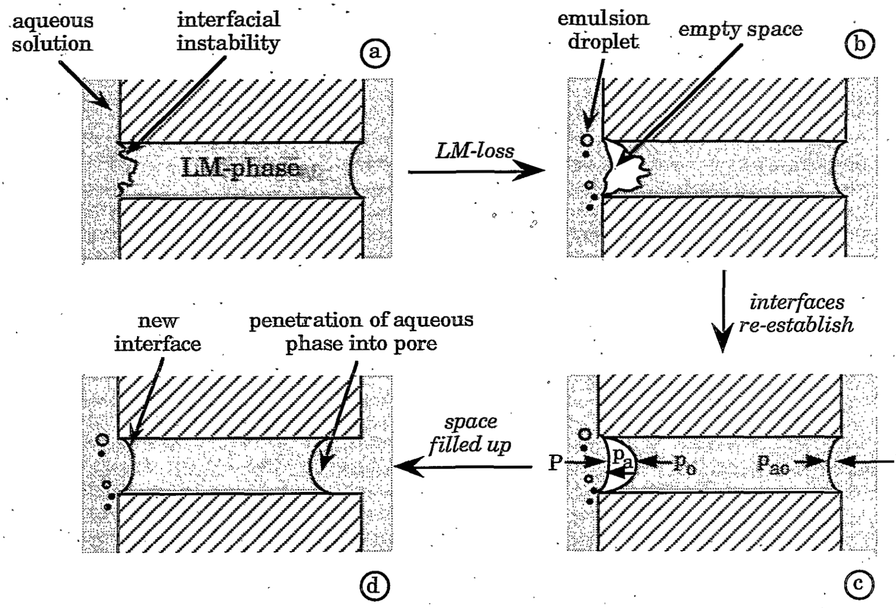
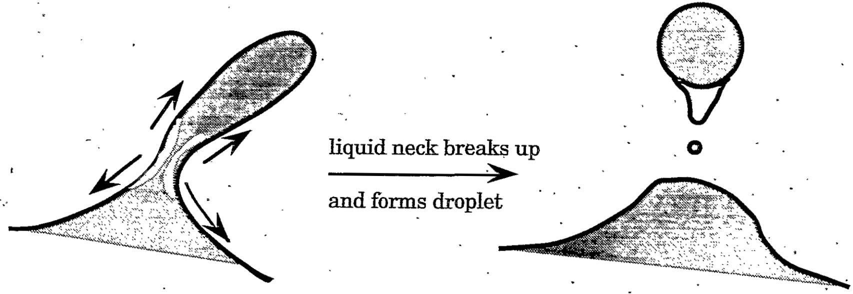


Figure 2.6. *LM-loss and re-establishment of the interfaces according to Zha [6]. P or P' = hydraulic pressure, p = capillary pressure, a = aqueous phase, o = LM-phase. Adapted from Zha [6].*

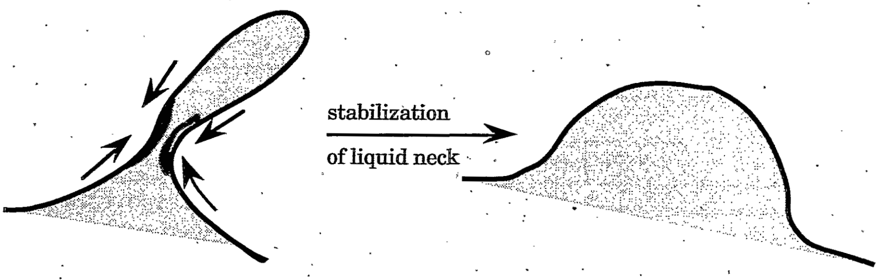
Once interfacial instabilities have caused emulsion droplets to be splitted off, the LM-meniscus will try to re-establish itself. This was worked out by Zha in more detail [6]. According to Zha, under influence of the surface tension the aqueous and organic surfaces will quickly re-establish to form minimum areas, after which the 'empty space' is filled with the solution exerting the greater force. This is schematically drawn in figure 2.6. After making a force balance over the two surfaces in figure 2.6c, assuming the membrane phase wets the membrane completely and the external pressures on both sides of the membrane are equal (P = P'), the empty space will be filled (partly) with organic liquid rather than by aqueous phase. This implicates that the aqueous phase will enter the membrane from the other side. That the aqueous phase will replace the organic phase is obvious. However, the whole idea of an 'empty space' between the aqueous and the organic surface is very doubtful in our opinion. It is completely unclear why, after shredding of an emulsion droplet from the LM-phase, two surfaces will develop since the system will strive for a minimum free energy. Furthermore, it is not clear where this 'empty space' is composed of: is it a vacuum, or dissolved gas? We reject this 'empty space' hypothesis, but agree on Zha's point that the lost liquid membrane phase lost might be replaced by one of the aqueous phases. By carrying out impedance spectroscopy experiments on SLMs for phenol removal, Zha confirmed this hypothesis [6,49]. Nevertheless, we believe that part of the LM-phase lost also might be filled up by LM-phase from other places in the support when the support membrane has an interconnected pore structure. This is promoted by vibrations of the membrane or by small pressure differences over the membrane. Once the LM-meniscus is in contact with the aqueous phases again, loss of LM-phase by formation of emulsion droplets might continue.

The effect of surface tension gradients (Marangoni effects), caused by the mass transfer process, on emulsion formation is drawn schematically in figure 2.7. In a surface tension negative system (γ^- system), the interfacial tension decreases as the mass transfer process reaches equilibrium, while in a surface tension positive system (γ^+ system) this interfacial tension increases. For a surface tension neutral system, the interfacial tension does not change. The 'system' mentioned includes the interface and two bulk phases that extend normal to it on both sides. Zha extended these terms for SLM-systems [6]. When the interfacial tension between organic and the feed phase is increased when more carrier-solute complex is present compared to the interfacial tension of pure water/membrane liquid without solute-carrier complex present, a γ^+ system is formed at the feed phase. The stripping process, as a consequence, should be a γ^- system because of the opposite direction of mass transfer.

When a surface tension gradient $\nabla\gamma$ is present, interfacial hydrodynamic instabilities might be either promoted or damped out, depending on the direction of the surface forces. According to Zha, the effect of $\nabla\gamma$ on SLM stability can be ascribed to two factors [6]. Firstly, an unstable interface between the LM-phase and the aqueous phase is caused by Marangoni effects due to interfacial turbulences. This normally occurs in γ^+ systems but is sometimes also found for γ^- systems. Secondly, emulsion formation might be promoted or suppressed. Suppose the SLM interface is instable and an amount of liquid is thrust outward from the bulk of the liquid membrane phase, while a narrow neck is formed (figure 2.7). Due to the high area to volume ratio of the neck, the neck is rich in solute to be transported. In the case of a γ^- system, the interfacial tension will be lowered in the neck compared to the bulk liquid. As a result, this low interfacial tension liquid will be taken into the bulk liquid in order to reduce its interfacial tension. Breakage of the neck is promoted and an emulsion droplet will be formed. So, a γ^- system should promote the loss of LM-phase by emulsion formation. The opposite is the case for γ^+ systems: the loss of LM-phase will be more difficult.



(a) surface tension negative system



(b) surface tension positive system

Figure 2.7. *Schematic drawing of the effect of surface tension gradients on the formation of emulsion droplets. The darker areas represent liquid of higher interfacial tension. The arrows indicate the direction of surface movement. Adapted from Zha [6].*

Zha studied the effect of surface tension gradients on SLM stability for two different systems [6]: nickel extraction by di-(2-ethylhexyl) phosphoric acid (D2EHPA) and copper transport by LIX 84. For the nickel system, interfacial tension measurements between pure water and membrane liquid showed that the interfacial tension γ decreased when the nickel concentration in the organic phase increased. The Ni-D2EHPA complex was even more surface active than D2EHPA itself and the system was defined as being γ^-. The opposite was found for copper and LIX 84. The interfacial tension increased when the copper/LIX-65 content in the membrane phase increased, indicating that the copper complex was less surface active than LIX 84 alone. The copper system is therefore an example of a γ^+ system. For the nickel system, it was found that in the absence of mass transfer, LM-loss was lower than in the presence of nickel transport, indicating that the transport causes Marangoni effects and $\nabla\gamma$ due to the mass transfer process.

Furthermore, for this system the effect of adding inorganic electrolyte to the aqueous solution was investigated by Zha [6] with the objective to increase the interfacial tension and suppress interfacial turbulences. However, Zha does not give any data on the increase of the surface tension as a function of the inorganic electrolyte concentration. This is necessary since the effect of salt on interfacial tension is small, as was measured for instance by Neplenbroek *et al.* for their SLM-system [2,4]. Furthermore, addition of salts has not only an effect on interfacial tension and turbulences, but it changes also factors like the solubility of the LM-components in the aqueous phases (salting in and salting out). This is not taken into consideration by Zha, so his results must be considered with some caution. Zha found that raising the ionic strength in the feed had a much more positive effect on SLM stability than the addition of salt to the strip, in accordance with their hypothesis: at the feed side, the system is a γ^- system and emulsion formation will be promoted at low ionic strengths.

For the γ^+ copper transport system, no difference in LM-loss was found with and without copper transfer. In this case, surface tension gradients had no effect on SLM stability. At the strip side, the system was γ^-, but here the salt concentration was high enough to suppress Marangoni effects completely according to the author. Addition of salt to the feed phase reduced LM-loss, in accordance with the emulsion formation hypothesis and the results of Neplenbroek *et al.* [37]. However, when the addition of salt to the aqueous phases decreases the solubility of the LM-components, their results can also be explained by this effect as will be discussed in chapter 7 of this thesis. The results indicated nevertheless that even in a γ^+ system loss of LM-phase, either by emulsion formation or by other mechanisms discussed before, is still a severe problem.

Summarizing, we can conclude that several mechanisms for the instability of supported liquid membranes are proposed in literature. It is very doubtful whether the pore blocking mechanism is correct. A pressure gradient over the membrane might have an influence on SLM instability, but can not be the major cause since the LM-liquid lost should have the same composition as the remaining LM-phase in the support which is not the case. This objection also holds for the mechanism of the wetting of the LM-pores by the aqueous phases. The osmotic pressure might have an effect on the instability of SLMs, but only in case the LM-phase can accommodate enough water. Most likely, either the solubility of the LM-components in the adjacent aqueous phases or an emulsification of the LM-phase due to lateral shear forces are the main mechanisms of SLM degradation. The work of Zha supports the emulsion formation hypothesis in several cases, but there are some errors and obscurities in his work.

2.3 Improvement of SLM stability

2.3.1 Effect of membrane materials and operating conditions on membrane stability

In the previous section, a number of possible mechanisms for SLM degradation are given. The causes for the SLM instability are related to both membrane materials and the operating conditions [17]. A proper choice of these factors might improve the lifetime of SLM systems.

Considering membrane materials, we can distinguish between the solvent for the carrier, the carrier itself and the support [17]. It is obvious that the *organic solvent* used has a large influence on membrane stability. From literature it can be concluded that in order to raise lifetimes of SLMs, the organic solvent should have a low solubility in water [20,26,55], and water a low solubility in the organic solvent [18,26,30,35]. The solvent should furthermore have a high interfacial tension between the solvent and the water phases [3,5,18,26,32,37] and a high boiling point [35].

The *carrier* lipophilicity and surface activity, together with its solubility in the membrane solvent, are of importance for the stability of the SLM. The more surface active the carrier is, the less stable is the membrane [31,37]. By attaching carriers onto a polymer [56,57] or when the carrier was covalently linked onto (long-chain) aliphatic chains [35,58], the partition of the carrier towards the aqueous phases could be decreased. Disadvantages of these techniques are the decrease of flux due to the increase in LM-phase viscosity and the limited solubility of the modified carriers in the membrane solvent. Visser succeeded in binding the carrier covalently to the membrane solvent and he improved in this way the compatibility of several carriers with the solvent [17]. Stability experiments with these solvent-bound carriers were promising, although at higher carrier concentrations the flux was low.

The type of *support* used influences SLM-stability in several ways. From the Laplace equation (equation (1) in this chapter), one can conclude that SLMs using supports with a lower pore size are in general more stable than those with a large pore size. In accordance with this, Danesi *et al.* advised the use of supports with a small pore size [18], although the surface porosity should be high enough to obtain a reasonable flux. Zha *et al.* recommended the use of supports with a morphology having a less connected network and sharp pore edges [33]. In the case of a connected network, once LM-loss has started the impregnating liquid in the neighboring branch pores will be dragged out continuously by the aqueous phase due to viscous forces. This should result in more passages for the aqueous phases. It is however not clear why the aqueous phase would pass through the bigger pores, and whether the viscous forces are strong enough. Contrary to Zha's advice, Neplenbroek *et al.* found that Accurel supports lead to substantially more stable SLMs than Celgard due to their larger thickness and interconnected pore structure [37]. Another important support characteristic is the wettability of the membrane. Only when the support is wetted sufficiently by the organic phase, imbibition of the aqueous phase into the SLM can be minimized [5,18]. According to Takeuchi *et al.* the organic LM-phase should have a surface tension smaller than the 'critical' surface tension of the support [5]. Although hydrophilic microfiltration membranes can be used as support [59,60], poor transport properties are obtained due to a poor wettability and immobilization of the impregnating liquid. Better results with hydrophilic supports were obtained when the LM-phase was impregnated in the form of an oil-in-water emulsion [59,60], but this seems not logical and the system used is not well described. In general, however, hydrophobic supports are better from a stability point of view.

Membrane thickness, stirring rate or pumping velocity, carrier concentration, aqueous solute concentration and operating temperature are operating conditions that influence membrane stability [17]. In general, the higher the *membrane thickness*, the more stable the SLM simply because the support contains more LM-phase and therefore it will take longer before the SLM breaks down [61]. However, feed and strip will be polluted with more LM-phase which might be unacceptable for several (pharmaceutical) applications. Chiarizia states furthermore that a larger thickness makes water bridging between feed and strip phases through membrane pores lacking some organic phase practically impossible [31]. Examples are the higher stability of SLMs with Accurel as support compared to the thinner Celgard membranes [37] or the improved stability when hollow fibers are used as support which have a larger thickness than flat sheet supports [31,62]. Teramoto *et al.* showed that a constant copper flux could be maintained for 30 hours when a Teflon® Gore-Tex TA-002 hollow fiber (thickness 400 μm) was used as support. Under the same conditions a thinner polypropylene KPF-400 fiber (33 μm) showed already a flux decrease immediately after the experiment was started [63].

In literature not much data were found on the influence of *stirring rate* on SLM stability. However, Neplenbroek *et al.* observed an increase in both carrier and solvent losses for flat sheet SLMs when the *pumping velocity* was increased [37]. It might be expected that an increase in stirring rate has the same effect on stability. This was confirmed by Zha *et al.* [6,49]. Izatt *et al.* concluded from their measurements on hollow fiber-SLMs the pumping velocity to have the same effect on flux as the stirring rate in flat sheet liquid membranes [25]. Furthermore, an increase in pumping velocity when hollow fibers are used as support, increases the pressure drop over the membrane. This may result in a larger loss of LM-phase when ΔP is larger than the minimum transmembrane pressure required to displace the impregnated phase out of the most susceptible pore. In case the outside and inside hydraulic pressures were balanced in a hollow fiber SLM, Danesi *et al.* observed a constant flux over a period longer than two months [3]. Takigawa designed a special spiral-type membrane module [59,60]. Strip and feed phases were flowing counter-currently through machined channels in two half-cell faceplates that were in a spiral, mirror-image pattern with respect to each other. In this way, the pressure difference between feed and strip could be minimized when the viscosities of the two phases did not differ much. Consequently, the membrane was much more stable than when other cell configurations were used.

In case the *carrier concentration* reaches the saturation limit, it might form solid or gelatinous precipitates in the membrane pores as was observed by Chiarizia [31]. Chiarizia thought this precipitation to be a convenient way for enhancing the stability of the membrane by preventing emulsion formation with the aqueous phase and by acting as a barrier against water bridging in semi-devoid pores. The exact mechanism of this stability improvement by carrier precipitation is not elucidated however. In case the carrier is surface-active, a higher carrier concentration will decrease the interfacial tension of the organic phase, which will in general lead to less stable membranes.

Neplenbroek *et al.* observed a decrease in SLM lifetime when the *solute concentration* in either feed or strip was decreased [4,37,48]. Partition of crown ethers towards the aqueous phases was increased when the pH was lowered to values below pH 10. This leaching of carrier decreased membrane stability [57].

Finally, the *operating temperature* might be of importance in determining membrane stability. Saito found the lifetime of SLMs for Zn^{2+} to be 60, 50 and 20 hours when the temperature was 25, 40 and 60 °C, respectively [64]. This was explained by an increased solubility of both membrane solvent and carrier in the aqueous phases at higher temperatures. It might also be expected that the water solubility in the membrane phase increases at elevated temperatures. In general, membrane lifetime is usually lower when temperature increases.

2.3.2 Methods of SLM-lifetime enhancement

Once an SLM system (support, carrier, organic solvent and aqueous phases) is chosen or fixed by the situation, there are several other methods, which can be found in literature, to enhance the stability. In this section, a number of them will be discussed in more detail.

2.3.2.1 *Reimpregnation of the support*

One of the methods described in literature is reimpregnation of the support. Babcock *et al.* reloaded both flat sheet and hollow fiber supports after they were decayed and their results showed a restoration of the flux after reimpregnation [41]. Several other authors use the regeneration technique for 'stabilizing' SLMs [8,20,22,47,65]. Teramoto and Tanimoto regenerated degraded hollow fiber liquid membranes by simply reimpregnating them with the original LM-phase which was forced to flow in the lumen side of the membrane for a few minutes instead of the aqueous acid solution [63]. Copper flux recovered immediately to the initial value. An alternative proposed by the authors for preventing the flux decrease was to add a small amount of LM-phase to the strip solution. The organic solution will flow through the inside of the fiber and refills the vacant pores continuously with fresh LM-phase. In this way, the pores are always filled with LM-phase and the flux will be constant for a long period of time. No experimental data on this alternative method were presented. This idea was also used by Takahashi and Takeuchi [7]. In a special LM-module with two channels on both sides of the impregnated support, the membrane solution was forced to flow with the strip solution to stabilize the SLM. By keeping the pressure in the feed channels higher than in the strip channel, leakage of membrane solution to the feed was avoided. Disadvantages of these techniques are the loss of extractant, which is as severe as in ordinary solvent-solvent extraction, and the necessity of an additional separation step to remove the membrane solution from the strip.

To avoid the additional separation step, a continuous impregnation of the membrane is possible. Such continuous impregnation methods are mainly applied for hollow fiber modules and can be found in different configurations. Nakano *et al.* designed a vertical hollow fiber module containing one single fiber, with a certain amount of liquid membrane phase at the bottom. This 'pool' of LM-phase was connected to a device to eliminate pressure differences between the membrane liquid and strip solution. The membrane liquid in the pool was soaked into the pores of the support and moved upwards through the porous support network by capillary and buoyant forces [19]. The same research group designed also a module on a larger scale, based on the same idea [21]. Chiarizia *et al.* also used a vertical membrane module, but in their case the LM-phase reservoir was placed on top of the module [65]. By gravitational and capillary forces, the organic phase was soaked into the membrane pores. Tanikagi *et al.* developed a horizontal liquid membrane module for continuous regeneration [20] in which, by means of a pressure difference, the liquid membrane phase was forced to refill the pores. One example of continuous regeneration of flat sheet SLMs is known. Fujinawa *et al.* reported that by laminating nonwoven polypropylene fibers containing membrane liquid to a Teflon® film, the SLM was recharged continuously [66]. However, the reimpregnation only lasted a limited time.

Continuous regeneration of liquid membranes works well, but still feed and/or strip solutions are polluted with the membrane liquid. Therefore, according to our opinion, these membranes are not 'stable'. Only the effects of LM-loss are cured, but the problem of instability itself is not tackled. Other disadvantages are the necessity to fill up the membrane liquid and the complex modules and procedures required [2].

2.3.2.2 *Sandwich-SLMs*

Zhu *et al.* reported a great prolongation of SLM lifetime when a suitable sandwich-SLM was used in operation [45]. By interposing a Celgard SLM between two pieces of hydrophilic lens paper, a stagnant aqueous layer was built up in the paper. According to Zhu *et al.*, in this way no micelles of carrier and water were formed at the interface and introduced into the SLM which would decrease the permeability of copper. Experimental results showed a 'longer membrane lifetime' at almost equal permeabilities, but this lifetime is not mentioned. Another objection against their idea is that the components necessary for micelle or aggregate formation (water and carrier) are still present. Whether the aggregates are formed or not, depends on the concentration of water and carrier and thermodynamical ability to form micelles. This has nothing to do with the presence of the lens paper. A similar system was used by Saito, who sandwiched the SLM between two hydrophilic dialysis membranes (15 μm thickness each) to prevent the loss of membrane solvent and carrier [64]. The lifetime of the sandwiched SLM was higher than that of the ordinary SLM, but still there were stability problems. Permeation velocity was decreased to one-fifth of the value for a single SLM. Therefore, until now, sandwich SLMs offered no solution to the instability problems.

2.3.2.3 *Gelation of SLMs*

The idea of using gelled membranes was proposed firstly by Bloch *et al.* in the late sixties [36]. Polyvinylchloride, PVC, was plasticized with several phosphate esters which could act as extractants for uranium. These so called solvent membranes had a lifetime which was insufficient due to a washout of extractant and subsequent impermeability of the PVC films. Solvent membranes will be discussed in more detail in chapter 6 of this thesis.

Babcock *et al.* tried to increase the viscosity of the organic solution with several polymers [42]. In this way, the high viscosity should be able to increase the mechanical strength of the liquid membrane and prevent separation or displacement by aqueous droplets (see their pore blocking mechanism described in section 2.2.2). Two polymers were studied: polyisoprene and polyvinylchloride.

Polyisoprene was added to the carrier solution, after which the supports were impregnated with the polymer/LM-phase mixture. No improvement in membrane lifetime was observed. When PVC was applied as polymer, it was dissolved in THF and the carrier, LIX 54, was added. After impregnating the support with this mixture and subsequent evaporation of THF, a gel was formed. Long term copper permeation test over a period of 28 days revealed a considerable stability improvement compared to other membranes without PVC. The absolute value of the initial flux nevertheless was somewhat lower.

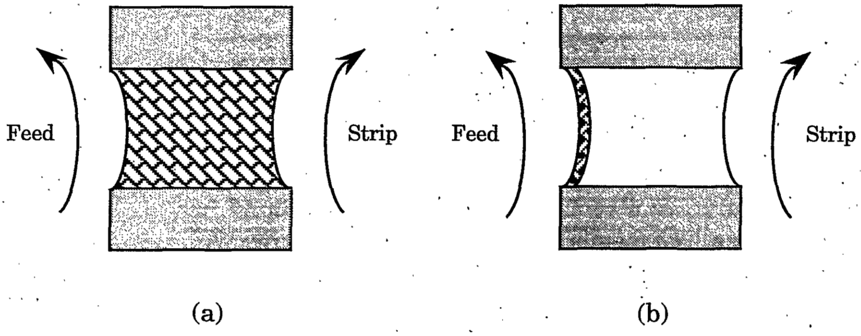


Figure 2.8. *Schematic drawing illustrating the stabilization of SLMs by gelation. (a) Homogenous gel network in the support pores. (b) Thin dense gel layer at feed side.*

Based on their emulsion formation hypothesis for membrane degradation, Neplenbroek *et al.* used gelation of the LM-phase to stabilize SLMs [9,48]. By gelling the membrane liquid, its macroscopic viscosity increases and the resistance against liquid displacement out of the support will be enhanced. By effectively preventing the LM-meniscus to deform, emulsion formation is prevented and as a consequence the SLM will be more stable. The stabilization of the liquid membrane by gelation with PVC was carried out in two different ways as shown in figure 2.8. Firstly, the whole LM-phase was gelled inside the pores of the support (figure 2.8a). Mechanical stability was increased as shown by liquid displacement experiments, while in the meantime LM-loss was less. At higher PVC concentrations, however, the initial nitrate flux was decreased. Neplenbroek *et al.*[9,48] assumed that this was due to the increase in tortuosity factor when the LM-phase was gelated. Better results were obtained when a thin PVC layer was applied as a thin layer (< 2 μm) on the feed side of the support and cross-linked after preparation (figure 2.8b). In this way the resistance towards transport was minimized. Furthermore, emulsion formation could be suppressed more effectively: the polymer concentration could be higher, and as a result the deformation of the LM-meniscus was prevented more effectively. Their results were very astonishing and promising. The best membranes showed no flux decrease after 80 hours under circumstances which enhanced significantly the degradation of the SLM, without a reduction in initial flux compared to SLMs without a gel layer. A membrane lifetime far over one year under normal circumstances was predicted by the authors [9,48]. The major disadvantage of this technique is the bad reproducibility. Furthermore, the coating of the membrane with the gel layer using their technique *i.e.* spreading of the gel with a tissue as smoothly as possible over the membrane surface, seems not to be suitable for large scale applications and the coating of hollow fibers. Based on Neplenbroek's promising results, Bromberg *et al.* [67] and Levin *et al.* [68] also homogeneously gelated their SLMs. Both authors, however, give no data on liquid membrane stability.

2.4 New liquid membrane configurations

Some authors tried to avoid the instability problems inherent to SLMs by developing new liquid membrane configurations. These configurations have all in common that they are a combination of supported liquid membranes and bulk liquid membranes. The membrane phase contains a carrier which binds with one of the components in the feed and transports it across the membrane to the receiving phase. In most cases, the authors claimed that these configurations combined the advantages of liquid membranes with an improved stability and avoidance of the disadvantages of extraction and absorption. In this section, these new liquid membrane configurations will be discussed in more detail.

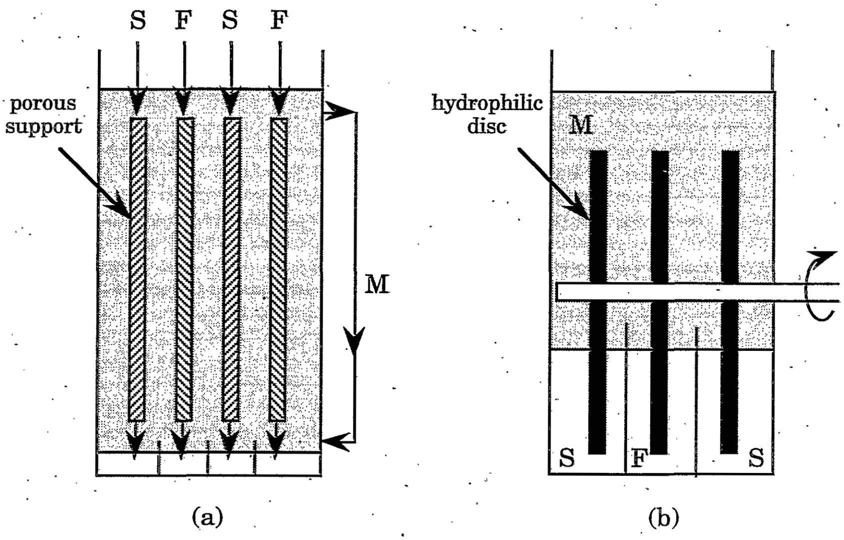


Figure 2.9. *Schematic drawing illustrating the operating principle of two types of film pertractors. (a) Creeping film pertractor. (b) Rotating film pertractor. M = membrane phase, S = stripping solution, F = feed solution. Adapted from Schlosser [12].*

In figure 2.9, two types of *film pertractors* are drawn. The creeping film pertractor (figure 2.9a) was developed by Boyadzhiev [69-71] and further investigated by Lazarova *et al.* [72,73]. In contradiction to the SLM process, besides feed and strip solutions the organic LM-phase is also in motion. Feed and strip flow down the vertical hydrophilic porous supports, placed in an alternating sequence. The whole pertractor volume is filled with the organic phase which is circulated in a cocurrent or countercurrent mode. Construction and operation of this pertractor is claimed to be simple, inexpensive, flexible and easy to scale up. Another advantage would be that the velocities of the three phases could be controlled independently, while the vertical flow and immiscibility and density differences ensure stable interfaces [24]. Continuous operation times of more than 3000 hours have been reported by Boyadzhiev without any efficiency loss or process deterioration [71]. However, Boyadzhiev did not give data on pollution of the feed and strip phases with the membrane liquid. Fraser *et al.* modified the creeping film pertractor to make it suitable for use with strongly alkaline stripping solutions [24].

Another variation on the film pertractor idea was the rotating film pertractor (figure 2.9b) developed by Schlosser *et al.* [12] and also used by Boyadzhiev *et al.* [74,75]. Hydrophilic discs were mounted on a horizontal shaft. The lower parts of the discs were dipped in compartments, alternately filled with strip and feed solutions. On these parts of the discs, due to rotation, films of water were formed which were immersed in the membrane phase where extraction and stripping took place. According to some studies, the rotating film pertractor offered a stable operation without side effects under both continuous and batch regimes [74]. No data on the lifetime were presented, however, and also here feed and strip might get contaminated with the membrane solution.

Two other variations on the pertractor idea are shown in figure 2.10. The *flowing liquid membrane* (FLM) configuration was proposed firstly by Teramoto *et al.* [76-78]. In this type of liquid membrane, the LM-phase flows in thin channels between two hydrophobic microfiltration membranes. These microfiltration membranes separate the LM-phase from feed and strip and, according to the authors, form in this way a stable liquid membrane. The flowing liquid membrane is shown schematically in figure 2.10a. Firstly, a spiral-type module was designed for the recovery of chromium and zinc [76]. Although this type of module was tested only for 100 hours, it was claimed to have a high stability. With flat sheet PTFE microfiltration membranes as support, the flowing liquid membrane was applied for the separation of ethylene from ethane and benzene from cyclohexane using silver nitrate as carrier [77,78]. Comparison of the flowing liquid membrane results with those of ordinary SLMs for ethylene/ethane separation revealed a higher stability for the FLM. The stability of the flowing liquid membrane for benzene transport was 11 days without a flux decrease, but here no comparison was made with supported liquid membranes. Furthermore, in FLMs leakage between aqueous and organic solutions frequently happens [6], which is undesirable.

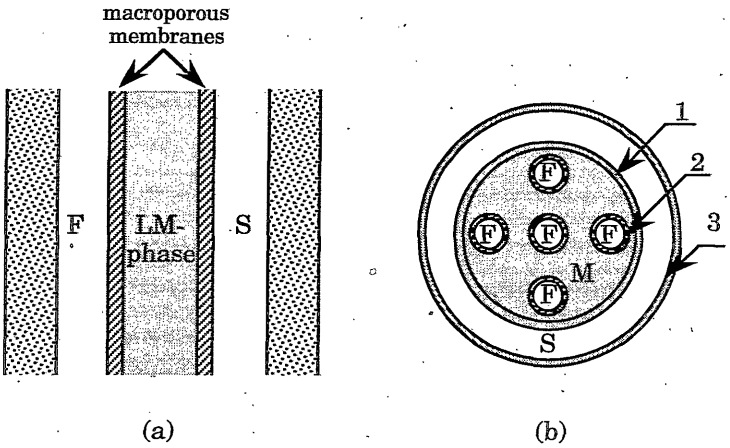


Figure 2.10. *(a) Flowing liquid membrane. F = feed channel, S = strip channel. (b) Top view of a hollow-fibers-in-tube type pertractor. F = feed solution, S = stripping solution, M = liquid membrane phase. 1 = tubular wall (hydrophilic polysulphone), 2 = hollow fiber, 3 = glass wall. Adapted from Teramoto et al. [77] and Schlosser et al. [79].*

Schlosser and Rothová recently published results of a new type of hollow-fiber pertractor (see figure 2.10b), which is in fact also a flowing liquid membrane since all three liquids are in motion and the membrane phase is not flowing through a porous support as is the case in creeping film pertractors [79]. The feed is flowing through hydrophobic hollow fibers, where it is extracted by the LM-phase. The stripping reaction takes place at the hydrophilic polysulphone tube. By pulsating the membrane phase, mass transfer is enhanced substantially. No data on membrane lifetime are given, nor were data given on loss of membrane liquid to the aqueous phases.

The hollow fiber pertractor of Schlosser and Rothová can also be regarded as a variation on the *contained liquid membrane*. The idea of contained liquid membranes (CLMs) was developed in the late eighties by the group of Sirkar [23,80-83]. In a CLM, two sets of hollow fibers are present which are schematically drawn in figure 2.11. Throughout the permeator, the hollow fibers are well mixed but they are separated at the end. The fibers can be either hydrophilic or hydrophobic. The aqueous feed and strip solutions flow through the lumen side of the fibers and, depending on the hydrophilicity of the fibers, fill the pores of the fiber (in the hydrophilic case) or the fibers are wetted by the organic membrane phase (when the fibers are hydrophobic). It is also possible to use organic solutions as feed and strip phases. In that case an aqueous or polar organic solution is applied as liquid membrane phase. The membrane phase contains a selective complexing agent which binds at the interface in one set of fibers with one of the components of the feed solution. Hereafter, the complex diffuses across the (organic) liquid membrane and dissociates in the other set of fibers where the component transported is released to the strip solution.

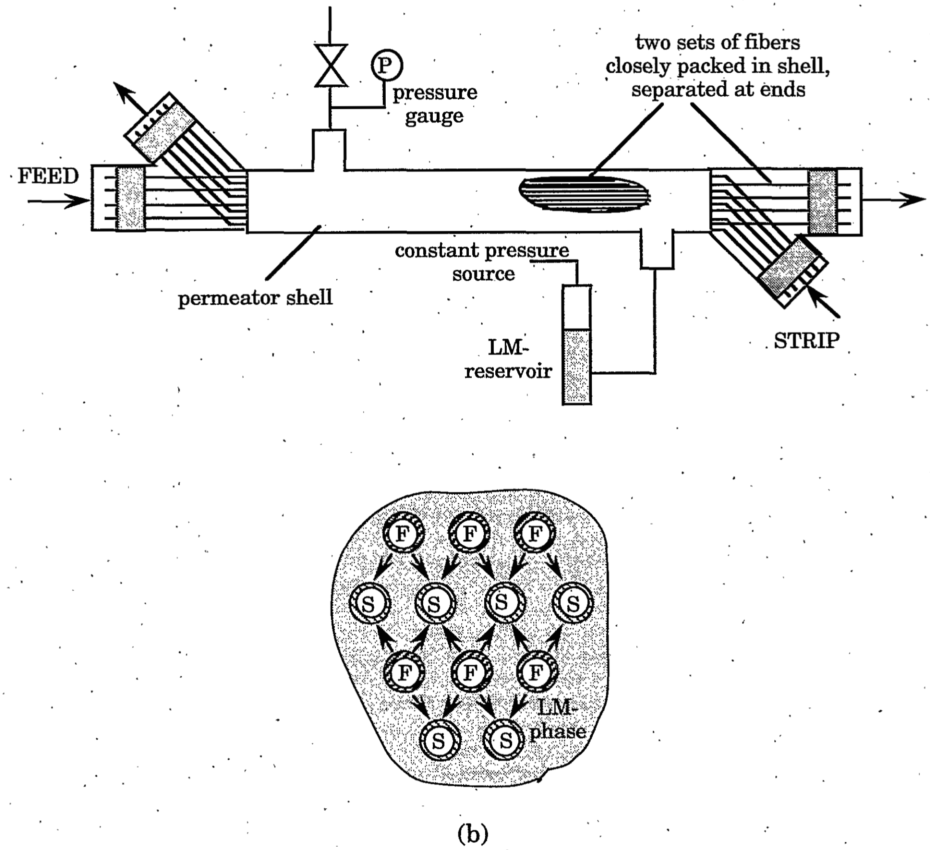


Figure 2.11. *Schematic drawing of an hollow fiber contained liquid membrane. (a) Side-view of the permeator. (b) Internal structure and arrangement of the fibers. Adapted from Sengupta et al. [80,81].*

Hollow fiber contained liquid membranes have been used for different applications. Sengupta *et al.* transferred phenol or acetic acid with hydrophobic and hydrophilic hollow fiber CLMs (HFCLMs) [80,81]. Citric acid was successfully separated from aqueous solutions by Basu *et al.* [82], while the recovery of pharmaceutical products by HFCLMs was studied by the same authors [23]. In all cases, an elimination of stability problems as encountered in supported liquid membranes is claimed. Stabilities up to 60 days are reported [82]. Nevertheless these long term experiments are somewhat misleading, since no explicit attention is paid to the fact that the contained liquid membranes all use a membrane reservoir to refill the permeator with fresh LM-liquid which was lost to the feed and strip phases.

This loss of LM-phase is also a problem for the flowing liquid membranes and the film pertractors. Sometimes even the use of an aqueous-organic separator is required [84]. Moreover, the processes are more complicated than SLMs, while the total resistance to permeation of solute from feed to strip is increased. Finally, these membrane configurations in general need a much larger amount of LM-phase than supported liquid membranes, which might be disadvantageous when expensive extractants are used.

A relatively new variation on liquid membranes is the so called electrostatic pseudo liquid membrane (ESPLIM) developed in China by Gu *et al.* [28,85]. The process is a combination of an electrostatic technique with the principle of a liquid membrane. The porous membrane in SLMs is replaced by a baffle which separates feed and stripping cell. When an alternating current (ac) high-voltage electrostatic field is applied simultaneously to both cells, the feed and strip solutions are dispersed into numerous droplets in the continuous organic phase containing the carrier. The complex, formed in the extraction cell, diffuses through the baffle plate into the stripping cell where the product is released. In general, fluxes are in the order of 10^{-7}-10^{-8} mol cm^{-2} s^{-1}, two magnitudes of order higher than in most SLMs. The authors claim the technique to be more stable than supported liquid membranes [28], but do not show any data on long term stability. Another disadvantage, again, is the complex operation of the process.

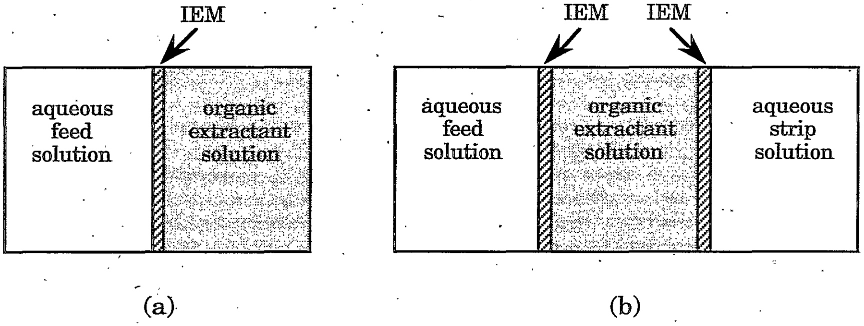


Figure 2.12. *The use of ion exchange membranes in extraction processes in a two chamber (a) or a three chamber cell (b). IEM = ion exchange membrane.*

Finally, Kedem and Bromberg describe the use of ion exchange membranes in extraction processes [86]. Ion exchange membranes were used to separate aqueous feed solution from the organic extraction phase as is schematically shown in figure 2.12. Three different techniques were used: a two chamber cell in which feed and extractant solution were separated by the ion exchange membrane (2.12a), a three chamber cell with an extra ion exchange membrane and a 'strip' solution (2.12b) and a variation on the first technique in which aqueous feed and organic extractant solution were flowing parallel to the membrane. In the case of copper transport, a cation exchange membrane separated the different solutions, and the removal of acid was conducted using anion exchange membranes. According to the authors, the ion exchange membranes could prevent the loss of extractant to the aqueous solutions with a solute flux similar to that of ordinary supported liquid membranes. However, this technique is new and still much research is needed on the transport mechanism and stability.

2.5 Conclusions

In this chapter a state of the art literature review was given on the stability of supported liquid membranes. Firstly, different possible causes of SLM instability were discussed. Only two mechanisms for SLM instability seem to be important and can explain the loss of membrane solvent and carrier in different ratios: the solubility of the LM-components in the adjacent feed or strip solutions and an emulsification of the LM-phase due to lateral shear forces. Secondly, a review is given on methods for SLM lifetime improvements. A careful choice of membrane conditions and materials is important and may enhance membrane stability. Once the system is fixed, several suggestions for lifetime improvement can be found in literature. Especially gelation of the LM-phase to prevent loss by emulsification is very promising.

2.6 References

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3

STABILIZATION OF SUPPORTED LIQUID MEMBRANES BY INTERFACIAL POLYMERIZATION

Part I: Screening of the monomers

SUMMARY

The first part of this chapter describes the backgrounds of interfacial polymerization and the use of this technique in membrane separation processes is discussed briefly. Using literature data, a series of monomers were selected which were known to have a low salt rejection and might therefore be of use to stabilize supported liquid membranes.

In the second part, interfacial polymerization reactions of a series of monomers on the surface of microfiltration membranes is described. The modified supports were used for the preparation of supported liquid membranes and tested for selective nitrate transport and stability. These screening experiments revealed that most applied toplayers did not hinder the transport of nitrate ions. However, only a few toplayers were able to improve the stability of the liquid membranes. Best results were obtained when piperazine and trimesoyl chloride were used as monomers. SEM showed the particular surface texture of layers prepared with these monomers.

3.1 Introduction

As has been pointed out in chapter 2, the major problem concerning supported liquid membranes is their instability due to the loss of carrier and membrane solvent to adjacent feed and strip phases. The loss of carrier is larger than might be expected on the basis of its concentration in the LM-phase. It is obvious that this loss should be reduced as much as possible in order to increase the lifetime of supported liquid membranes and to assure their commercial application in future. One way to deal with this problem was discussed in chapter 2. In order to minimize the loss of liquid membrane phase by emulsion formation, Neplenbroek *et al.* applied thin, crosslinked PVC gels on the feed side of their membranes [1,2]. These toplayers were very effective in stabilizing supported liquid membranes for nitrate removal from water without a measurable influence on the flux. However, this technique has several disadvantages. Because the gel layers were applied by spreading them on the membrane surface by means of a tissue, reproducibility of the results was poor. Furthermore, this method is only suitable for coating flat membranes and cannot be applied at the lumen side of hollow fibers. The industrial applicability of this stabilization technique is therefore doubtful.

This thesis is mainly focussed on applying thin layers on top of porous membranes by means of the interfacial polymerization technique. The thin layer should prevent loss of LM-phase just like occurred with the gel layers of Neplenbroek *et al.* [1,2]. In the ideal case, transport of nitrate ions across the layer is not hindered to retain a high nitrate flux. On the other hand, the layer should be impermeable for the LM-components to prevent loss by dissolution in the adjacent phases.

An interfacial polymerization reaction is chosen for the application of the toplayer since the technique is expected to be better reproducible and easy to scaled up to an industrial scale. By means of an interfacial polymerization reaction, it is also possible to coat the lumen side of hollow fibers.

In this chapter, the basics of interfacial polymerization will be discussed briefly. Furthermore, a number of monomers is polymerized on the surface of microfiltration membranes in order to obtain suitable candidates for the stabilization of supported liquid membranes. The results of these experiments are given in this chapter.

3.2 Interfacial polymerization

3.2.1 Polymer chemistry

Interfacial polymerization is the formation of a condensation polymer at the interface of two non- or slightly miscible phases each containing one of the monomers [3]. The chemistry behind this technique is very simple and a typical example is shown in figure 3.1. A solution of sebacoyl chloride in a water-immiscible solvent (e.g. CCl_4 or hexane) is brought into contact with an aqueous solution of hexamethylenediamine in water. The polycondensation reaction takes place at the interface of the two solutions and a film of polymer is formed which is strong enough to be removed from the interface as a collapsed sheet or tube. Therefore, this reaction is also known as the nylon rope trick. While the polymer is removed, the reaction continues and more polymer is formed. This can be continued over a period of many hours [4]. The byproduct HCl is neutralized by reacting with an acid receptor like NaOH. When no acid receptor is added, the HCl will react with the $-NH_2$ group of the diamine to form diamine hydrochlorides ($-NH_3^+Cl^-$). The reaction cannot proceed further with all amine groups protonated since it is believed that the reaction mechanism is of the S_N2 type [5].

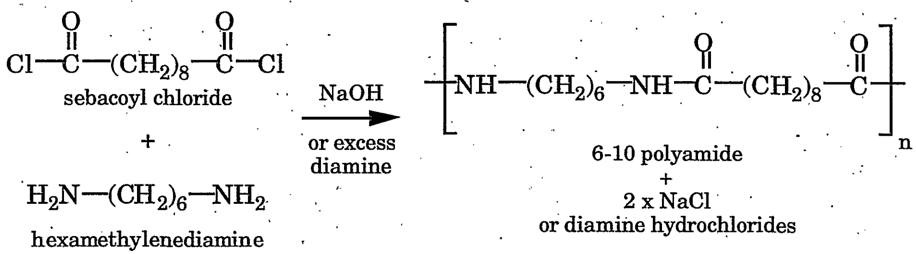


Figure 3.1. *The formation of nylon-6,10 by an interfacial polymerization reaction.*

Morgan *et al.* were the first to describe the principles and backgrounds of interfacial polymerization [5-7]. Their proposed mechanism will be reviewed briefly. We restrict ourselves however to unstirred polyamidation systems. After the two phases containing the monomers are brought into contact with each other, both reactants and solvents will have a tendency to be transferred to the opposing phase. Usually, the acid chloride is hardly soluble in the water phase. The diamine, however, shows a clear partition towards the organic phase. Measured partition coefficients for diamines in suitable organic phases were in the range 400 to less than one ($c_{H2O}/c_{organic}$) [5]. The first diamine transferred to the organic phase will meet a high concentration of acid chlorides and react almost immediately to form acid chloride terminated oligomers. The transport of following diamine will be hindered by a layer of these oligomers. The oligomers will be coupled by the diamine, and in this way they grow in length. Finally, the concentration and size of oligomers will increase until a layer of high M_W polymer is formed which will precipitate depending on the polymer-solvent interaction. Once the polymer has precipitated, the rate of polymerization is decreased drastically because of the low mobility of the polymer chains and the decrease in diffusivity of the intermediates.

The polycondensation reaction takes place where both reactants meet each other. This might be exactly at the interface, or either in the organic or in the aqueous layer. However, in general it is assumed that most polymers in interfacial polymerization form and grow at the organic solvent side of the interface [5,6]. This was shown for instance by the introduction of insoluble, coloured powders on the polymer interface at the aqueous side of the polymeric interface during the polymerization process. No polymer was formed at the aqueous side since all coloured powder remained clearly on top of the film. Also changes in polymerization conditions could be explained best when it was assumed that the reaction took place at the organic solvent side of the interface. Some authors however claim to have reasons to believe that reactions might also occur at the aqueous side, for instance when one of the reactants is not a monomer but an oligomer like polyethylenimine PEI [8,9]. MacRitchie concludes that the location of the polymerization is in a mixed monolayer of the adsorbed monomers [10].

As already mentioned before, one of the possible side reactions during interfacial polymerization is the formation of diamine hydrochlorides. However, the most important side reaction is the hydrolysis of diacid chlorides. In the hydrolysis reaction, the acid chloride group is replaced by a carboxylic acid group, either by a reaction with water or by a reaction with hydroxyl ions [5,6]. Not only the polymerization rate, but also the molecular weight of the polymer is decreased by hydrolysis since the diacid chloride is converted into monofunctional reactant. The hydrolysis reaction almost exclusively takes place in the aqueous phase [6,11]. This means that the hydrolysis rate is dependent on the system investigated: short chain aliphatic diacid chlorides have a higher water solubility than other diacid chlorides, and are therefore more sensitive to hydrolysis. For polyamidations, in general the polymerization rate is two orders of magnitude higher than the hydrolysis rate and therefore hydrolysis might be neglected in some cases [12,13]. However, no general rules can be given when hydrolysis can be neglected. This will depend on *e.g.* the monomers, solvents and reaction conditions.

The properties of the interfacially synthesized polymer will depend on several variables [5,6], including:

- the chemical reaction rate
- partition coefficients of reactants
- concentration ratio of phases

- hydrolysis of acid chlorides
- presence and transfer rate of additives (salts, acid receptors, surfactants)
- polarity of solvents
- stirring
- impurities in reactants and solvents.

All these factors influence, in their own way, the final molecular weight of the obtained polymer. For a detailed description of the above mentioned variables one is referred to Morgan *et al.* [5,6].

3.2.2 Interfacial polymerization in membrane technology

Interfacial polymerization is a technique which also can be applied for the preparation of membranes. In literature one can distinguish between three different methods.

Firstly, interfacial polymerization can be used to synthesize polymers. After dissolving the synthesized polymer in a suitable solvent, a membrane can be obtained by a phase inversion process induced by solvent evaporation or immersion precipitation. In this way, Credali *et al.* [14-16] synthesized a number of polypiperazineamides with the general formula given in figure 3.2. These polymers were used to prepare dense and homogeneous films for reverse osmosis applications. Joshi *et al.* [17] synthesized six different polyureas by an interfacial polymerization reaction. The polymers were dissolved in concentrated sulphuric acid together with some additives. Membranes were prepared according to the phase inversion method by solvent evaporation and polymer precipitation in a nonsolvent medium. The obtained membranes were tested for their performance in reverse osmosis and ultrafiltration.

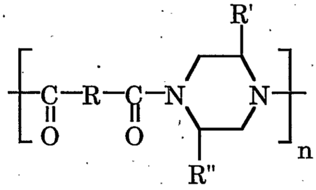


Figure 3.2. *General formula of substituted polypiperazineamides as prepared by Credali et al. [15].*

The second way interfacial polymerization is used in membrane technology is in the direct synthesis of polymeric membranes. Enkelmann and Wegner [18-21] placed solutions of sebacoyl chloride in chloroform and hexamethylenediamine in water on top of each other. After the polymerization process is stopped by adding

HCl to the water phase, the organic phase was removed carefully, the membrane isolated, washed with acetone and water and kept in distilled water to prevent irreversible shrinkage and change of structure. By adding a trifunctional acid chloride to the organic phase, they were able to synthesize chemically and mechanically stable membranes for dialysis, ion exchange and reverse osmosis applications. The method is not commercialized since only membranes with a small area could be prepared. Chern *et al.* [22,23] prepared aromatic polyimide films out of two different diamines and 1,2,4,5-benzenetetra acyl chloride to investigate the effects of heat treatment and reaction conditions on temperature and organic solvent resistances. Chai *et al.* [24] developed a light-reflectometry measurement technique and a pendant-drop technique to elucidate the interfacial polymerization process for the monomers *m*-phenylenediamine and trimesoyl chloride. These unsupported polyamide films were also investigated by scanning electron microscopy. The authors claimed that the above mentioned techniques are very useful techniques for studying the very fast interfacial polymerization technique, although their results are not always that clear.

The preparation of microcapsules by interfacial polymerization is also an interesting application. Microcapsules are small particles, liquid droplets or gas bubbles surrounded by a coating and with a size between 1 and 1000 μm [25]. They are used for controlled release and transfer of drugs, inks, proteins, pesticides etc. By either stirring both reaction mixtures [26,27] or injecting small droplets of one solution with a needle in the second solution [25,28], a polymeric wall is formed around the droplets. Since the walls of the microcapsules show selective permeability for certain molecules, one can consider microcapsules as membranes.

Thirdly, and most important, interfacial polymerization is used in the preparation of *thin film composite membranes*. This type of membranes is characterized by a thin separating layer, preferentially 0.5 μm or thinner, supported on an asymmetric porous substrate made out of a different material. The substrate is sometimes bound to a nonwoven to give the actual separating membrane the required mechanical strength. In between the actual separating layer and the substrate, other polymeric layers might be present as a result of the preparation method, *e.g.* a layer of unreacted polymeric or monomeric material [29] or a gel layer of water-insoluble polymer [30].

Schematically, the deposition of the thin toplayer on a porous support is shown in figure 3.3. The process starts with the immersion of the support in a solution of reactant A in liquid 1. Usually, the supporting material is a microfiltration or ultrafiltration membrane. Depending on the hydrophilicity of the support, it is immersed in either the aqueous or the organic solution of the reactant A. After the support is impregnated, it is immersed in a solution of the second reactant. At the interface of the two phases -at the support surface- the interfacial polymerization takes place forming a dense polymeric layer. Sometimes a heat treatment is applied afterwards to complete the reaction or crosslink the prepolymer or the water-soluble monomers. Because the reaction is self-inhibiting since the already formed polymeric layer limits the supply of reactants, extremely thin layers down to 50 nm thickness can be obtained.

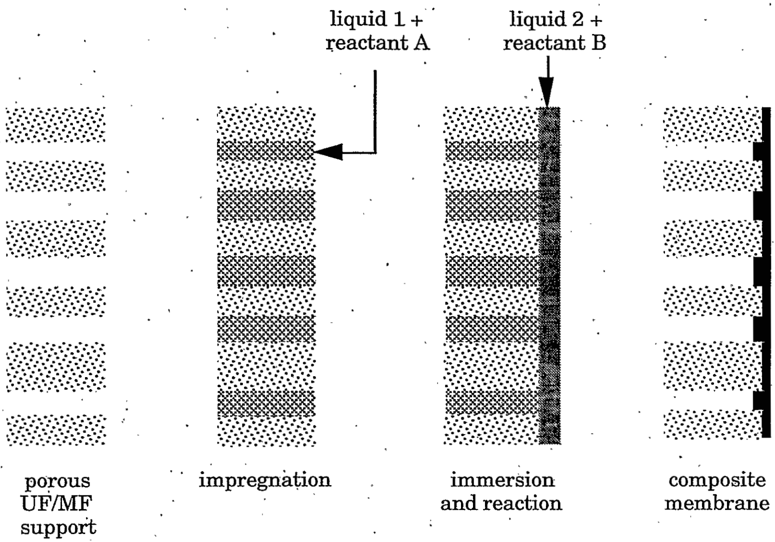


Figure 3.3. *Schematic drawing illustrating the preparation of thin film composite membranes by interfacial polymerization. The two monomers, reactant A and reactant B, are dissolved in liquid 1 and 2, respectively.*

There are numerous recipes for the preparation of thin-film composite membranes by an interfacial polymerization method in literature. One of the first commercial reverse osmosis membranes made this way at the North Star Research Institute, based on Cadotte's work, is the NS-100 membrane [31,32,36]. The NS-100 membrane is based on an interfacially polymerized toplayer of polyethyleneimine (PEI) and toluenediisocyanate (TDI), on top of a polysulfone microporous support. This membrane was crosslinked by heat-curing at 110 °C. In a later version of this membrane, designated NS-101, the TDI was replaced by isophtaloylchloride (IPhCl), thereby generating a polyamide [31]. By replacing the PEI in the NS-101 membrane by a polyetheramine, Riley *et al.* developed the PA-300 membrane [33]. This membrane was superior to the NS-100 since higher membrane fluxes were possible at equivalent salt rejections.

Unfortunately, the NS-100, NS-101 and PA-300 membranes were not resistant to low levels of chlorine in reverse osmosis feed water. In order to improve chlorine resistance, the NS-300 and FT-30 membranes were developed at North Star and FilmTec Corporation, respectively [8,34-37]. These membranes are based on work by Credali *et al.* [14-16] and Parrini [38], who demonstrated that polypiperazine-amides show a better chlorine resistance due to the absence of hydrogen at the amide bond. The NS-300 membrane is prepared by the interfacial polycondensation reaction of piperazine (PIPA) and a mixture of trimesoyl chloride (TMCl) and IPhCl on a polysulfone support. In order to obtain reproducible results and high salt rejections, the addition of acid receptors and surfactants to the amine solution is necessary..Compared to the 'NS' series of membranes, the FT-30 thin-film composite membrane is superior in resistance towards high and low values of pH, temperature and the presence of chlorine in the feed phase. The FT-30 membrane is prepared by using aromatic amines and aromatic acid halides, in contradiction to the 'NS' series where only aliphatic amines were applied. The best results are obtained using trimesoyl chloride TMCl alone as acid halide, and 1,3-benzenediamine as aromatic amine. A heat-cure is not necessary, neither is the addition of surfactant and acid receptor. Due to a partly hydrolysis of the acid halide groups, the polyamide toplayer is mildly anionic in charge, and thus susceptible to binding and fouling by cationic surfactants. For a complete overview of thin-film composite membranes for reverse osmosis membranes, one is referred to Petersen [29].

Interfacial polymerization is not only applied in membrane technology to prepare thin-film composite reverse osmosis membranes. By choosing the right monomers and reaction conditions, different types of membranes can be prepared. FilmTec prepared composite membranes in which the barrier layer consisted of a fully aromatic crosslinked polyamide (the actual composition has never been disclosed). These membranes, the NF-50 and NF-70, are used for nanofiltration applications. Chern *et al.* [39] used an interfacial polymerization reaction between 4,4'-methylenedianiline or ethylenediamine and 1,2,4,5-benzenetetraacylchloride to apply a polymeric toplayer on a porous PSf support. After a heat treatment at 135 °C in a N_2 atmosphere to imidize the polyamide, the membranes were suitable for gas separation applications. Ultrathin films containing oxygen-complexing functional groups (e.g. Schiff bases and metallophtalocyanines) were synthesized by means of an interfacial polymerization on a microporous polypropylene support by Lonsdale at Bend Research [40]. The materials could be used as selective membranes or as selective sorbents. Another patent of Lonsdale *et al.* describes the preparation of ultrathin (20 to 2000 nm thick) films that contain functional groups [41]. These groups were capable of electron transfer, of chelation or complexation, of enzymatic activity, of photochemical activity or of biological activity. Various applications were enclosed, like membrane electrodes, selective membranes and sorbents and targeted drug delivery.

For the application of a toplayer on SLMs in order to stabilize them, the third method (directly on top of the support) seems the most suitable one. The method is relatively simple and easy to apply at larger (industrial) scale. The question now is which monomers to use for the interfacial polymerization reaction. This will be discussed in the next section.

3.2.3 Choice of reagents for SLM toplayers

It is important to make a proper choice of the monomers and solvents to be used in the interfacial polymerization for the application of the protective toplayer on the macroporous liquid membrane support. There is an enormous amount of suitable monomers and solvents available, each combination resulting in a specific polymer with certain properties. It is therefore important to specify the properties the polymeric toplayer should have and to translate these properties in the proper chemicals.

Firstly, the polymeric toplayer should prevent the loss of carrier molecules and liquid membrane solvent immobilized inside the pores of the support. This means that the layer should be dense enough to prevent dissolution of both components in the aqueous phases. When the solubility of carrier and solvent in water is very low, the layer might be somewhat opener, but should at least prevent the loss of membrane phase by emulsion formation, as already explained in chapter 2. Secondly, however, if the toplayer is too dense or too thick the transport of ions through the layer is hindered and the overall flux will decrease. This means that the layer should be thin and 'loose'. Furthermore, a negatively charged toplayer also might hinder the transport of nitrate ions. Therefore, it is preferred to have an uncharged or positively charged toplayer.

In the last paragraph, it became clear that interfacial polymerization is mainly used to prepare thin-film composite reverse osmosis membranes. In reverse osmosis, the membrane should have a high water flux and a *high salt retention*. Such membranes are not suitable for our purposes, since a high salt retention decreases the ion flux too much. It must be stated here that reverse osmosis operating conditions are quite different from those during liquid membrane operation, but at least an idea of the salt permeability can be obtained. Therefore, literature was checked on low salt rejection RO membranes. We restricted ourselves to polyamide membranes since this class of polymers is most widely applied. Care must be taken when data from different references are compared, since test conditions (feed pressure, feed composition) or membrane preparation (type and properties of support, interfacial polymerization reaction conditions, membrane thickness) might be quite different.

Enkelmann and Wegner used sebacoyl chloride and hexamethylenediamine as monomers for the direct synthesis of nylon-6,10 membranes [19,21]. Since the objective of their research was to investigate the mechanism of interfacial polycondensation, no RO membranes were prepared and no salt rejection data were given. From salt diffusion experiments however, diffusion coefficients were calculated. Using a 0.2 M NaCl solution on one side and distilled water on the other side, a diffusion coefficient of $4.0 * 10^{-10}$ cm^2 s^{-1} was found. It was observed that the direction of transport was important. The surface of the membrane exposed to the water phase during synthesis contained only amino endgroups, while the opposite surface was rich in carboxyl endgroups. Due to these weakly basic and acidic endgroups, the material exhibited ion-exchange properties which were a function of the pH. In between the two membrane surfaces, both density and sign of the fixed charge changed continuously from anion exchange to cation exchange properties, like in a bipolar membrane. Current-voltage characteristics were found to be asymmetric. In a review article by Blais [42], nylon-6 and nylon-6,10 were considered to be not suitable as salt barrier materials due to their low ratio between water and salt permeabilities Linear polyamides (nylons) therefore are possibly a suitable candidate for our stabilizing toplayers.

Credali *et al.* [15] investigated the salt rejection properties of a class of polypiperazineamides. All these membranes were obtained by phase inversion and not supported by a nonwoven or a porous UF membrane. Water permeabilities and salt rejections are given in table 3.1. It can be concluded from their data that, depending on the monomers used, some membranes posses a low salt retention.

Table 3.1. *Reverse osmosis properties of polypiperazineamide membranes. Pressure: 50-80 atm. Feed 0.5 % w/v NaCl. Film thickness 20-40 μm. Adapted from references 15 and 38.*

monomer 1*	monomer 2*	P_{water} [μg cm^{-1} s^{-1}]	P_{water}/P_{NaCl} [g cm^{-3}]	salt rejection [%]
PIPA	IPhCl	0.35-0.51	1600-2000	98-99
MPIPA	FMCl	2.2-2.3	50-100	80-85
dMPIPA	FMCl	1.0-1.4	280-330	91-95
dMPIPA	MCCl	1.4	100-120	81-85
dMPIPA	APCl	0.5	120	81
dMPIPA	IPhCl	0.49	25-40	65
dMPIPA	TPhCl	0.50	500-600	94-95

*PIPA: piperazine, MPIPA: 2-methylpiperazine, dMPIPA: trans-2,5-dimethylpiperazine, IPhCl: isophthaloyl chloride, FMCl: fumaryl dichloride, MCCL: mesaconyl dichloride, APCl: adipoyl chloride, TPhCl: terephthaloyl chloride.

As mentioned before in paragraph 3.2.2, Cadotte and coworkers investigated composite membranes consisting of polyamide toplayers on polysulphone supports for their reverse osmosis properties [8,34,36,43]. Low salt rejections were observed when terephthaloyl chloride was polymerized with several diamines like 1,3-propanediamine, 1,6-hexanediamine, 1,3-diaminobenzene and 1,4-diaminobenzene. Since their objective was to obtain a high salt retention membrane, piperazine and polyethyleneimine were examined in more detail. By changing the ratio trimesoyl chloride (TMCl) to isophthaloylchloride (IPhCl), the salt rejection for synthetic seawater could be varied. The lowest salt rejection of 64 % was observed for a ratio TMCl:IPhCl of 75:25, while the highest salt rejection of 98 % was obtained at a ratio of 0:100. By changing the amount and type of acid receptor, salt rejection could be varied between 88 % and 28 % for the piperazine/trimesoyl chloride system in the order no acid receptor > Na_2CO_3 > NaOH. The opposite order was found when the TMCl was replaced by IPhCl. From the above it can be concluded that the combination of piperazines with aromatic acid halides offers interesting possibilities due to their low salt retention.

In microencapsulation technology, permeability of the capsule walls towards their contents (*e.g.* salts, pesticides, herbicides, pharmaceuticals or dyes for carbonless copying) is very important. One way of preparing microcapsules is by interfacial polymerization. Both polyamides and polyurethanes are used as polymeric materials for encapsulation [44]. Acid chlorides employed include sebacoyl chloride, terephthaloyl chloride and trimesoyl chloride because of their low hydrolysis rate. The polyurethanes are usually based on *p,p'*–diphenylmethaneisocyanate, toluenediisocyanate (TDI) or hexamethylenediisocyanate (HMDI) as isocyanates. Amines such as ethylenediamine (EDA), hexamethylenediamine (HMDA) or triethyltetramine (TETA) are most widely applied to produce polyamides. Ishizaka *et al.* compared permeability coefficients of different hydroxides in poly(1,4-terephthaloylpiperazine) and poly(1,6-hexamethylenesebacamide) microcapsules [45]. The first one showed 50 to 350 times higher permeability coefficients for the hydroxides than the latter one. According to the authors, this was due the water structure in and around the microcapsules which determined the resistance towards transport of ions. Mathiowitz and Cohen investigated a series of microcapsules made from several multifunctional (*i.e.* with two, three or four primary or secondary amine groups) linear amines and terephthaloyl chloride or trimesoyl chloride [46]. The higher the porosity of the polymeric material, the faster the core solvent was released from the capsules. The results showed that crosslinked membranes were much less permeable than the other capsules tested. The same conclusion was drawn by Janssen *et al.* who studied the influence of the addition of diamines to aqueous phase of diethylenetriamine (DETA) during encapsulation with terephthaloyl chloride [25,47]. The higher the ratio of diamine to triamine, the less crosslinking took place and the higher was the permeability for DETA.

The literature discussed above clearly shows that it is possible to prepare interfacially polymerized layers or 'walls' which are permeable towards salt or other molecules. Therefore, a selection of the above mentioned monomers were tested on their suitability as stabilizing and permeable toplayer. The attention was focussed on the polyamides, since the necessary reactants are less toxic than those for the preparation of polyurethanes.

Table 3.2. *Physical properties of some potential organic solvents suited for interfacial polymerization. Data taken from reference 49, unless indicated otherwise.*

solvent	boiling point [°C]	vapor pressure* [mm Hg]	solubility in H_2O [%w/w]	solubility of H_2O in solvent [%w/w]
chloroform	61.2	194.8	0.815	0.072
1,2-dichloroethane	83.5	83.35 (20 °C)	0.81	0.15
carbon tetrachloride	76.8	115.2	0.077	0.010
cyclohexane	80.7	97.6	0.010	0.0055
n-hexane	68.7	151.3	0.00095	0.0111
n-octane	125.7	14.0	$6.6 * 10^{-5}$	0.0095
n-decane	174.1	1.3	$1.5 * 10^{-6}$ †	0.0072
n-dodecane	216.3	0.12	$3.7 * 10^{-7}$ †	0.0065
m-xylene	139.1	8.3	0.0196	0.0402
benzene	80.1	95.2	0.1780	0.063
dimethylphthalate**	283.7	$3.07 * 10^{-3}$	0.427	1.6
dibutylphthalate	340.0	$1.09 * 10^{-5}$ ††	< 0.01	0.46
dioctylphthalate**	384.0	$7.22 * 10^{-8}$	$4.1 * 10^{-6}$	-

*: vapor pressure at 25 °C. **: data from references 50 (boiling points, calculated vapor pressures), and 51 (solubilities). †: data from reference 51, error (for n-decane) $\pm 0.5 * 10^{-6}$ %w/w. ††: calculated from reference 50. - = unknown.

Apart from the reactants, another factor influencing polymer properties is the organic solvent used. The organic solvent influences the partition coefficient for the reactant dissolved in the aqueous phase and its solubility. Consequently, the final molecular weight of the polymer produced is affected. The higher the solubility of the polymer in a solvent, the thicker and less porous the membrane is expected to be, other parameters being equal [48]. In general, aliphatic hydrocarbons like n-hexane and cyclohexane or halogenated hydrocarbons such as chloroform, dichloroethane and carbon tetrachloride are used [5,6]. Other solvents applied include for instance xylene [5,48,52,53], benzene [52,53] and phthalates like dimethylphthalate or dibutylphtalate [25,47]. However, most of these solvents are relatively volatile and evaporate too fast from the pores of the hydrophobic supports used in this work. Since the reaction usually takes place in the organic phase, this means that there is no reaction medium left for the polymerization process to continue. Therefore, other organic solvents with a low vapor pressure had to be chosen. Additional requirements are a sufficient solubility for the acid chlorides investigated, and low or no solubility of the organic solvent in water and vice versa. In table 3.2, several solvents and their properties are given. Apart from their high vapor pressure it was decided to avoid the use of halogenated solvents from an environmental point of view. After some preliminary experiments, dodecane was chosen as organic solvent for most of the polymerizations described throughout this thesis. Despite their lower volatility, dioctylphthalate (DOP) and dibutylphthalate (DBP) were not used primarily because of their higher viscosity (16.63 cP and 55.41 cP respectively) compared to dodecane (1.41 cP) which might slow down the transfer of the amines to the organic phase [50].

3.3 Experimental

3.3.1 Materials and membranes

Support

Two hydrophobic microfiltration membranes were used as supports for the polymer preparation experiments: Accurel 1E-PP and Celgard 2500. These two supports are both flat sheet membranes, and made from polypropylene. Accurel is prepared by means of a thermally induced phase separation process, while Celgard membranes are made by stretching a homogeneous polypropylene film in one direction. The Accurel membranes have an interconnected pore structure while the Celgard membranes have not. Furthermore, the Celgard supports have slit-shaped pores, Accurel has round pores at its surface. Some characteristics of these membranes as obtained from the manufacturers are given in table 3.3.

Table 3.3. *Characteristics of the supports as obtained from the manufacturers.*

trade name	supplier	pore diameter [μm]	thickness [μm]	overall porosity [%]
Accurel 1E-PP	Akzo	0.2 (nominal)	95	69
Celgard 2500	Hoechst	0.075 x 0.25 (W x L)	25	45

Interfacial polymerization

Interfacial polymerization reactions were carried out using multifunctional amines and acid chlorides or amines and isocyanates. Piperazine (PIPA), 1,6-hexamethylenediamine (HMDA) and diethylenetriamine (DETA) were obtained from Fluka. Trans-2,5-dimethylpiperazine (DMPIPA) and 1,12-diaminododecane (DAD) from Janssen Chimica were used. Polyethyleneimine (Aldrich), abbreviated as PEI, is a polymer containing primary, secondary and tertiary amine groups. PEI is delivered as a 50 wt% solution in water with an average molecular weight of 50,000-60,000 g mol^{-1}. All amines were used without further purification. Hexamethylenediisocyanate (HMDI) and toluyene-2,4-diisocyanate (TDI) were obtained from Fluka. Multifunctional acid chlorides used are sebacoyl chloride SBCl (Janssen Chimica), terephthaloyl chloride TPhCl (Fluka) and trimesoyl chloride TMCl. Due to several supply problems, TMCl from three different sources was used (Fluka, Aldrich and Janssen Chimica), but these three all had the same product specifications. TMCl was placed in an oven (50 °C) to liquify it just before preparation of the solutions. After the oven treatment, the TMCl (melting point 34.5-36 °C) remained in the liquid state, possibly due to impurities present. Nevertheless, all monomers were used as received.

Generally, as organic solvent dodecane (Janssen Chimica) was applied. TPhCl did not dissolve in dodecane, so dibutylphthalate (Janssen Chimica) was used. The multifunctional amines were dissolved in either demineralized water or in Milli-Q water (Milli-Q water is demineralized water purified by means of a Milli-Q Plus Water Purification System from Millipore®). Diaminododecane was not soluble in water, so a nonaqueous solvent known from literature [6], ethyleneglycol (Merck) was used, although the solubility of DAD in this solvent was also limited. As acid receptor, sometimes sodiumhydroxide (Merck) was added. All the organic solvents and additives were used without further purification.

Carrier and solvent

As liquid membrane solvent, *o*-nitrophenyloctylether (*o*-NPOE) was taken because of its low solubility in water [1]. *o*-NPOE was obtained from Fluka and used without further purification. The carriers used were both long chain quaternary ammonium salts. Most experiments were carried out with trioctylmethylammoniumchloride, abbreviated to TOMA. The other carrier was tetraoctylammoniumbromide (TeOA). Both carriers were obtained from Fluka (purity TOMA and TeOA ~ 97 % and > 98 %, respectively) and used without further purification. In all cases, a carrier concentration of 0.2 M in *o*-NPOE was applied which is the same as applied by Neplenbroek *et al.* [1,2,54-56]. The *o*–NPOE/TOMA mixture was warmed slightly which was necessary to dissolve all the carrier. The carrier solutions were stored under nitrogen to prevent degradation of the *o*-NPOE. Since the colour of the carrier solution did not change in time, it was assumed that the *o*-NPOE did not degradate in time.

3.3.2 Membrane preparation and characterization

Interfacial polymerization

A circular piece of glass, having the size of the liquid membrane module, was used to cut a round part of support material out of a flat membrane sheet by means of a scalpel. For scanning electron microscopic characterization, a smaller piece was used. Care was taken not to touch its surface, and the polymerization always was performed on the same side of the support. Especially for Accurel the latter was important, since the two sides of the membrane were not identical as was revealed by scanning electron microscopy. Polymerization was always carried out on the 'shiny' side of the membrane. The membranes were impregnated with the acid chloride or diisocyanate solution (concentration usually 0.2 M). The acid chloride solutions were prepared just before use and care was taken to seal the bottles carefully in order to prevent as much as possible hydrolysis of acid chlorides. Excess solution was wiped off the surface of the membrane with a paper tissue. Immediately hereafter, the membrane was placed on top of a 0.2 M amine solution in water (PEI was dissolved in water in a concentration of 2.5 wt%), usually without acid receptor unless mentioned differently. After 15 minutes, the membrane was removed from the amine solution and washed with water and ethanol to remove unreacted materials and solvent from the composite membrane. Finally, the support with the toplayer was dried in air at room temperature. In all cases, to avoid damaging of the toplayer care was taken as much as possible not to touch the composite membrane.

It is questionable whether the relatively large pores of the underlying microfiltration membranes can be covered in one step without any large defects in the toplayer. Therefore, to obtain an indication of the presence of large defects and to get an impression of the thickness of the toplayer, part of the composites were examined with scanning electron microscopy (SEM). Cross section samples were prepared by cryogenic breaking, i.e. the sample was immersed for 5 minutes in a water/ethanol mixture and subsequently broken in liquid nitrogen. Flat samples were 'glued' on the sample holder using conducting carbon. After sputtering the samples with gold (Balzer Union SCD 040 sputtering apparatus, 3 minutes, 15 mA), they were examined with a Jeol JSM T 220A scanning electron microscope (at 20 kV).

Gas permeation experiments were carried out too to get an impression whether the toplayer contained large defects. Circular pieces of the composites were placed in a gas permeation cell, after which gas fluxes were measured with pure O_2 and N_2 at a pressure of 1 bar using soap film capillaries. All tests were performed at room temperature.

Pore size analysis of uncoated membranes was carried out on a Coulter® Porometer II (ASTM F316-80, 1980; B.S. 6410-1980). As pore wetting liquid, Coulter® Porofil was used. The diameter of the sample holder was 25 mm.

3.3.3 Permeability measurements

SLM preparation

A small amount of carrier solution (either 0.2 M TOMA or 0.2 M TeOA in *o*–NPOE) was spread on the bottom of a petri-dish. The SLMs, either with or without toplayer, were prepared by soaking them in this solution for at least 15 minutes. When a toplayer was present on the support, this toplayer was directed upwards. Supports with a toplayer needed a longer impregnation time, up to at least one hour, since the enclosed air in the pores could not escape so easily. When the SLM was completely transparent, it was removed from the petri-dish. Attached liquid was removed from the surface of the membrane by wiping it very carefully with a tissue. The amount of soaked LM-liquid was calculated by determining the mass of the membrane before and after impregnation.

Flux determination

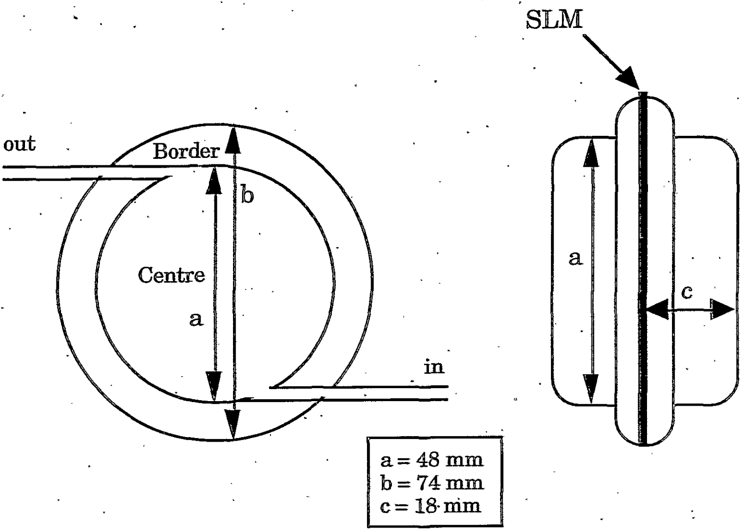


Figure 3.4. *Dimensions of the membrane module. Adapted from references 1 and 54.*

After impregnation, the liquid membrane, with the toplayer to the feed side, was clamped between two cell halves as shown in figure 3.4. The membrane module was placed in one of the experimental set-ups drawn in figure 3.5. Buffer vessels, pulsation damping vessels and the membrane module were all made of glass and connected to each other by silicone rubber tubes. Initially, experiments were carried out using set-up (a) in figure 3.5. which did not contain pulsation dampers and was placed in a thermostated room of 25-26 °C. The feed volume was always 100 ml, the strip volume 90 ml. Later on, set-up (b) was used for the experiments. This set-up contained thermostated buffer vessels keeping feed and strip (both 130 ml) at a constant temperature of 25 °C. Furthermore, pulsation damping vessels made out of extra thick glass to reduce heat effects were present which minimized pulsations caused by the peristaltic pumps.

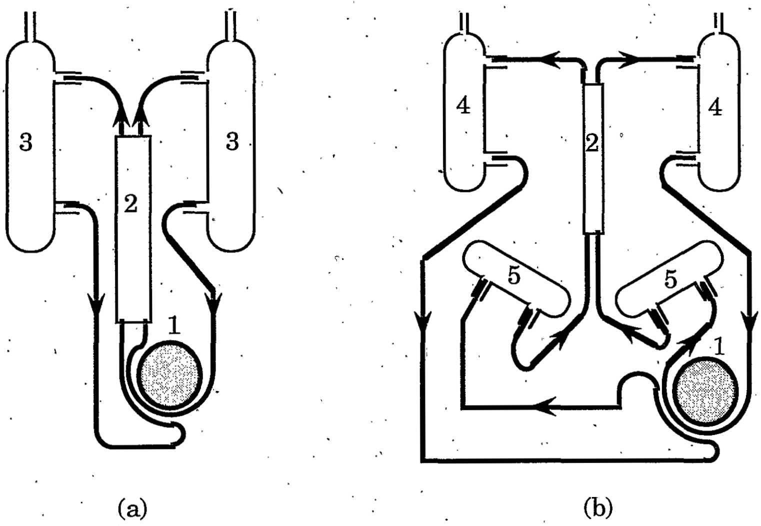


Figure 3.5. *Schematic representation of the experimental set-up for nitrate flux measurements. (a) set-up, placed in a thermostated room, (b) set-up with thermostated buffer vessels and pulsation buffers (1 = pump, 2 = membrane module, 3 = buffer vessel, 4 = thermostated buffer vessel, 5 = accumulator).*

After the membrane module was placed in the set-up, the system was filled with the aqueous feed and strip solutions. The feed consisted of a 4 * 10^{-3} M $NaNO_3$ solution (Merck), while a 4 M aqueous solution of NaCl (Merck) was applied as strip phase. By means of Masterflex® peristaltic pumps feed and strip were circulated around with a constant water flow velocity of 5.5 ml s^{-1}. Aqueous boundary layer resistances were minimal at this velocity [1,54]. In the membrane module, the aqueous phases were flowing parallel to the membrane. Periodically, samples of about 1 ml were taken from the feed buffer vessel. Nitrate and chloride concentrations in these samples were measured by HPLC (Waters IC-PAK™ anion column using a Millennium™ data station). By assuming a constant feed volume, the nitrate flux J through the liquid membrane can be calculated by

$$J = -\frac{d[NO_3^-]}{dt}\frac{V}{A}, \qquad (1)$$

where J is the nitrate flux in mol cm^{-2} s^{-1}, $d[NO_3^-]/dt$ the linear decrease of the nitrate feed concentration in time, V the feed volume (in ml) and A the membrane area in contact with the aqueous phase (18.1 cm^2).

3.3.4 Stability measurements

To simulate long term experiments, the following procedure was followed. After determination of the initial flux, the feed solution was replaced by a 10^{-4} M aqueous nitrate solution. Application of the SLM to a feed solution with a low salt concentration increases the instability of the membrane, as explained in chapter 2. After 20 to 21 hours of 'destabilization', both feed and strip were replaced by fresh $4 * 10^{-3}$ M NO_3^- and 4 M Cl^- solutions, respectively. The flux was determined again as described before in section 3.3.3. As will be shown later, in this way an uncoated membrane using TOMA as carrier lost all its flux within 1 day, so a fast check on stability improvement is possible. To obtain an indication of loss of LM-phase from the support, the masses of the SLMs before and after the flux measurements were determined. The difference between the two masses is defined as the the LM-loss.

3.4 Results and discussion

3.4.1 Uncoated membranes

Support characterization

In table 3.4, results of the pore size determination test of the supports as obtained by Coulter® porometry are given.

Table 3.4. *Pore sizes as determined by Coulter® porometry.*

membrane	min. pore size [μm]	max. pore size [μm]	MFP† [μm]	pore size given by supplier [μm]
Accurel	0.177	0.275	0.247	0.2
Celgard 2500	0.063	0.083	0.077	0.25 x 0.075

†: mean flow pore size

For the Accurel membrane, agreement with the manufacturer's data is rather well. In the calculation of the pore sizes from the measurements, it is assumed that the pores have a cylindrical shape. Because pores of the Celgard membrane are slit-shaped, care must be taken with the interpretation of the Coulter results. The obtained pore sizes for this membrane are the smallest dimensions of the pores, in this case the width of the pore. These agree with the supplier's data.

Nitrate fluxes and LM-loss

The results for uncoated SLMs using Accurel or Celgard as support are summarized in table 3.5. Initial fluxes of TeOA and TOMA SLMs are in the order of 16-20 * 10^{-10} mol cm^{-2} s^{-1}, which is in reasonable agreement with data presented by Neplenbroek *et al.* [1,54,55,57]. Small differences between our measurements and those of Neplenbroek *et al.* are due to the fact that the different batches of support film used have slightly different properties. It is known that because TOMA-Cl is much more surface active than TeOA-Br, SLMs with the first carrier are much less stable than the latter ones. Indeed this is shown by the data in table 3.5. SLMs containing TOMA as carrier, have zero flux after one day, in contradiction to TeOA membranes which show only a very small decrease in flux. So, by using TOMA as carrier and applying 'destabilization' conditions in between two flux measurements, stability experiments can be carried out in a fast way. In general, the data in table 3.5 show a good reproducibility within 10 % accuracy.

Table 3.5. *Nitrate fluxes and stability of uncoated SLMs.*

support	carrier	initial flux [10^{-10} mol cm^{-2} s^{-1}]	flux after 1 day [10^{-10} mol cm^{-2} s^{-1}]	LM-loss [wt%]
Accurel	none	0	0	3.4
	none	0	0	3.4
Accurel	TeOA	20.4	18.6	n.d.
		19.9	18.5	n.d.
		20.4	18.4	5.9
		22.2	17.9	4.1
Accurel	TOMA	19.2	1.6	5.5
		17.1	~0	6.9
		18.9	~0	5.9
Celgard	TOMA	16.2	1.4	n.d.

n.d. = not determined

When no carrier was present the LM-loss, or the loss of *o*-NPOE, after 1 day of degradation was in the order of 10-15 mg (3.4 wt%). This is remarkably high considering its very low solubility [1]. Other effects might be important. LM-phase might be pressed out of the support due to the way the two cell halves are squeezed together. In almost all cases, a slightly yellow substance was observed at the outside of the cell. Since the LM-phase used is always yellow of colour, this might indicate that this substance is coming from the pores of the support. Consequently, the observed mass decrease is not only due to loss of LM-phase into the aqueous feed or strip phases. Care must therefore be taken in the interpretation of LM-loss data throughout the rest of this thesis. LM-losses of the carrier containing membranes were all in the order of 6 wt%, slightly higher than that of SLMs containing solely *o*-NPOE.

3.4.2 Influence of support modification on nitrate flux and membrane stability

This section covers the characterization of a number of SLMs with different toplayers at the feed side. Initial nitrate fluxes through these modified SLMs are determined, as are their stabilities. The objective was to find candidates for the stabilization of SLMs.

Initial nitrate fluxes

In table 3.6, results of SLMs with a toplayer are summarized. From a comparison of these data with those in table 3.5, it can be seen that the majority of the applied toplayers do not seriously affect the initial nitrate flux. In most cases, the nitrate flux is equal or only slightly lower than the flux for an uncoated SLM. This indicates that most of the transport of anions is not hindered by most of the investigated toplayers. This might be due to a sufficient large mesh- or pore size as a result of the swelling of the toplayers in the aqueous feed phase to such an extent that the ions can pass easily. Only nylon-6,10 toplayers prepared with HMDA and SBCl as monomers clearly show an initially lower flux. This seems contradictory to the conclusion of Blais that nylon-6,10 is not a suitable material for reverse osmosis membrane because of its low salt retention [42]. However, our results show that in those cases where the toplayer is not suitable for RO applications, the resistance to transport in liquid membranes might still be too high. The lower flux might indicate either an increase in toplayer thickness compared to the other materials, or a more compact layer, which both result in a decrease of salt permeability. As will be shown in section 3.4.3, the thickness of nylon-6,10 toplayers is not significantly different from the other composites, so a denser structure seems more logical. Lower permeabilities for nylon-6,10 microcapsules, compared to PIPA/TPhCl ones, were observed by Ishizaka *et al.* [45]. They contributed this to a difference in the water structure in and around the microcapsules. The nylon-

6,10 membranes were considered to be more dense, and therefore the effect of water structure is more important. The polymer chains of nylon-6,10 capsules were thought to be more entangled, restricting swelling of the membrane and thus lowering the permeability for ions.

Table 3.6. *Nitrate fluxes and stabilities of coated SLMs: polymer selection. LM-phase: 0.2 M TOMA in o-NPOE. Support: Accurel.*

toplayer	acid receptor*	initial flux [10^{-10} mol cm^{-2} s^{-1}]	flux after 1 day [10^{-10} mol cm^{-2} s^{-1}]	LM-loss [wt%]
HMDA/SBCl	NaOH	8.3	1.7	8.6
	NaOH	6.9	1.6	10.1
	-	11.3	1.6	7.1
	-	12.4	1.7	13.8
DAD/SBCl†	-	12.7	n.d.	7.2
	-	16.3	0	9.3
DETA/TPhCl[1]	-	19.8	1.8	7.9
	-	19.8	1.3	9.0
PEI/TMCl[2]	-	23.0	1.3	7.3
PEI/TMCl[2,3]	-	19.7	12.4	5.3
		21.5	7.1	7.0
PIPA/TMCl	NaOH	14.8	2.7	12.2
	NaOH	13.9	2.1	9.7
	-	15.7	12.2	14.3
	-	15.3	13.5	12.1
DMPIPA/TMCl	-	15.1	1.1	12.3
HMDA/HMDI[1]	-	15.4	1.6	5.6
	-	13.2	0	13.9
EDA/TDI[1]	-	16.2	1.8	5.8

*: concentration 0.4 M. †: DAD 0.15 M in ethyleneglycol, SBCl 0.3 M in dodecane. [1]: organic solvent: DBP. [2]: PEI 2.5 wt% in water. [3]: crosslinked 1 hour, 80 °C. n.d. = not determined.

The addition of an acid receptor to the aqueous amine solution reduces salt permeability as is shown clearly by the HMDA/SBCl data. The effect of acid acceptors on salt rejection was also observed in reverse osmosis membranes, *e.g.* for the system PIPA/TMCl, by Cadotte *et al.*, who subscribed the effect of acid acceptors to an increase in acid chloride hydrolysis [8]. This would lead to a lower salt rejection. Nevertheless, no clear evidence of an increase in hydrolysis was presented. The effect of acid receptors on properties of the toplayer, is treated in more detail in chapter 4.

Remarkable results were obtained for the system polyethyleneimine and trimesoyl chloride. Initial nitrate fluxes for both membranes were significantly higher than those for uncoated membranes (see table 3.5). The heat-cured membrane showed a somewhat lower nitrate flux than the other PEI/TMCl membrane due to internal crosslinking of the polymer chains. The observed flux increase with respect to uncoated supports is contradictory to our expectations. Both PEI and TMCl have the capability of crosslinking, either because of their functionality larger than two or by a post-treatment by heat-curing. It is believed that the higher the crosslinking density, the more effective the membrane is in solute rejection [30]. However, it is not expected that the nitrate flux is *higher* than that of an uncoated membrane, when the resistance towards transport is fully determined by the diffusion of the carrier through the membrane, as assumed by Neplenbroek *et al.* [1,54]. The presence of an extra resistance, such as a toplayer, consequently can only result in a flux decrease. This indicates that the overall resistance is not only determined by a diffusional resistance in the liquid membrane. The presence of a toplayer on the feed side might influence the reaction between carrier and nitrate, or influence the supply of nitrate ions. As will be shown later, interfacially polymerized toplayers have a certain surface roughness. If the carrier has the possibility to penetrate into this layer, the effective membrane area increases which might, in some cases, result in a flux increase. It is however not clear why this effect is not observed for other toplayers.

Stability

Fortunately, most supported liquid membranes with a toplayer show a good nitrate flux. However, in almost all cases the nitrate flux, measured after one day with a fresh feed solution was nil. The heat-cured PEI/TMCl toplayer has still a reasonable flux after 1 day of degradation, although the flux loss is already at least 37 %. Best results, however, were obtained when a toplayer of piperazine and trimesoyl chloride was applied on the support and no acid receptor was added to the diamine solution. After one day, flux decreased only with approximately 17 %. Toplayers of PIPA and TMCl, prepared under these conditions, have the right properties to retain the carrier inside the liquid membrane and suppress the formation of emulsion droplets. Therefore, it was decided to investigate this system in more detail. The results are described in chapter 4.

Theoretically, every applied toplayer should be able to prevent emulsion formation since the deformation of the liquid membrane meniscus is decreased and loss of LM-phase by emulsion formation hindered. The fact that nearly all investigated materials do not show any stability improvement, might be explained in several ways. Firstly, the toplayers might be too open to prevent completely the deformation of the LM-meniscus, so loss of carrier still takes place. Neplenbroek *et al.* showed already that the stabilizing effect of PVC toplayers is dependent on the mesh size of the PVC [1,2]. The smaller this mesh size (the less 'open' the PVC gel), the better the stabilization. Secondly, the systems with TOMA as carrier might be too instable. If there is a stabilizing effect by application of a toplayer, it might not be seen at all when all the carrier is still lost after 1 day of degradation and thus also no flux can be detected. Milder degradation conditions or flux measurements after a shorter period might give a decisive answer.

Thirdly, loss of membrane liquid might not only occur by means of emulsion formation. As mentioned in chapter 2, carrier molecules can be lost from the membrane phase by simply dissolving into the aqueous feed or strip phases. Neplenbroek *et al.* found the solubility of the quaternary ammonium carriers applied to be sufficiently low [1]. For TOMA-Cl, literature values for the solubility in the range 10^{-2} - 10^{-3} M are reported by Okahata *et al.*, although the purity of their TOMA-Cl and the exact method of the solubility determination were not given [58]. Taking the low absolute amount of carrier present in the LM-phase at the beginning of the experiment in consideration ($5.6 * 10^{-5}$ mol for an Accurel membrane and a 0.2 M carrier solution), together with the feed and strip volume, this is far below the maximum solubility in water. Although nothing is known about distribution coefficients of the carrier between *o*-NPOE and water, the effect of carrier dissolving in the water phase might not be neglected. When the LM-phase or the carrier alone can penetrate into the polymeric toplayer, this layer might not prevent the loss of carrier by dissolution. A reconsideration of the LM-degradation mechanism is presented later on in this thesis in chapter 7.

The effect of acid receptor addition to the PIPA solution on stability 'improvement' is astonishing. By adding 0.4 M NaOH to the aqueous amine solution during the preparation of the toplayer, the flux is completely lost after 1 day. As mentioned before, it is known that the presence of acid receptors during polymerization influences the properties of reverse osmosis membranes. In chapter 4 this effect is studied in more detail.

It should be pointed out that it is not likely that PIPA and TMCl is the only monomer pair which improves the stability of SLMs in our nitrate removal system. Interfacial polymerization of other monomers might result in an increased stability, but maybe at other conditions than investigated during the polymer screening described here. The organic solvent, the concentration ratio between the reactants, the addition of phase transfer catalysts or the absolute monomer concentrations are for instance factors which can be varied. From literature it is known that such variables influence polymer properties as the inherent viscosity (thus the molecular weight) and the polymer yield [5,6].

Reproducibility

Comparing the reproducibility of coated and uncoated SLMs (tables 3.5 and 3.6), it is clear that the data of coated membranes are more difficult to reproduce. Especially the LM-losses are widely scattered for one and the same system. It lasted longer before the SLMs obtained a stable weight after the flux determination. This is due to the more hydrophilic character of the toplayer, which absorbs water which will not be released immediately after the experiment is stopped. It is however not certain whether one measures only the mass of modified support and LM-phase or whether also residual water is included. The same is valid for the determination of the mass of the support before impregnation with LM-phase: residual organic or aqueous phase might still be present after the polymerization. This all indicates that the determination of LM-loss by simply weighing is much more inaccurate in the case of coated supports. Therefore, the LM-losses are not discussed into detail. It is only mentioned here that there is a tendency for coated SLMs to have a larger LM-loss than uncoated membranes.

3.4.3 Characterization

Gas permeability

Table 3.7. *Oxygen and nitrogen fluxes and selectivity α of several interfacially polymerized supports. Support: Accurel. Thickness of the composites 96-105 μm.*

toplayer	O_2 flux [$cm^3\ cm^{-2}\ s^{-1}\ bar^{-1}$]	N_2 flux [$cm^3\ cm^{-2}\ s^{-1}\ bar^{-1}$]	α (O_2/N_2)
none	n.d.	8.4 [59]	-
PIPA/TPhCl	2.6	2.7	0.96
PIPA/TMCl	0.0083	0.0093	0.89
PIPA/SBCl	0.12	0.13	0.92

n.d. = not determined.

Results of some gas permeation measurement using PIPA as amine are given in table 3.7. These data show that the prepared toplayers do not show gas separation properties due to the presence of defects and/or pores. The fluxes were the lowest when PIPA and TMCl were used as monomers, possibly due to their ability of crosslinking. The crosslinking reduces the possibilities of polymer chains to allow the passage of gas molecules. The ratio of oxygen to nitrogen fluxes is almost the same as the Knudsen selectivity (0.94 for O_2/N_2). Not too many conclusions can be drawn from these measurements. The actual situation as protecting barrier in an SLM is quite different from the gas permeation conditions. It is not our goal to prepare dense gas separation membranes since the layers should allow the transport of ions.

SEM characterization

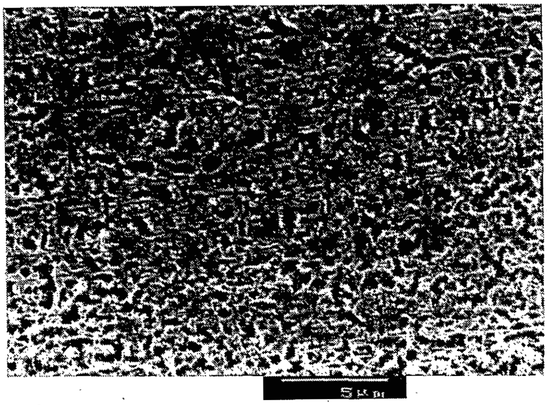
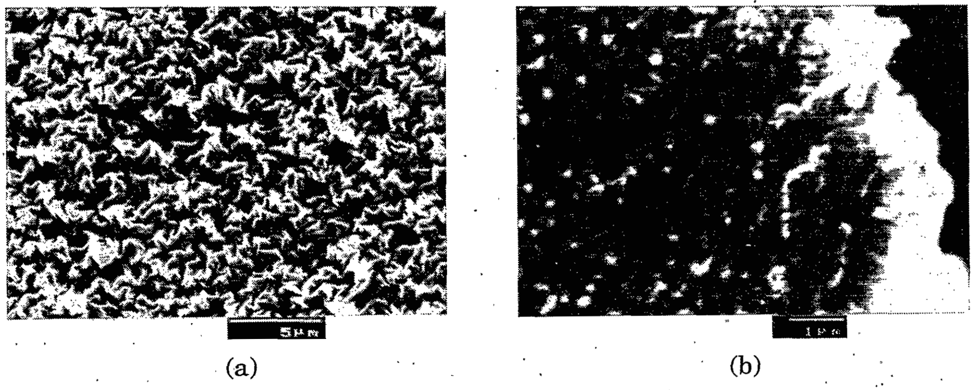


Figure 3.6. *SEM photograph of Accurel 1E-PP. Uncoated, 'shining side' (5,000x).*

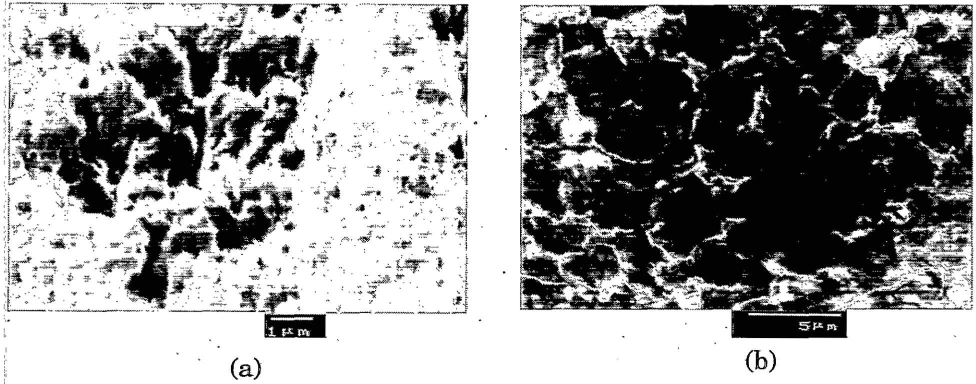


(a) (b)

Figure 3.7. *SEM photographs of Accurel + PIPA/TMCl toplayer (no acid receptor). a) Surface view (5,000x). b) Cross section (15,000x).*

Scanning electron microscopy (SEM) was used to observe toplayer morphology, thickness of the toplayer and the presence of large defects. In figure 3.6, a surface view of the support membrane is shown. The dark parts are the pores, the lighter parts the membrane material, polypropylene. The high surface porosity can be seen which is necessary for SLMs to obtain a high area where ions and carrier can get in contact.

In figure 3.7, scanning electron microscopy photographs of a toplayer of piperazine and trimesoyl chloride are given. The membrane surface texture is quite particular with its folds and waves. Such structures are also observed by Cadotte *et al.* [8] for PIPA/TMCl reverse osmosis membranes and for Toray's UTC-70 RO membranes [30]. It is believed that this membrane surface texture is a result of swelling phenomena during polymerization. This swelling results in an expansion of the membrane in the plane of its formation. When the polymerization continues within the swollen membrane, this structure is permanent, also after drying for SEM preparation. This structure was also observed when PIPA and TMCl were polymerized on Celgard as support. From figure 3.7b it can be seen that the thickness (of the dried toplayer) is 3 to 5 μm.



(a) (b)

Figure 3.8. *SEM photographs of Accurel + toplayer. a) Nylon-6,10, polymerized with 0.4 M NaOH as acid receptor (10,000x). b) PEI + TMCl heat-cured 1 hour at 80 °C (5,000x).*

When different monomers were used for the interfacial polymerization, in general different surface morphologies were observed with SEM. This is illustrated in figure 3.8 for nylon-6,10 and heat-cured PEI/TMCl. Although nylon-6,10 toplayers show surface roughness, it is clear that the typical 'hill and valley' structure, as observed with PIPA/TMCl layers, is not present. SEM reveals many holes or spots in the toplayer, from which one might not conclude however that the toplayer contains large defects since nothing is known about the polymeric layer directly under the surface. Figure 3.8b shows even an almost flat toplayer containing a defect, possibly due to the heat treatment. In general, toplayer thicknesses were all in the range of 2 to 5 μm. An exception were the PEI toplayers with thicknesses below 1 µm. It is difficult for PEI to pass the initially formed polymeric layer to react with the other monomer since PEI is a polymer. Therefore, at equal polymerization times, less polymer is formed and the thickness will be lower when densities of the polyamides do not differ too much.

3.5 Conclusions

A number of toplayers was successfully applied on top of Accurel microfiltration membranes by means of the interfacial polymerization technique. Although the pores of the underlying support were significantly larger than usual in the synthesis of reverse osmosis membranes, all pores were covered by the polymeric layer. SEM could not reveal any large defects, although gas permeation measurements showed the presence of a pore structure

The modified supports were used for the preparation of supported liquid membranes for nitrate transport. Most of the toplayers did not hinder the transport of nitrate and chloride ions, since their fluxes were almost equal to those of uncoated SLMs. However, only a few toplayers could increase the stability of the investigated liquid membranes. Toplayers of piperazine and trimesoyl chloride gave the most promising results and will be investigated in more detail in the following chapters.

3.6 References

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Appendix to chapter 3

Structural formulas of the applied monomers

$H_2N-(CH_2)_2-NH_2$

ethylenediamine (EDA)

$H_2N-(CH_2)_6-NH_2$

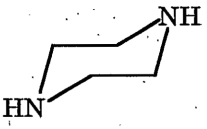
hexamethylenediamine (HMDA)

$H_2N-(CH_2)_{10}-NH_2$

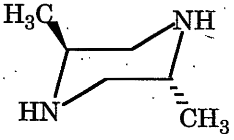
diaminododecane (DAD)

$H_2N-(CH_2)_2-NH-(CH_2)_2-NH_2$

diethylenetriamine (DETA)



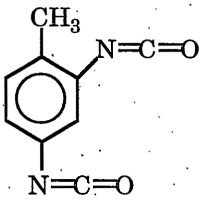
piperazine (PIPA)



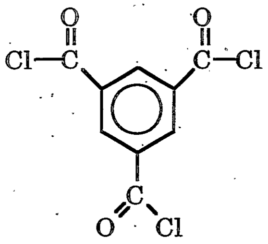
trans-2,5-dimethylpiperazine (DMPIPA)

$O=C=N-(CH_2)_6-N=C=O$

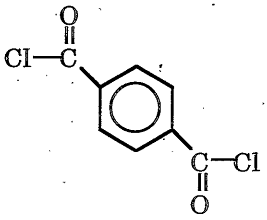
hexamethylenediisocyanate (HMDI)



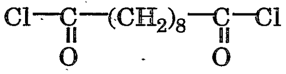
toluyene-2,4-diisocyanate (TDI)



trimesoyl chloride (TMCl)



terephthaloyl chloride (TPhCl)



$$\mathrm{Cl-\underset{\underset{O}{\|}}{C}-(CH_2)_8-\underset{\underset{O}{\|}}{C}-Cl}$$

sebacoyl chloride (SBCl)

4

STABILIZATION OF SUPPORTED LIQUID MEMBRANES BY INTERFACIAL POLYMERIZATION

Part II: Investigation of piperazine / trimesoyl-chloride toplayers

SUMMARY

In this chapter, the influence of piperazine/trimesoyl chloride (PIPA/TMCl) toplayers on nitrate flux and SLM stability is investigated. A number of reaction parameters is varied systematically to optimize the system. Furthermore, several techniques (SEM, ATR-FTIR, XPS) are used to characterize the modified supports

The long term experiments were very promising. For Accurel supports with a PIPA/TMCl toplayer, the best results did not show any flux decrease after 350 hours, whereas an uncoated membrane lost its flux completely within 1 day. Coated teflon membranes still had a reasonable flux after 650 hours. Other toplayers, prepared with piperazine-like monomers and TMCl, also showed stability improvements. The low initial nitrate fluxes without any improvement of the membrane stability when an acid acceptor was added to the amine solution during the interfacial polymerization reaction, could not be explained.

4.1 Introduction

It was demonstrated that interfacially polymerized layers of piperazine (PIPA) and trimesoyl chloride (TMCl) are able to improve the stability of supported liquid membranes (SLMs) for the removal of nitrate from water [1]. A few preliminary experiments showed a very low flux decrease after 1 day of operation, while uncoated membranes had no flux at all after the same period. However, no long term experiments were carried out. Furthermore, the polymerization reaction for PIPA/TMCl might be optimized. Other monomer pairs, in chemical structure almost identical to PIPA or TMCl, might be found which also might improve the stability of SLMs for nitrate removal.

It is known that the properties of an interfacially synthesized polymer depend on a large number of factors, including [2,3]

- chemical reaction rate
- polymerization time
- partition coefficients of reactants
- absolute concentration levels of reactants
- concentration ratio of reactants
- hydrolysis of acid chlorides
- polarity and type of solvent used during the reaction
- presence and transfer rate of additives (acid acceptors, surfactants)

Each of these factors influences in its own way the final molecular weight of the polymer and the optimal reaction conditions. The effect of all these variables is described by Morgan *et al.* [2,3].

In this chapter, a systematic investigation is presented of some of the above mentioned variables in order to optimize the PIPA/TMCl system and investigate their influence on long term stability. Furthermore, these monomers are varied systematically to investigate the influence of small variations in monomer structure on the stabilization of SLMs. Supports with a toplayer are chemically analyzed by means of infrared spectroscopy and X-ray photoelectron scattering (XPS). The thickness and surface texture of the toplayers are investigated using scanning electron microscopy (SEM) and high resolution-SEM (HR-SEM). Finally, the support material is varied to elucidate its influence on nitrate flux and stability.

4.2 Experimental

4.2.1 Materials and membranes

Support

In table 4.1, for the complete set of supports that are used in this investigation, the properties as obtained from the manufacturer are given. Most experiments were carried out with Accurel 1E-PP as support. The Z2D1 and Z2E1 membranes were kindly supplied by the Dutch State Mines (DSM) and are not commercially available. Pore sizes and pore size distributions of these supports were measured on a Coulter® Porometer II (ASTM F316-80, 1980; B.S. 6410-1980), using Coulter® Porofil as pore wetting liquid.

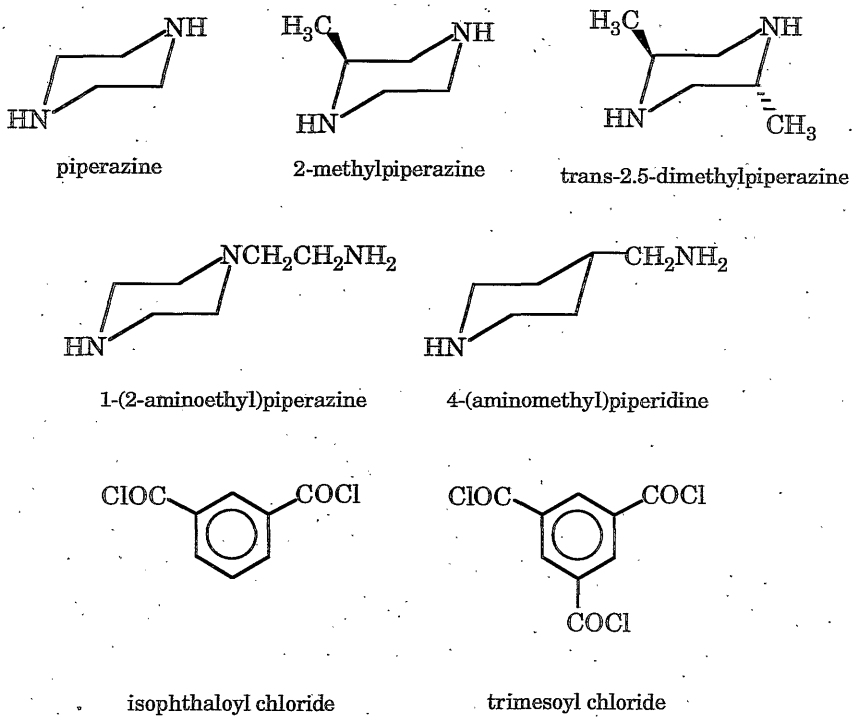
Table 4.1. *Overview of the supports used. Pore sizes, porosities and thicknesses as obtained from the manufacturer.*

trade name	supplier	material	pore size [μm]	porosity [%]	thickness [μm]
Accurel 1E-PP	Akzo	PP	0.20	69	95
Durapore GVHP	Millipore	PVDF	0.22	75	125
Durapore HVHP	Millipore	PVDF	0.45	75	125
SM 11807	Sartorius	PTFE	0.2	-	65
Z2D1	DSM	PE	± 0.5	-	-
Z2E1	DSM	PE	<< 0.5	-	-

-: not given by the supplier.

Interfacial polymerization

Throughout this chapter, interfacial polymerization reactions were carried out using several diamines and multifunctional acid chlorides. Piperazine (PIPA) and 1–(2-aminoethyl)piperazine (AEPIPA) were obtained from Fluka. 2-Methylpiperazine (MPIPA) and trans-2,5-dimethylpiperazine (DMPIPA) from Janssen Chimica were used. 4-(Aminomethyl)piperidine (AMPIP) was obtained from Aldrich. Isophthaloyl chloride IPhCl (Janssen Chimica) and trimesoyl chloride TMCl were used as acid chlorides. TMCl from three different suppliers was used (Fluka, Aldrich and Janssen Chimica) due to several supply problems. They all had the same product specifications. TMCl was heated in an oven (50 °C) to liquefy it for a better handling. The different piperazines and acid chlorides applied are given in figure 4.1.



piperazine 2-methylpiperazine trans-2.5-dimethylpiperazine

1-(2-aminoethyl)piperazine 4-(aminomethyl)piperidine

isophthaloyl chloride trimesoyl chloride

Figure 4.1. *Structure of the piperazine, - derivatives and acid chlorides as used in this chapter.*

Usually, dodecane (Janssen Chimica) was used as solvent for IPhCl and TMCl unless mentioned differently. To investigate the influence of the organic solvent on the properties of the toplayers, experiments were carried out using decane, tetradecane, dimethylphthalate (DMP), dibutylphthalate (DOP) and dioctylphthalate (DOP), all obtained from Janssen Chimica, as organic solvents for the interfacial polymerization. The diamines were dissolved in demineralized water or in Milli-Q water (Milli-Q water is demineralized water purified with a Milli-Q Plus Water Purification System from Millipore®). All solvents were used without further purification.

Several polymerizations were carried out in the presence of acid acceptors or other additives. Acid acceptors used were K_2CO_3 and NaOH (both Merck). In a few cases, hydrochloric acid (Merck, 37%) was added to the aqueous amine solution.

Carrier and solvent

As organic solvent for the carrier, *o*-nitrophenyloctylether (*o*-NPOE) was taken because of its low solubility in water [4]. Part of the experiments were carried out with *o*-NPOE obtained from Fluka which was used without further purification. Later on *o*-NPOE was not available anymore on the commercial market. Therefore, it was synthesized in our laboratories according to the recipe given in appendix A. The synthesized *o*-NPOE was a yellow, viscous liquid with a purity of 99.8 % (as determined by gas chromatography with a capillary column type Z5) and yielded equal nitrate fluxes as the 'Fluka' *o*-NPOE SLMs.

The carriers used were all quaternary ammonium salts. Both trioctylmethylammoniumchloride (TOMA) and tetraoctylammoniumbromide (TeOA) were obtained from Fluka and were used as received. Both carriers were solids and had purities of ~ 97 % (TOMA) and > 98 % (TeOA). A carrier concentration of 0.2 M in *o*-NPOE was used throughout the experiments described in this chapter. Carriers and organic solvent are identical to those applied by Neplenbroek *et al.* in their studies [4-9].

4.2.2 Interfacial polymerization

The majority of the interfacial polymerizations were carried out in the same way as described before [1]. A circular part of the support material (diameter 74 mm) was impregnated with the organic acid chloride solution (in general, a concentration of 0.2 M was used). Excess solution was wiped off the surface of the impregnated support with a paper tissue. Immediately thereafter, the support was placed on top of the diamine solution. Unless indicated differently, a diamine concentration of 0.2 M was used. For Accurel membranes, care was taken that the polymerization took place at the 'shiny' side of the membrane, since the two sides were not identical. Scanning electron microscopic investigations showed this 'shiny' side to be completely flat while the 'dull' side was more lumpy. It was expected that the polymerization reaction was more reproducible when carried out on the 'shiny' side. After a certain polymerization time, typically 15 minutes unless mentioned differently, the membrane was removed from the diamine solution. After washing the membrane one time with ethanol and water to remove unreacted species, the composite membrane usually was dried in air overnight. To investigate the influence of drying, several experiments were carried out where the supports were dried in a vacuum oven (30 °C) after polymerization. The mass of the toplayer on the support was determined by weighing the support under dry conditions before and after polymerization.

When the above mentioned polymerization method was used, it was observed that the membranes had the tendency to curl up during polymerization, especially at higher monomer concentrations or when the support was relatively thin. This made further characterization rather difficult and resulted in an unequal thickness of the prepared toplayer. Furthermore, reproducibility of the SLM flux measurements might become problematic. Therefore, a mould was designed to clamp the membrane (see figure 4.2). It consisted of an open glass cylinder with a tube to withdraw the reactants. The application of the toplayer was as follows. Firstly, the support membrane was washed with ethanol and ether to remove dust particles and dirt, and subsequently dried. Thereafter, the support was impregnated with the organic monomer solution, excess solution was wiped away by means of a tissue and the support was clamped in between the flat, clean glass plate and the cylinder. Next, 40 ml Milli-Q water was introduced carefully into the mould. Under stirring (ca. 60 rpm), in one minute 10.00 ml PIPA solution (1 M) was introduced in the mould after which the reaction took place for another 14 minutes (still stirring with 60 rpm). Then the amine solution was removed from the mould via the tube. By rinsing the composite in the mould with approximately 0.5 l Milli-Q water, remaining amines were removed from the surface. Finally, the membrane was taken out of the mould and placed in a petri-dish containing ethanol to remove residual reactant and organic solution from the pores of the support. The membrane was stored in ethanol until further use to prevent drying effects. The mould was only used in those cases when stated explicitly.

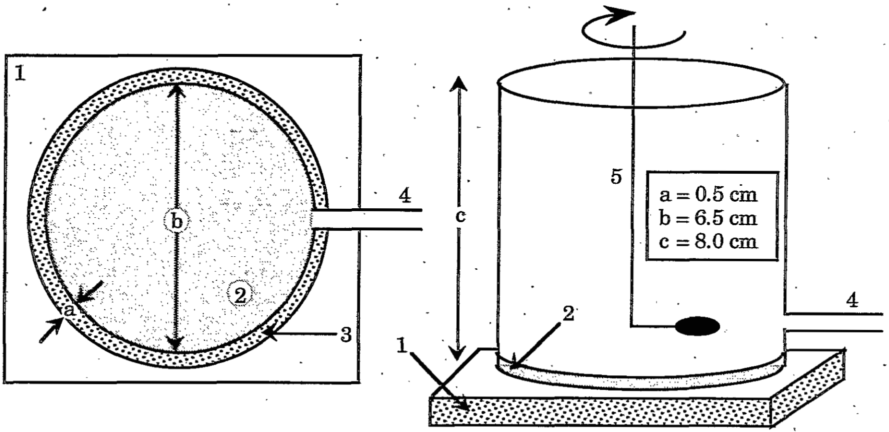


Figure 4.2. *Mould used for the preparation of composite membranes by interfacial polymerization. Left side: top view. Right side: side view (1 = glass plate, 2 = membrane, 3 = glass-wall, 4 = outlet for reactants, 5 = stirrer).*

4.2.3 Characterization

The supports with a toplayer were characterized by different means to elucidate toplayer thickness, surface texture and chemical composition. By placing the membranes in an ethanol/water bath for about 5 minutes and breaking them in liquid nitrogen, cross section samples for scanning electron microscopy (SEM) investigation were prepared. Flat samples were simply fixed to the sample holder using conducting carbon. After sputtering the samples with gold (Balzer Union SCD 040 sputtering apparatus, 3 minutes, 0.1 mbar, 15 mA), they were examined with a Jeol JSM T 220A scanning electron microscope (accelerating voltage 20 kV). To obtain higher resolution images at lower accelerating voltages, field emission SEM (FE-SEM), or high resolution SEM (HR-SEM), was used. Cross section samples were freeze-dried, broken and glued on the sample holder by means of conductive carbon. Before examination on a Hitachi S800 HR-SEM, the samples were sputtered with Au-Pd in a sputtercoater. During sputtering, the samples were cooled to obtain a very fine distribution of the gold. Accelerating voltages were usually between 4-6 kV.

To obtain information on the chemical composition of the toplayers, X-ray Photoelectron Scattering (XPS) and Attenuated Total Reflectance-FTIR (ATR-FTIR) were used. The XPS measurements were done on a Kratos DS800 (Mg-Kα X-ray source). ATR-FTIR was carried out on a Bio-Rad FTS-60 FTIR spectroscope using a KRS-5 crystal.

4.2.4 SLM preparation

A small amount of carrier solution, either TeOA or TOMA in *o*-NPOE (concentration 0.2 M), was spread on the bottom of a petri-dish. A dry support membrane was placed in the carrier solution. When a toplayer was present, it was kept upwards. For uncoated membranes an impregnation time of about 15 minutes was used. For supports with a toplayer longer impregnation times (up to one hour or even more) were necessary. When the support was fully transparent, it was assumed to be fully impregnated and it was removed from the petri-dish. Residual LM-phase was wiped away very carefully with a tissue. The amount of soaked liquid membrane phase was determined by weighing the membrane before and after impregnation.

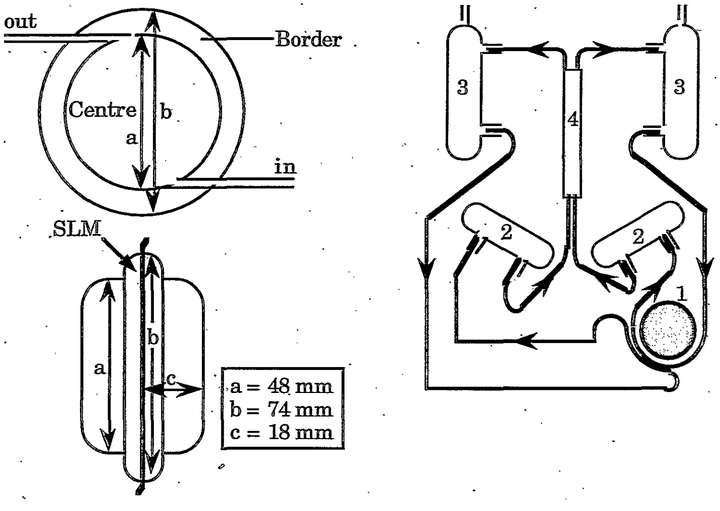
In case the composite supports were kept in the wet state (the polymerizations using the mould), a somewhat different impregnation method was applied. The composite membrane was removed from the ethanol bath and placed in ether, which replaced the ethanol in the pores. The support with ether was placed in a petri-dish containing the carrier solution. The ether evaporated and, as a result, the carrier solution was forced into the pores of the support. Because the support was always kept in the wet state, the absolute amount of LM-phase could not be determined since the mass of the empty composite support was not known.

In some cases, double layer SLMs were tested. These were prepared by impregnating two coated supports with the LM-phase. Subsequently, the two SLMs were laminated together using a droplet of LM-phase to 'glue' them. These results are given in appendix B of this chapter.

4.2.5 Permeability and stability measurements

Flux determination

After impregnation, the SLM (with the toplayer to the feed side) was clamped between the two cell halves as drawn in figure 4.3a. The membrane cell was placed in the experimental set-up (figure 4.3b), after which the system was filled with 130 ml 4 * 10^{-3} M $NaNO_3$ (feed) and 130 ml 4 M NaCl (strip) solutions. Peristaltic pumps circulated feed and strip solutions with a constant flow velocity of 5.5 ml s^{-1}, high enough to minimize the resistance of the aqueous boundary layers [4,6]. By means of the thermostated buffer vessels, feed and strip were kept at a temperature of 25 °C. Periodically, samples (about 1 ml) were taken from the feed solution and analyzed by HPLC (Waters IC-PAK™ anion column) on nitrate and chloride concentrations. From the linear decrease of the nitrate concentration in time, assuming a constant feed volume, the nitrate flux was calculated.



(a) (b)

Figure 4.3. *(a) Membrane cell as used for the flux measurements. The SLM is clamped between the two glass cell halves. (b). Schematic representation of the experimental set-up for flux measurements (1 = pump, 2 = accumulator, 3 = thermostated buffer vessels, 4 = membrane cell).*

Stability measurements

Long term permeability experiments were simulated by exposing the feed side of the SLM to an aqueous solution with a low salt content in between two flux measurements. This enhances degradation of SLMs with TOMA or TeOA as carrier [4,8,10]. After a flux measurement the membrane cell was emptied by the pump and the feed was replaced by a 10^{-4} M $NaNO_3$ solution. To measure the nitrate flux again, both feed and strip solutions were replaced by fresh $4 * 10^{-3}$ M $NaNO_3$ and 4 M NaCl solutions, respectively. Usually, the SLMs were tested for 1 day ('flux after 1 day'), but also simulated long term experiments up to 1 month were carried out. In order to obtain an impression on LM-loss, in a number of cases the masses of the SLMs before and after flux measurements were determined by weighing the SLM on an analytical balance. The LM-loss is the difference between the two masses.

4.3 Results and discussion

In the following section, only the results of coated SLMs are discussed. The uncoated SLMs with TOMA as carrier and Accurel as support, all showed initial nitrate fluxes in the order of $16\text{-}19 * 10^{-10}$ mol cm^{-2} s^{-1}, and after 1 day the flux was smaller than $1 * 10^{-10}$ mol cm^{-2} s^{-1}. The exact data are given in table 3.5.

4.3.1 PIPA/TMCl toplayers

In this section, the results of flux and stability measurements on SLMs with a toplayer of piperazine and trimesoyl chloride are discussed. Several reaction parameters were varied, and their influence on flux and SLM stability are elucidated.

Influence of polymerization time on yield

Usually, a standard polymerization time of 15 minutes was used in the experiments described in chapter 3. However, after the initial fast formation of the toplayer at the moment the reactants meet each other at the interface, a barrier will be formed. This means that mass transfer of the diamine through the toplayer will become the rate controlling step in the polymerization process [3] and the increase in weight of the membrane with time will decrease. This was supported experimentally by Enkelmann *et al.* [11,12] who showed that the membrane will reach a final thickness after a certain time.

In this study, these ideas are worked out further. Several experiments were carried out using the polymerization time and TMCl concentration as variables. The results are shown in figure 4.4, in which the relative mass increase of the Accurel supports after polymerization is given. TMCl concentration and reaction time were both varied. All composites were dried in a vacuum oven at 30 °C over night to obtain a constant weight.

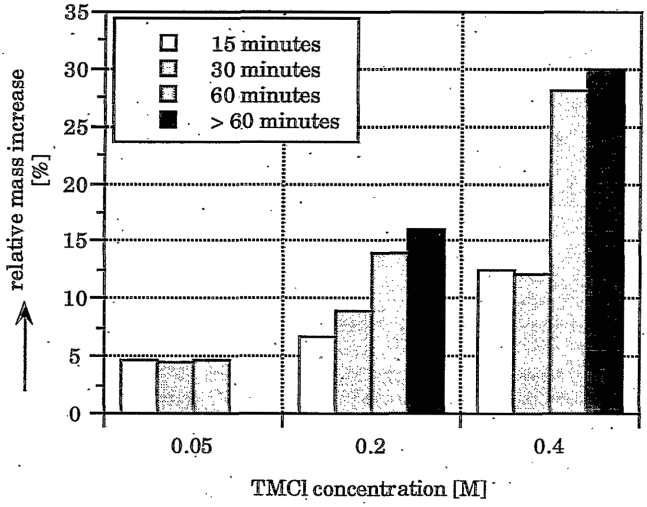


Figure 4.4. *Relative mass increases of Accurel supports as a function of polymerization time and TMCl concentration (0.05 M, > 60 min not measured). Support: Accurel + PIPA / TMCl layer. PIPA concentration 0.2 M. LM-phase: 0.2 M TOMA in o-NPOE.*

Figure 4.4 clearly shows the influence of polymerization time and TMCl concentration on the mass of the toplayer. For a TMCl concentration of 0.05 M, after 15 minutes no further mass increase can be observed, indicating that either the maximum amount of polymer is reached, or that the toplayer completely hinders the transport of both reactants to reach each other. This is not the case for 0.20 and 0.40 M TMCl. Polymerization times exceeding one hour are necessary to complete the interfacial polycondensation. SEM observations revealed an increase in toplayer thickness with increased TMCl concentration, confirming the hypothesis of Enkelmann *et al.* [11,12]. For 0.20 M, the observed maximum weight increase is about 16 %, for 0.40 M TMCl this value is 30 %. From the porosity and thickness of Accurel, from the surface area as used for the polymerization, from the concentration TMCl and from the molecular weights of PIPA and TMCl, one can calculate the maximum amount of polymer to be formed, assuming all three acid chloride groups participate in the reaction. For 0.05 M TMCl one finds a maximum weight increase of approximately 4 mg, for 0.20 M TMCl 16 mg and for 0.40 M 32 mg. The values in figure 4.4 agree rather well with the calculated ones. So, we can reach the maximum yield and therefore the circumstances used during polymerization are ideal. When nitrate fluxes are low or instable membranes are obtained, it is therefore not due to our polymerization method.

In figure 4.4, the PIPA concentration was kept constant. Nevertheless, the amount of polymer increased when the TMCl concentration is increased. So, at this PIPA concentration the absolute amount of TMCl is the limiting factor. This was expected, since only a small amount of acid chloride can be present in the support, in contradiction to the much higher absolute amount of PIPA in the petri-dish. Later on in this chapter, experiments with varying PIPA concentration are described.

Influence of the drying method

Table 4.2. *Influence of drying of the composite supports after preparation on nitrate flux and stability. Drying conditions: yes = 1 night a a vacuum oven at 30 °C, no = in air at room temperature. Support: Accurel + PIPA / TMCl. LM-phase: 0.2 M TOMA in o-NPOE.*

polym. time [min]	dried [yes/no]	initial flux [10^{-10} mol cm^{-2} s^{-1}]	flux after 1 day [10^{-10} mol cm^{-2} s^{-1}]	LM-loss [%]
15	no	17.1	12.6	18.5
	no	15.7	13.4	14.3
	yes	13.7	9.6	11.7
	yes	14.9	10.4	11.0
30	no	15.5	13.0	8.6
	no	11.8	8.9	11.1
	yes	10.9	8.0	7.3
60	no	8.1	6.2	12.0
	no	11.0	5.8	13.6
	yes	9.2	7.0	8.1
	yes	10.6	5.2	5.6

After the interfacial polymerization reaction had taken place and reactants and solvents were removed, the composites were dried in air at room temperature. However, to determine the amount of polymer deposited on top of the support, the composites had to be dried in a vacuum oven at 30 °C to obtain a stable and realistic weight (based on the maximum amount of polymer that could be formed). To investigate whether this drying of the composite supports had an influence on nitrate flux and stability of SLMs, experiments were carried out using 'dried' and 'undried' composites. These composites all were prepared using PIPA and TMCl concentrations of 0.20 M. The 'undried' supports were kept one night in a closed bottle, the 'dried' supports one night in a vacuum oven at 30 °C. Results are given in table 4.2. From this table, it can be concluded that drying of the membranes in a vacuum oven results in lower nitrate fluxes, especially for polymerization times of 15 and 30 minutes. The lower fluxes might be due to an irreversible densification of the toplayer during drying in the oven, which increases the transport resistance and therefore lowers the flux. Longer polymerization times result in a higher amount of polymer formed, as was shown in figure 4.4, and this gives SLMs with lower initial fluxes as is reported in table 4.2.

The stabilities of the SLMs all increased considerably due to the application of a PIPA/TMCl toplayer. For undried SLMs (polymerization time 15 minutes) the initial nitrate flux is almost equal to that of an uncoated SLM. In chapter 3 it was demonstrated that an uncoated SLM lost all its flux within 1 day (table 3.5), while in table 4.2 all SLMs still show an appreciable flux after 1 day. Considering the absolute values of the nitrate fluxes, a polymerization time of 15 minutes and drying the membranes in air seems optimal. Higher polymerization times or drying in an oven all result in lower fluxes. Surprisingly, LM-losses for oven dried and membranes polymerized during longer times are considerably lower. It was already mentioned in section 3.4.2 that the determination of LM-loss by simply weighing is not reproducible enough for an accurate and correct determination, especially when a toplayer is present on the support. Furthermore, when the membranes are not washed well enough and dried after polymerization, still reactants or solvents can be present in the toplayer. These might be washed out during flux determination, giving a LM-loss which is in fact too high. Some of the membranes in table 4.2 indeed showed toplayer masses which were much too high when the amount of reactants and the accuracy of the weight determination (± 1 mg) was taken in consideration.

Influence of piperazine concentration

Generally, it is assumed that the interfacial polycondensation process takes place in the organic phase [3]. This means that the amine has to transfer from the aqueous phase to the organic phase and that factors like the transfer rate of the amine and the partition coefficient are of importance for the final properties of the polymer. Increasing the amine concentration will increase the amount of amine present in the organic phase when the driving force for the amine to migrate to the organic phase is constant. Therefore the amount of amine available for polymerization with the other monomer is also higher, resulting in a higher mass of the toplayer. When the toplayer mass increases, it is expected that the resistance towards nitrate transport also increases. Consequently, the nitrate flux through the SLM should decrease with increasing PIPA concentration.

Table 4.3. *Influence of PIPA concentration on toplayer mass, nitrate flux and stability. Support: Accurel + PIPA/TMCl. TMCl concentration: 0.2 M in dodecane. LM-phase: 0.2 M TOMA in o-NPOE.*

PIPA conc. [M]	mass toplayer [mg]	initial flux [10^{-10} mol cm^{-2} s^{-1}]	flux after 1 day [10^{-10} mol cm^{-2} s^{-1}]	LM-loss [%]
0.20	5.6	15.1	13.6	11.0
	5.8	16.5	16.6	9.2
0.30	6.3	16.7	19.4	9.1
	7.0	19.0	22.0	16.2
0.40	5.9	14.9	14.6	9.2
	6.2	18.2	19.5	10.2
0.50	7.9	18.1	20.8	9.6
	7.0	20.2	23.6	10.6
0.60	8.1	17.8	18.1	9.3
	8.2	18.3	20.5	10.1
0.80	8.2	18.3	21.8	8.3
	9.7	17.7	20.6	15.3

The influence of piperazine concentration in the aqueous phase on nitrate flux and stability is listed in table 4.3. As expected, the mass of the toplayer increases when the PIPA concentration increases (see figure 4.5), although this effect is small. From table 4.3, however, no clear trend can be observed for the initial nitrate fluxes contrary to our expectations. Despite the higher toplayer mass, initial fluxes are almost identical to those of uncoated membranes. Only at higher PIPA concentrations a slight increase of the initial flux is found, at least compared to the 'standard' concentration of 0.2 M. Assuming a constant density of the polyamide toplayer, a higher PIPA concentration would result in an increase of the toplayer thickness. From this point of view, the slight flux increase is somewhat surprising. Possibly, properties like porosity and swelling of the toplayer also change. The application of the toplayer results in a stable SLM after one day. Fluxes after 1 day are slightly higher than the initial ones, an effect encountered more clearly in long term experiments and therefore not discussed here. However, no definite conclusions can be drawn from these results because of the standard error of approximately 10 % in each flux measurement and ± 1 mg in the toplayer mass determination. The same applies for the LM-losses. Also in this case the values scatter too much to draw explicit conclusions.

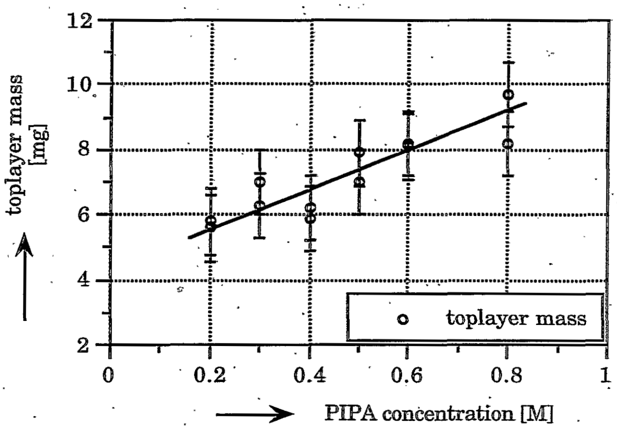


Figure 4.5. *Toplayer mass as a function of PIPA concentration. data from table 4.3.*

Influence of trimesoyl chloride concentration

In figure 4.4 it was shown that the TMCl concentration during polymerization had a large influence on the amount of polymeric toplayer formed. Therefore, it might be expected that nitrate flux and stability also change when the TMCl concentration is varied. Experimental results are given in table 4.4 for the standard procedure (drying in air overnight).

From the results in table 4.4 it can be concluded that the application of the toplayer results in SLMs with an improved stability without a reduction in initial flux compared to uncoated membranes. It is difficult to more draw conclusions from the data in table 4.4. The 0.05 M TMCl data seem to be an exception, since the flux after one day is higher than the initial flux. This might be due to a loss of LM-phase, resulting in a decrease of the liquid membrane thickness. For long term experiments (section 4.3.2.1) this effect is more pronounced. All the other data do not differ that much from each other and show only a small flux decrease after one day. Experiments over a longer period of time show more differences as shown in section 4.3.2. Such experiments will be discussed later on. Fluxes are all about the same as the initial flux of an uncoated SLM. Taking into account the inaccurate determinations of the amount of LM-phase present in the membrane, the losses are in the same order of magnitude as for uncoated membranes.

Table 4.4. *Influence of TMCl concentration on nitrate flux and stability. Support: Accurel + PIPA / TMCl. PIPA concentration: 0.2 M in water. LM-phase: 0.2 M TOMA in o-NPOE.*

TMCl conc. [M]	initial flux [10^{-10} mol cm^{-2} s^{-1}]	flux after 1 day [10^{-10} mol cm^{-2} s^{-1}]	LM-loss [%]
0.05	15.9	19.9	9
	16.6	19.8	11
0.10	15.3	14.3	12
	18.4	15.8	12
0.20	15.7	12.2	14
	15.3	13.5	12
	17.4	16.5	15
0.40	17.6	15.6	13
	17.2	15.2	14

Influence of organic solvent for TMCl in the polymerization reaction

Varying the organic solvent used for preparation of the acid chloride solution will change the driving force for migration of the amine, the interaction between polymer and organic solvent (precipitation rate of polymer) and the mutual solubilities of water and organic solvent. Therefore, two series of solvents were tested: decane, dodecane and tetradecane in one series and dimethylphthalate (DMP), dibutylphthalate (DBP) and dioctylphthalate (DOP) in another. All these solvents have a sufficient low vapor pressure. Apart from DMP, the mutual solubility of water and these solvents is low in order to prevent mixing of the reactants and penetration of the organic phase by water, which would increase hydrolysis of the acid chloride. The exact properties of these solvents are listed in table 3.2. All other variables were kept constant. The permeation results are shown in figure 4.6.

For decane and tetradecane as solvent, similar flux and stability results were expected as presented before for dodecane since these solvents are very similar in structure and physical properties. The phthalate series have a larger viscosity than dodecane (see section 3.2.3). Migration of the reactants to the reaction site will be more difficult due to the larger resistance towards transport. Formation of a toplayer will be more difficult, and the stabilizing effect of these membranes is expected to be less than that of the alkanes series.

As can be seen in figure 4.6, the reproducibility of the membranes prepared with DBP or DOP as organic solvents is rather poor. Nevertheless, initial fluxes for DBP and DMP are comparable to those of the alkanes. Contrary to the expectations, the DOP membrane has a low initial flux, but shows such an increase of flux after 1 day. It might be possible that the more hydrophobic DOP is not well enough removed from the toplayer or the pores after polymerization (because of its high viscosity) and thus hinders the transport. After a while during the flux measurements, all remaining DOP is removed by the flowing feed phase and therefore the flux increases again.

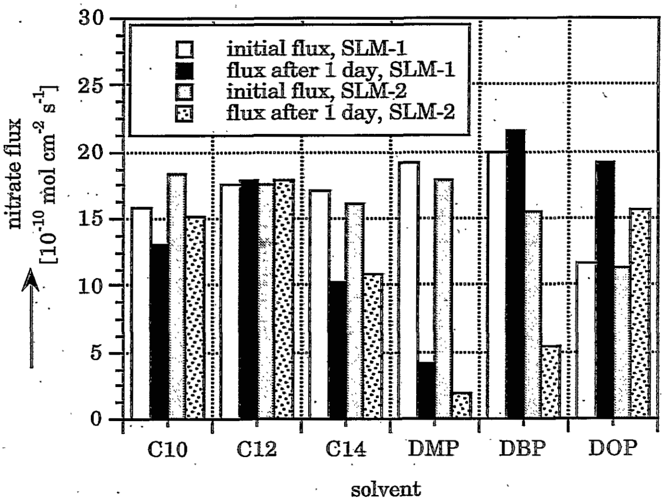


Figure 4.6. *Influence of the organic solvent for TMCl used during interfacial polymerization on nitrate flux and stability. C10 = decane, C12 = dodecane, C14 = tetradecane. Support: Accurel + PIPA/TMCl. LM-phase: 0.2 M TOMA in o-NPOE. For each solvent, two membranes were measured (SLM-1 and SLM-2).*

The alkane series gives a better reproducibility. There is not much difference between the different alkanes when the initial fluxes are considered. After one day, the 'regular' solvent, dodecane, gives the best results since the decrease in flux is the smallest. Therefore, as organic solvent for TMCl, dodecane will be used.

Influence of acid acceptors

In table 3.6 it was seen that the presence of an acid receptor in the aqueous amine solution reduced the permeability for nitrate ions. For the system PIPA/TMCl, addition of an acid receptor resulted in instable SLMs, in contradiction to situations where no acid acceptor was present. Acid acceptors might be added to the aqueous amine solution during interfacial polymerization to remove HCl, formed in the reaction and transferred to the aqueous phase after elimination. The hydrochloric acid is also able to react with the amine, which is a weak base. Once reacted with

HCl, the multifunctional amine hydrochloride is not acylatable anymore [2,3] and as a result less amine is available for polymerization.

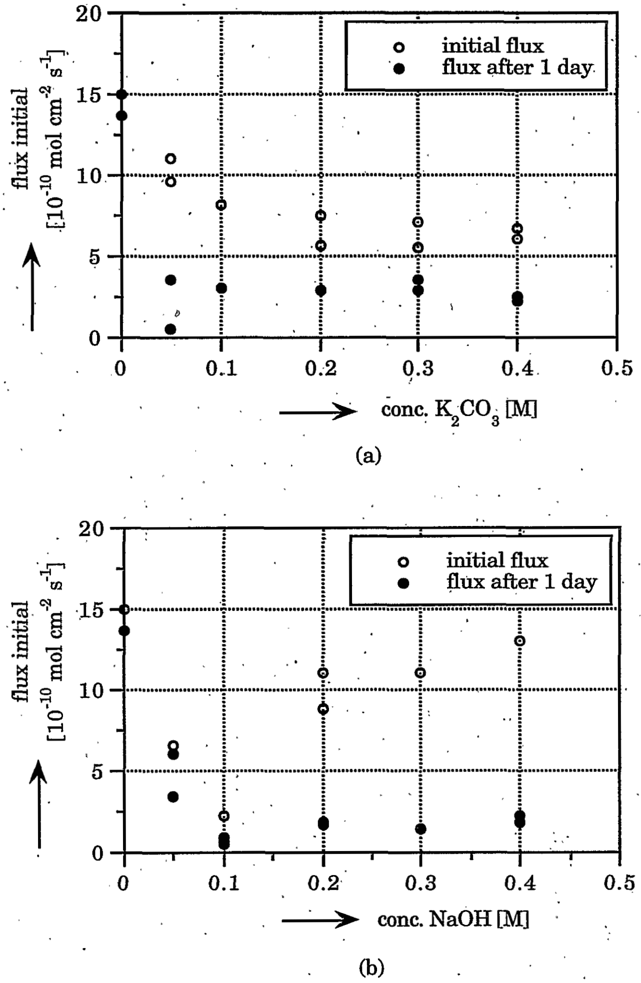


Figure 4.7. *Nitrate flux and stability as a function of the concentration acid acceptor. (a) K_2CO_3. (b) NaOH. Support: Accurel + PIPA/TMCl toplayer. LM-phase: 0.2 M TOMA in o–NPOE.*

In the preparation of reverse osmosis membranes, the addition of an acid acceptor is quite normal [13,15]. To investigate the effect of acid acceptors on flux and stability of our SLMs more thoroughly, experiments were carried out using K_2CO_3, a weak base, and NaOH, a strong base, as additives to the aqueous amine phase in different concentrations. The results are plotted in figure 4.7.

Considering the results when no acid receptor is used, one would expect a gradual decrease from stable, high nitrate flux membranes towards membranes with lower initial nitrate fluxes and low stability, when the acid acceptor concentration increases from zero to higher values. This is indeed observed when K_2CO_3 is applied as acid acceptor. There is a tendency towards a decrease in initial flux when the concentration of K_2CO_3 increases. Fluxes after 1 day are all in the same, low range of 2.5 - 4 * 10^{-10} mol cm^{-2} s^{-1}, even at low concentrations which are somewhat lower than the initial values. So, when the flux decrease is taken in consideration, these membranes are not so bad but the absolute flux values are somewhat low compared to PIPA/TMCl layers polymerized in absence of acid acceptors.

The membranes prepared using NaOH as acceptor show a minimum in the initial flux at a sodium hydroxide concentration of approximately 0.10 M. Above this concentration, initial fluxes increase again, but for all NaOH concentrations investigated, no stable membranes are obtained. Going towards lower concentrations (0.050 M), a marginal increase of the stability is observed compared to higher NaOH concentrations, although the nitrate fluxes are 2-3 times lower then when no acid acceptor is used.

For the minimum in initial flux no explanation has been found yet. The increase in initial flux beyond 0.1 M NaOH could be an indication for a less tight toplayer structure or a smaller toplayer thickness. It is known that the addition of salts and bases influences the driving force for migration of the diamine and the transfer rate of diamine to the organic phase. Salts shift the partition of diamine toward the organic phase [2,3]. A change in these variables will also alter the polymerization rate and thus the final molecular weight and amount of polymer formed. However, the influence of NaOH is not known for this system, and care must be taken in interpreting such data from other systems.

In figure 4.8 the masses of the toplayers from the membranes used in figure 4.7 are plotted. The 0.05 M NaOH membranes show a large mass increase compared to the increase of other membranes. This might indicate the presence of residual reactants or indicating a thick or dense toplayer hindering nitrate transport as was indeed observed in figure 4.7b. Nevertheless, the 0.1 M data are in contradiction to the flux measurements: as the toplayer mass is low, a high flux should be expected which is not the case. Possibly, the 0.1 M data are somehow an exception and the experiment should be repeated. The other data show a gradual decrease in mass with increasing NaOH concentration, in agreement with the gradual increase in flux observed. The K_2CO_3 data in figure 4.8 are almost constant, while the flux showed first a decrease with increasing K_2CO_3 concentration and later on an almost constant flux. The decrease in flux indicates, for some reason, a higher resistance to nitrate transport. It is however not understood why the higher resistance towards nitrate transport does not result in an increased stability of the SLM.

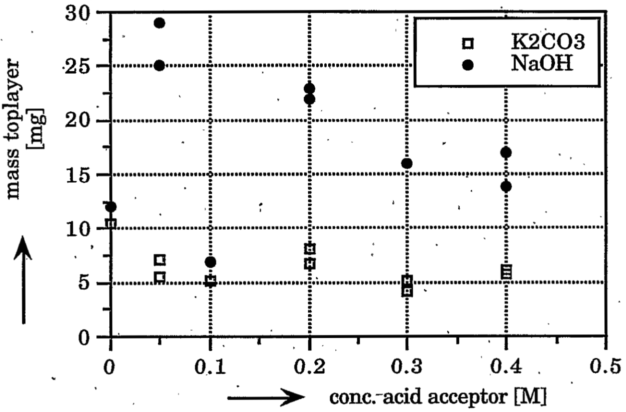


Figure 4.8. *Mass increase of the support due to the application of the toplayer as a function of the concentration acid acceptor used. Data for the membranes used in figure 4.7.*

The most striking effect of the addition of acid acceptor during polymerization is the disappearance of the stabilizing effect of PIPA/TMCl toplayers and the decrease in initial flux. The influence of acid acceptors on membrane performance was also observed by Cadotte *et al.* [14,15]: PIPA and TMCl or IPhCl, in the presence of NaOH or Na_2CO_3 were applied on top of polysulfone supports by an interfacial polymerization reaction to obtain reverse osmosis membranes. For trimesoyl chloride, the salt rejection decreased in the order: none>Na_2CO_3>NaOH (88 %, 54 % and 28 %, respectively), while the reversed order was observed for isophthaloyl chloride under identical conditions. Although the system is quite different from ours, it might be clear that the addition of acid acceptors during polymerization has a large influence on the reverse osmosis properties of the membranes. Cadotte *et al.* explained this phenomenon assuming the acid acceptors to promote the hydrolysis side reaction on TMCl, leading to a less tight membrane and thus to a lower salt rejection [14,15]. However, no experimental evidence for this hypothesis was presented, and the reversed order found for IPhCl was not explained.

For TMCl, the hydrolysis reaction is shown in figure 4.9. The hydrolysis reaction takes place almost completely in the aqueous phase by a reaction with water or by the faster reaction with hydroxyl ions [3,16-18]. This means that the solubility of the acid chloride in the aqueous phase is the main factor determining the hydrolyzation of acid chlorides. No data on reaction rates for the hydrolysis of TMCl are known. However, for terephtaloyl chloride (TPhCl, the structure is given in appendix A of chapter 3), which is very similar in structure to TMCl, hydrolysis rates in microcapsules were measured. The hydrolysis rate of encapsulated TPhCl by H_2O was 0.15 * 10^{-2} mol m^{-2} s^{-1}, while with a 1 M NaOH solution the rate of hydrolysis was 3.87 * 10^{-2} mol m^{-2} s^{-1} [17,18]. After hydrolysis part of the reactive acid chloride groups is not available anymore for polymerization.

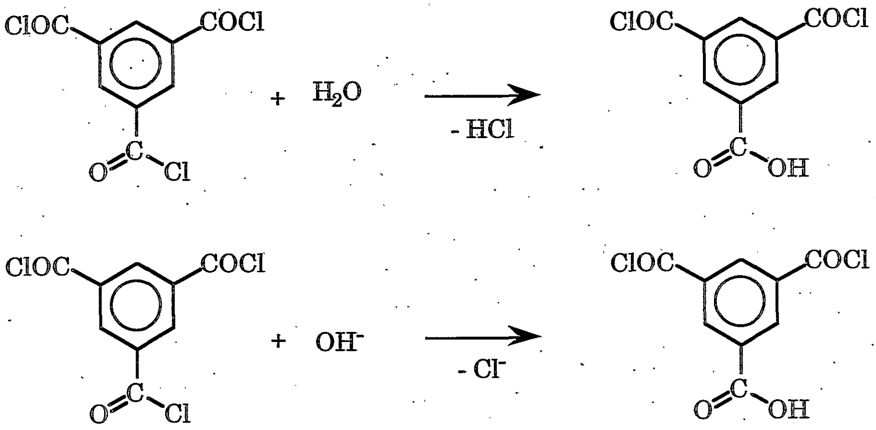


Figure 4.9. *Hydrolysis reaction of trimesoyl chloride by water (upper) or by hydroxyl ions (lower).*

The hydrolysis reaction is the most important side reaction during interfacial polymerization. Chern *et al.* [19,20] investigated the hydrolysis reaction in interfacially polymerized films of 1,2,4,5-benzenetetraacyl chloride and ethylenediamine with and without addition of a phase transfer catalyst (a quaternary ammonium salt) or an acid acceptor (Na_2CO_3). The amount of carboxyl groups was determined by ATR-FTIR. According to the authors the hydrolysis reaction is promoted by the presence of HCl which is produced during the interfacial polymerization. When the hydrochloric acid is not removed by a reaction with an acid acceptor more hydrolysis will take place than in the presence of an acid acceptor. This was confirmed experimentally by the ATR spectra, where the intensity of the peak at 1720 cm^{-1} (acid, C=O) was lower when Na_2CO_3 was present. This is contrary to the idea of Cadotte *et al.* mentioned before. Another difference is that Chern and Chen assume the hydrolysis reaction to take place partly in the organic phase and not, as generally assumed, fully in the aqueous phase.

Suppose in our system (PIPA/TMCl) hydrolysis of TMCl takes place. This might change the properties of the polymeric toplayer (*e.g.* the degree of crosslinking or the tightness of the layer). When the toplayer has a more open structure, the loss of LM-phase might be higher. A second effect is that carboxylic acid groups formed by the hydrolysis reaction can be ionized thereby introducing negative charge in the toplayer. The transport of negative ions will be hindered somewhat more, and the flux of nitrate and chloride ions will decrease. However, since the polymerization reaction is much faster than the hydrolysis reaction, it is expected that the amount of hydrolyzed groups is very small. The drastic effect of acid acceptor addition on nitrate flux and membrane stability is difficult to explain by assuming that hydrolysis plays an important role.

To investigate the effect of partly hydrolyzed TMCl on toplayer properties, the following experiment was carried out. Several solutions of TMCl in dodecane (0.2 M) and aliquots of demineralized water were stirred for certain time periods in between 45 minutes and 3 hours. In this way, the TMCl was hydrolyzed. After separation of the two phases and filtrating the white precipitate, the concentration of hydrolyzed groups was determined by a titration of the aqueous phase with NaOH (1.000 M) and bromothymolblue as indicator to determine the amount of HCl formed. The precipitate consisted of fully hydrolyzed TMCl, as revealed by analysis of the precipitate by FTIR. The partly hydrolyzed TMCl was used to prepare toplayers with PIPA on Accurel, after which the composites were used as support for SLMs. The nitrate fluxes and SLM stabilities are given in table 4.5. Thicknesses of the toplayers, as revealed by SEM, were in the order of 1-2 μm, somewhat smaller than the ordinary PIPA/TMCl toplayers (3-5 μm), while the surface morphology was the same.

Table 4.5. *Nitrate fluxes and flux stabilities of Accurel SLMs coated with a PIPA / partly hydrolyzed TMCl toplayer. LM-phase: 0.2 M TOMA in o-NPOE.*

percent. hydrolysis [%]*	initial flux [10^{-10} mol cm^{-2} s^{-1}]	flux after 1 day [10^{-10} mol cm^{-2} s^{-1}]	LM-loss [%]
42.1	15.1	13.9	11.8
	16.0	13.3	11.9
100.5	17.4	19.7	12.1
	17.7	13.7	10.4
170.9	15.6	14.9	10.8
	20.0	20.3	13.4

*: 100 % = all TMCl has one acid chloride group fully hydrolyzed.

From the data in table 4.5 it is clear that the hydrolyzed TMCl does not show lower initial fluxes. Furthermore, in contrast with the data given in figure 4.7 the flux stability is improved and resembles the data obtained for SLMs with a PIPA/TMCl toplayer polymerized in the absence of acid acceptors. This is an indication that hydrolysis of TMCl is not responsible for the low fluxes and instable membranes prepared in the presence of acid acceptors, and that hydrolysis only takes place when no base is present. ATR-FTIR measurements, presented later on in this chapter, support this hypothesis. This means still no explanation for the strange phenomena in figure 4.7 has been found.

Copolymers with IPhCl

Isophthaloylchloride (IPhCl) is a bifunctional acid chloride and is therefore unable to crosslink the polymer chemically. In this way the influence of crosslinking on stability and flux of PIPA/TMCl toplayers could be investigated.In table 4.6, results of copolymerization reactions of PIPA with mixtures of TMCl and IPhCl are given.

Table 4.6. *Nitrate fluxes and stabilities of Accurel SLMs coated with a PIPA/TMCl + IPhCl copolymeric toplayer. LM-phase: 0.2 M TOMA in o-NPOE.*

IPhCl/TMCl conc.* [M]	initial flux [10^{-10} mol cm^{-2} s^{-1}]	flux after 1 day [10^{-10} mol cm^{-2} s^{-1}]	LM-loss [%]
0.10/0.10	8.5	6.7	10.5
	8.9	5.4	10.6
0.05/0.15	8.8	10.3	8.4
	11.9	9.1	7.2

*: total concentration of acid chloride 0.2 M

The substitution of a part of trifunctional TMCl by bifunctional IPhCl reduces the initial nitrate flux when the data in table 4.6 are compared to those in table 4.3 or 4.4. SEM showed the layers to have a thickness between 1 and 3 µm. Apparently, IPhCl substitution results in denser layers. Since it might be assumed that the IPhCl containing polymer is less stiff than chains containing only the crosslinked TMCl, possibly the packing density of the latter is lower and a somewhat opener structure is the result. The nitrate flux is higher in that case. The less IPhCl is present, and consequently the more the toplayer resembles the PIPA/TMCl layer, the more stable is the membrane.

Other additives

When HCl is added to the aqueous amine solution part of the piperazine is converted into the hydrochloride salt which is believed to be less reactive [19] or even not reactive at all [2,3]. In table 4.7 results are given for interfacial polymerization reactions of PIPA with TMCl, with certain amounts of HCl added to the aqueous amine solution. Since less PIPA is available for the polymerization reaction, it is expected that the amount of polymer on the support is lower and the stabilizing effect less compared to the HCl-free case. Indeed this was observed for higher hydrochloric acid concentrations. For the lower concentrations, there was not much difference in stability. Possibly, the layer is thick or dense enough to retain the carrier in the membrane and open enough for a high flux, despite the presence of HCl during the polymerization. As was expected on forehand, for the highest HCl concentration used the flux stability was the lowest.

Table 4.7. *Nitrate flux and SLM stability of coated SLMs. Polymerizations in the presence of HCl in the aqueous PIPA solution. Support: Accurel + PIPA / TMCl toplayer. LM-phase: 0.2 M TOMA in o-NPOE.*

HCl concentration [M]	mass toplayer [mg]	initial flux [10^{-10} mol cm^{-2} s^{-1}]	flux after 1 day [10^{-10} mol cm^{-2} s^{-1}]
0	4.9	17.3	10.8
0.012	5.3	15.4	12.2
	5.8	16.7	14.1
0.121	4.7	14.1	12.6
	5.1	15.1	11.4
0.242	1.7	15.1	2.9
	2.5	18.7	< 1

4.3.2 PIPA/TMCl layers: long term experiments

In all previous experiments, only short term stabilities over a period of one day were presented. More important however is the behaviour of the coated supported liquid membranes when they are used for longer periods. The results of optimizing the polymerization process are easier to judge when the degradation times are longer. In this section these long term experiments will be discussed. The degradation time mentioned in the figures is the time the SLM is exposed to an aqueous feed with a low salt concentration to enhance the degradation of the membrane.

4.3.2.1 TOMA as carrier

The stability of coated SLMs as a function of TMCl concentration is shown in figure 4.10. It is clear from this figure that the application of a toplayer of PIPA and TMCl does not hinder the transport of nitrate- and chloride ions, since the initial fluxes of all coated membranes are the same as that of the uncoated membrane. In all cases, initial fluxes are in the order of 19 - 20 * 10^{-10} mol cm^{-2} s^{-1}.

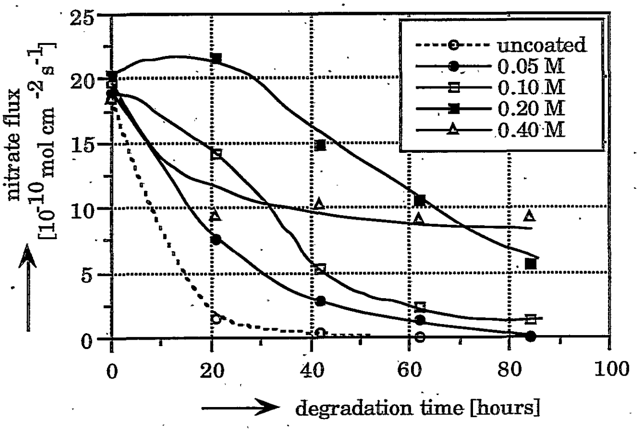


Figure 4.10. *Long term stability of SLMs with toplayers made with different TMCl concentrations. Support: Accurel + PIPA/TMCl toplayer. PIPA concentration: 0.2 M. LM-phase: 0.2 M TOMA in o-NPOE. The displayed points are mean values of various measurements.*

For uncoated membranes, no flux can be detected anymore after 1 day of degradation. It is clear that the application of a toplayer results in much more stable membranes. Especially when the TMCl concentration is higher than 0.2 M, after 4 days still a reasonable flux is present. Up to 3 days of degradation, the membrane with a toplayer prepared with 0.2 M TMCl gives the best results. However, after 4 days the best membrane seems to be the one polymerized with the highest concentration of TMCl.

After polymerization, the composites are usually washed with water and ethanol to remove residual reactants. It is not quite sure whether one single, washing step is enough to remove all unreacted monomers and solvents. Therefore, several experiments were carried out using composites which were washed eight times in fresh Milli-Q water and three times in ethanol after polymerization. As reference, at the same time composites were prepared which were washed according to the ordinary procedure mentioned before. The results are given in figure 4.11. There seems to be a tendency for the 'normal' membranes to have a lower nitrate flux over the whole range, but in this case the reproducibility of the flux measurement is better in comparison with the situation where washing of the membranes was performed. This might be an indication that irreproducibilities are not only a result of remaining reactants, but that other factors also play a role *e.g.* the introduction of defects by the drying procedure or the damage of the toplayer by less careful handling of the composite. Of course, the more washing steps are carried out, the higher is the chance that the toplayer is damaged resulting in a poor reproducibility.

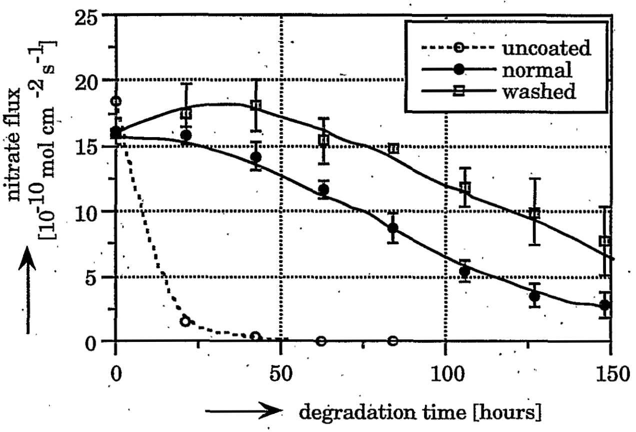


Figure 4.11. *Influence washing step on long term stability of SLMs. Support: Accurel + PIPA/TMCl toplayer (PIPA and TMCl concentrations 0.2 M) LM-phase: 0.2 M TOMA in o-NPOE. The 'normal' membranes are washed after polymerization according to the usual procedure (see section 4.2.2), the 'washed' ones are washed eight times in fresh Milli-Q water and three times in ethanol. The fluxes are mean values with the error bars indicating the minimum and maximum values.*

4.3.2.2 TeOA as carrier

All previous experiments were carried out with TOMA as carrier, resulting in a relatively instable system. Neplenbroek *et al.* [4,9] found very stable membranes using TeOA as carrier when a PVC gel layer was applied at the feed side. In order to compare the interfacially polymerized layers with the gel layers, experiments were carried with TeOA as carrier. The results are given in figure 4.12.

An uncoated membrane shows a flux reduction in time. The initial fluxes of coated and uncoated membranes, show that for the coated membranes these are somewhat lower. Nevertheless, in the long run the first series of experiments with coated membranes (PIPA/TMCl-1 in figure 4.12) show an almost constant nitrate flux for more than 150 hours when degradation conditions are used. The results of Neplenbroek *et al.* were stopped after 70 hours [4,9], so a good comparison with their results is not possible.

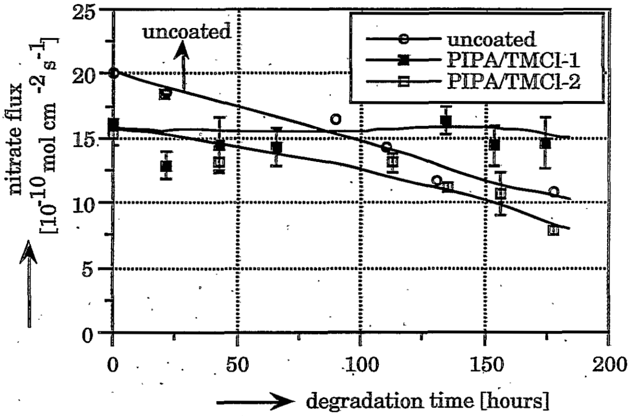


Figure 4.12. *Nitrate flux and stability of TeOA-SLMs. Support: Accurel + PIPA/TMCl toplayer. LM-phase: 0.2 M TeOA in o-NPOE. Error bars indicate maximum and minimum values for a series of experiments. The lines are just to guide the eye.*

In order to check the reproducibility of the measurements, a second set of membranes was polymerized in exactly the same way. Stability measurements in this case, however, resulted in membranes which were less stable in time (after approximately 130 hours) than uncoated SLMs. This again makes clear that there are problems in reproducing the results. More experiments should be carried out to investigate the backgrounds of these irreproducibility problems. One of the ideas is that the use of a mould during application of the toplayer might solve (part of) the problem. Experiments using the mould are described in section 4.3.4.

4.3.3 Other piperazines

In the previous sections it was shown that toplayers of piperazine and trimesoyl chloride were very effective in stabilizing SLMs for the removal of nitrate ions from water. Especially the lifetime improvement of relatively instable SLMs with TOMA as carrier is remarkable. Credali *et al.* [21] and Parrini [22] already showed that large differences in salt rejection and flux were obtained when a specific acid chloride monomer was polymerized with a series of piperazines with small side group variations. Therefore, four more piperazine-like monomers, (see figure 4.1), were polymerized with TMCl on Accurel, after which the modified supports were impregnated with the LM-phase and tested on nitrate flux and SLM stability. The results are given in table 4.8.

Table 4.8. *Influence of the type of piperazine on nitrate flux and SLM stability. Support: Accurel + amine / TMCl toplayer. Amine concentration: 0.2 M in water. LM-phase: 0.2 M TOMA in o-NPOE.*

amine*	initial flux [10^{-10} mol cm^{-2} s^{-1}]	flux after 1 day [10^{-10} mol cm^{-2} s^{-1}]	LM-loss [%]
MPIPA	24.0	15.8	8.2
	23.0	17.9	10.0
	26.4	21.4	6.7
DMPIPA	15.1	1.1	12.3
	13.8	2.4	11.0
AEPIPA	20.2	25.1	11.0
	19.8	25.5	13.2
	20.1	26.1	10.6
	20.6	23.7	9.2
AMPIP	14.9	15.5	4.0
	14.5	16.5	12.7

*: MPIPA = 2-methylpiperazine, DMPIPA = 2,5-dimethylpiperazine, AEPIPA = 1-(2-aminoethyl)piperazine, AMPIP = 4-(aminomethyl)piperidine (see figure 4.1).

Table 4.8 shows that a piperazine with one methyl group also raises the stability of the membrane and even shows an increase of the initial flux compared to an uncoated support (from 16 - 19 * 10^{-10} mol cm^{-2} s^{-1} for an uncoated membrane to 23 - 24 * 10^{-10} mol cm^{-2} s^{-1} for MPIPA). The same effect is observed for AEPIPA. This rather striking increase is not fully understood yet. A number of explanations can be given. Firstly, both monomers have more hydrophobic groups (a methyl or ethyl group) compared to PIPA. Possibly, the toplayers therefore are somewhat more hydrophobic and the LM-phase might penetrate into these toplayers to a larger extent. A second explanation might be that the effective surface area was larger since SEM-observations revealed the typical rippled surface texture mentioned already in chapter 3. This results in an increased flux.

Nevertheless it is difficult to explain why the incorporation of an extra resistance *i.e.* by the toplayer results in fluxes higher than those of an uncoated SLM. The flux increase for the AEPIPA membrane after 1 day might also be explained by a decrease in actual membrane thickness due to a loss of LM-phase exceeding the carrier loss. Attaching two methyl groups to the piperazine ring results in instable membranes. Compared to PIPA, DMPIPA is more hydrophobic and bulkier. This will change the driving force of migration of the diamine to the organic phase. It is not understood exactly why this results in instable membranes, and also not why the difference between one (MPIPA) and two methyl groups (DMPIPA) is so large. At least, one might conclude from table 4.8 that not only the combination PIPA/TMCl results in stability improvement, but the polymerization of TMCl with several other monomers also gives the same effect or even membranes with better properties (higher fluxes). Some of these monomers are investigated in more detail in the following section.

4.3.4 The use of a mould

Previously, some problems with reproducing the measurements were encountered. The reason for this is difficult to trace since many factors during polymerization and flux measurements influence the final stabilizing properties of the toplayer. The layers might be damaged after polymerization by the drying method, incautious handling or by the method the fluxes are measured. When feed or strip are replaced this causes the membrane to vibrate and subsequently the layer might be damaged or LM-phase might be pressed out of the support. To carry out at least the polymerization in a more reproducible way without the curling of the support a mould was used as described in section 4.2.2.

The use of a mould improved the reproducibility of the measurements, as well as the lifetime of the SLMs. However, still the test results for several polymerizations, with exactly identical supports and reactants, could be quite different. This is illustrated by figure 4.13. All these membranes were prepared using the mould with the same reactants and support, but the stabilizing effect for the three coated membranes is different. While one of the membranes is very stable for the first 300 hours of the degradation test, the other two then already lost most of their flux. This could be an indication that part of the observed instability might be inherent to the flux measurement procedure (the emptying of the membrane cell by the pumps). This was also observed by measurements on hollow fibers as described in chapter 5 of this thesis. Looking back, it might have been better to modify the experimental set-up or flux measurement procedures to minimize their effect on SLM stability. Nevertheless, all the flux and stability experiments described are carried out in the identical way as described in the experimental section.

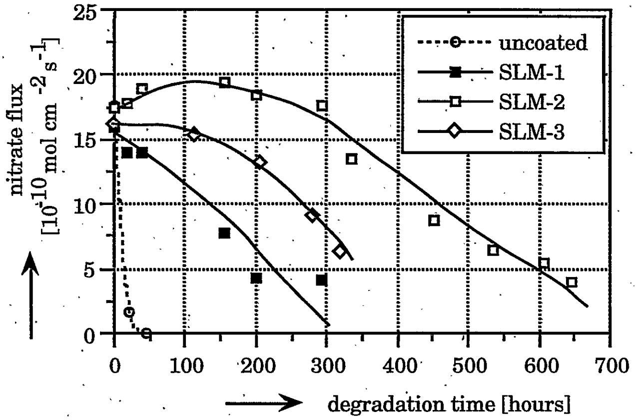


Figure 4.13. *Reproducibility problems for coated membranes. Support: Accurel + PIPA / TMCl. Composites prepared using a mould. LM-phase: 0.2 M TOMA in o-NPOE.*

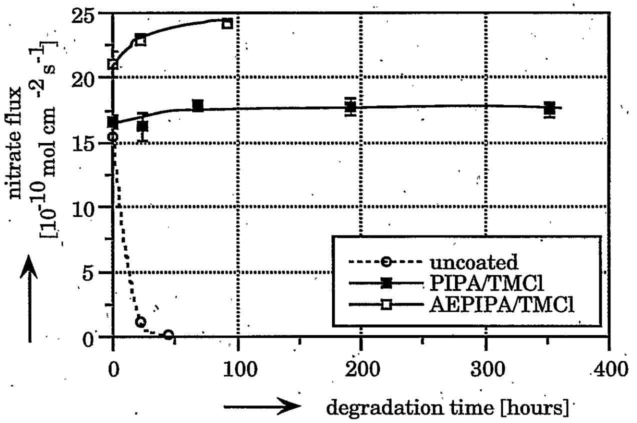


Figure 4.14. *Nitrate flux and long term stability for coated membranes. Support: Accurel + toplayer. Composites were prepared using a mould. LM-phase: 0.2 M TOMA in o-NPOE.*

In figure 4.14, the most promising results obtained for Accurel are given for polymerizations carried out with the mould. For PIPA/TMCl coated supports, it is clear that the initial flux is equal to that of an uncoated standard membrane. However, the uncoated SLM already shows a very low nitrate flux after 1 day of degradation. The SLMs with a PIPA/TMCL toplayer, on the other hand, show no flux decrease for a period of about 350 hours (about two weeks). Although these PIPA/TMCl results are the best ones measured, they are very promising. Therefore, in the following section PIPA/TMCl toplayers are used for the stabilization of SLMs with various other support membranes. The AEPIPA/TMCl toplayer has a higher initial flux, which increases in time. This was already observed in short term experiments (see table 4.8). The experiments were stopped after almost 100 hours due to experimental problems, but the results are of course very promising for further investigations.

4.3.5 Other supports

Previously, it was shown that applying a toplayer obtained by the polymerization of PIPA (or several similar monomers) and TMCl on an Accurel support membrane enhanced the quality of SLMs for nitrate removal from water. It is questionable whether these systems also work when other supports are used. In this section several other supports are tested and optimized. The properties of these membranes were given in table 4.1, while the pore size characteristics as measured by Coulter Porometry are shown in table 4.9. One must bear in mind that these pore sizes are calculated assuming a spherical shape of the pores, and this is not the case for the DSM and Sartorius membranes which are stretched and therefore have slit-shaped pores.

Table 4.9. *Pore sizes of different supports as determined by Coulter® Porometry.*

support	min. pore size [μm]	max. pore size [μm]	MFP* [μm]	pore size** [μm]
Durapore GVHP	0.259	0.469	0.386	0.22
Durapore HVHP	0.666	1.030	0.849	0.45
DSM Z2D1	0.171	0.324	0.262	± 0.5
DSM Z2E1	0.064	0.100	0.087	<< 0.5
Sartorius SM 11807	0.292	0.447	0.372	0.2

*: mean flow pore size. **: as obtained from the supplier

PVDF and PE supports

The results of the flux measurements are summarized in table 4.10. It is clear that toplayers of piperazine or methylpiperazine and trimesoyl chloride also are able to improve the stability of SLMs when Durapore is used as support. Using Durapore supports, initial fluxes are lower compared to the Accurel membranes (compare data in table 4.10 with those in section 4.3.1). This is due to the larger thickness of the Durapore membrane (125 μm against 95 μm) and a difference in internal pore structure causing differences in tortuosity. Also for Durapore membranes with a PIPA/TMCl toplayer, no influence of this toplayer on the initial flux was found compared to uncoated membranes. After one day, the flux decrease was very low, in contrast to the uncoated Durapore SLMs. For toplayers out of MPIPA and TMCl, an initial flux increase compared to uncoated supports was measured, as observed before for Accurel with a MPIPA/TMCl layer (see table 4.8).

When Z2D1 was coated with PIPA and TMCl, large defects were present (as revealed by SEM). This is due to the large pores (> 1 μm) present and the surface roughness which makes it difficult to prepare a 'smooth' thin defect free layer on top of the Z2D1 membrane. Therefore, the Z2D1 membrane could not be used as support. The measurements on Durapore membranes were quite reproducible. This, however, was not the case with the DSM membrane. SEM photographs showed a very irregular toplayer, due to the surface roughness of the uncoated membrane. This makes it difficult to obtain a defect free toplayer with reliable properties. These supports were also difficult to handel due to their small thickness (approximately 30 μm as measured with a digital Mitutoyo micrometer) and limpness (resulting in an enormous curling during the polymerization reaction). Therefore, no additional experiments were carried out with DSM Z2E1 as support membrane.

Table 4.10. *Influence of support and coating on nitrate flux and stability. LM-phase: 0.2 M TOMA in o-NPOE. Amine and acid chloride concentrations 0.2 M in water and dodecane, respectively.*

support	toplayer*	initial flux [10^{-10} mol cm^{-2} s^{-1}]	flux after 1 day [10^{-10} mol cm^{-2} s^{-1}]	LM-loss [%]
Durapore GVHP	none	9.6	5.3	4.7
		9.9	3.1	5.3
	PIPA/TMCl	11.2	11.5	7.1
		9.8	9.1	7.8
	MPIPA/TMCl	16.1	17.2	12.1
		16.3	19.4	13.0
Durapore HVHP	none	13.9	2.7	3.9
		13.5	4.6	5.0
	PIPA/TMCl	15.8	13.9	9.4
		15.9	15.0	12.0
Z2E1	none	19.6	3.5	26.3
	PIPA/TMCl	18.8	14.1	30.9
		19.8	< 1	30.1

*: PIPA = piperazine, MPIPA = 2-methylpiperazine, TMCl = trimesoyl chloride.

Polytetrafluoroethylene (PTFE)

The impregnation of this support with the liquid membrane phase caused some problems. Due to the low surface energy of PTFE, the liquid did not enter the pores of the support and remained as droplets on top. Therefore, another way of impregnation of the membranes had to be found. A suitable method was the following: firstly, the liquid membrane phase was diluted with ether. Next, an uncoated support was placed in the diluted liquid membrane solution. The ether evaporated and meanwhile the liquid membrane phase filled the pores of the support. In this way, the teflon membranes were impregnated with ca. 290-300 mg of liquid membrane phase which is about the same as the maximum amount in Accurel membranes. The coated supports were prepared with the mould. When the membrane was stored in ethanol after preparation, the ethanol was replaced by ether and the ether by the LM-phase. When the coated supports were dried after polymerization, the impregnation method was identical to that of an uncoated teflon support.

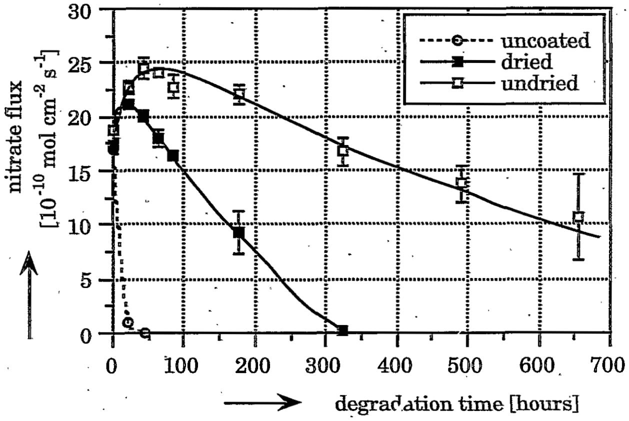


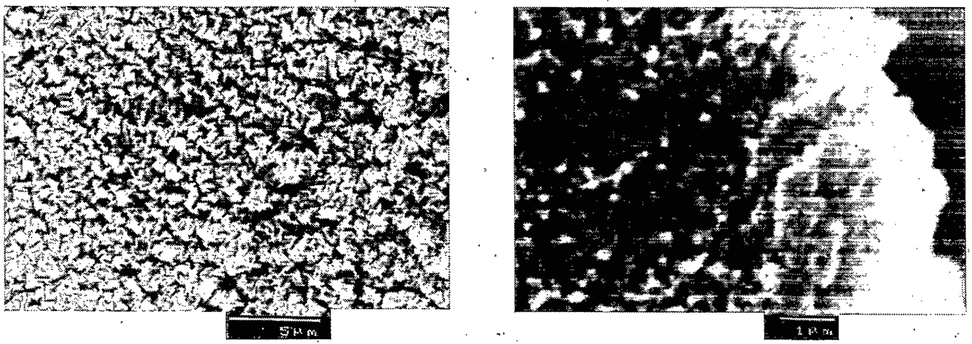
Figure 4.15. *Long term experiments with teflon membranes. Support: Sartorius SM 11807 + PIPA/TMCl toplayer. LM-phase: 0.2 M TOMA in o-NPOE. The composites were prepared using the mould described in section 4.2.2. Dried membranes were dried in air after polymerization. Undried membranes were kept in ethanol after polymerization until use. Error bars indicate maximum and minimum values obtained in a series of experiments.*

In figure 4.15 the results of flux measurements are drawn. Without a toplayer, the nitrate flux is reduced to almost zero within one day. Coated membranes, however, show a large increase in stability due to the presence of the toplayer. When a dried composite membrane is taken as support, no flux can be detected just after a period of 325 hours. Very promising results are obtained when the composites are not dried after preparation, but stored in ethanol in which way the toplayer remains in the wet state. In this way, the membrane does not have the opportunity to curl after polymerization or to induce defects in the toplayer because of the drying. After 325 hours of degradation, the flux is still the same as the initial flux of an uncoated SLM. After 650 hours (almost 1 month) the experiment was stopped. At this point, the flux was still about half the initial flux. The differences between dried and undried composite supports might indicate that drying is a very critical point in the preparation, and that drying is one of the causes of the reproducibility problems. It must be mentioned however that the undried results in figure 4.15 are mean values of the best results. Also here, different SLMs prepared exactly the same way, could show stabilities which differ by a factor two or more. This again indicated that the problems in reproducibility not only result from the interfacial polymerization itself. Other factors like replacing feed and strip for a flux measurement or small pressure differences across the SLM can introduce defects in the toplayer or press LM-phase out of the support.

4.4 Characterization

4.4.1 Scanning electron microscopy

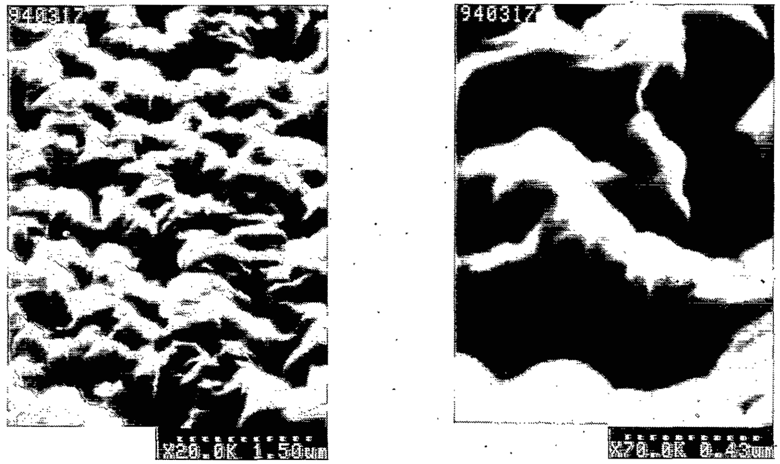
In figure 4.16, SEM photographs of PIPA/TMCl toplayers on Accurel are shown. This typical, rippled and folded surface structure (figure 4.16a) was always found with these monomers on Accurel. Similar structures were also observed by Cadotte *et al.* for PIPA/TMCl reverse osmosis membranes [15] and for Toray's UTC-70 RO membranes [23]. Cadotte *et al.* believed that this structure was the result of swelling phenomena during polymerization. When the polymerization continued within the swollen membrane, the structure could be permanent, even if the membrane is dried for SEM observation. The drying itself might also induce this rippling by a partly collapse of the swollen toplayer. In figure 4.16b one can see that the toplayer has a thickness of several microns (3-5 μm). The toplayer thickness is higher when the TMCl concentration increases. Although there are minor differences, the toplayers prepared with the mould have about the same surface morphology as the ones prepared in petri-dishes.



(a) (b)

Figure 4.16. *SEM photographs of Accurel + PIPA/TMCl toplayers. (a) Surface view (5,000x). (b) Cross section (15,000x).*

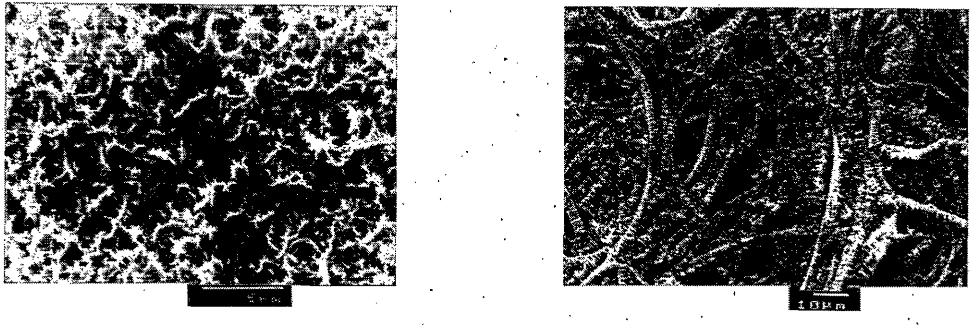
FE-SEM photographs of PIPA/TMCl layers on Accurel given in figure 4.17. The photographs are taken under an angle of 45 degrees to obtain information on differences in height in the toplayer. These differences are clearly visible. With magnifications of 70,000 no 'pores' or defects could be detected in the toplayer with FE-SEM. No differences between freeze-dried and normal dried samples could be detected. This might be an indication that the rippled structure is a permanent one, as already assumed by Cadotte *et al.* [15]. However, when the freeze-drying was carried out too slowly the swollen structure might get lost and no differences between dried and freeze-dried samples can be seen.



(a) (b)

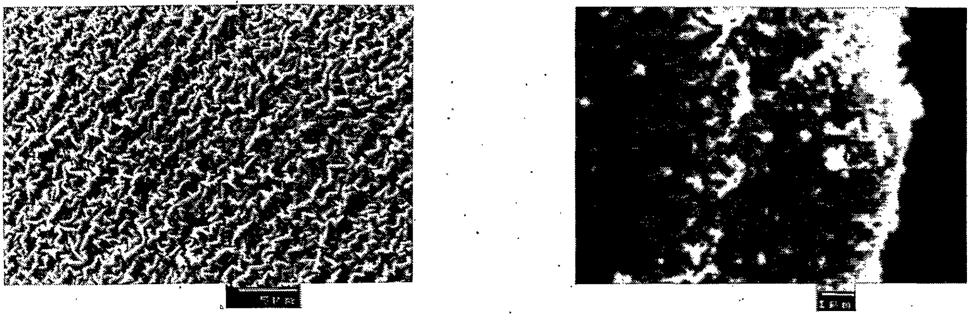
Figure 4.17. *Surface view FESEM images of Accurel + PIPA/TMCl toplayer. (a) magnification 20,000x, angle 45 °. (b) magnification 70,000x, angle 45 °.*

The influence of the support on toplayer morphology of PIPA/TMCl layers can be seen in figure 4.18. When Durapore is used as support, no folded structure is observed, but a much less smooth structure is observed compared to the situation with Accurel (see figures 4.16 and 4.18a). This might be due to differences in pore structure and membrane material (PVDF instead of PP). In figure 4.18b, the surface roughness and its impact on toplayer texture is clearly visible. The support material itself (DSM Z2E1) is biaxially stretched and has a rough surface. Although no large defects in the toplayer could be detected with SEM, it is clear that this surface roughness might cause defects in the toplayer, and as a result, problems in reproducing flux and stability measurements are encountered.



(a) (b)

Figure 4.18. *SEM pictures of PIPA / TMCl layers on two other supports. (a) Durapore GVHP (5,000x). (b) DSM Z2E1(1,000x).*

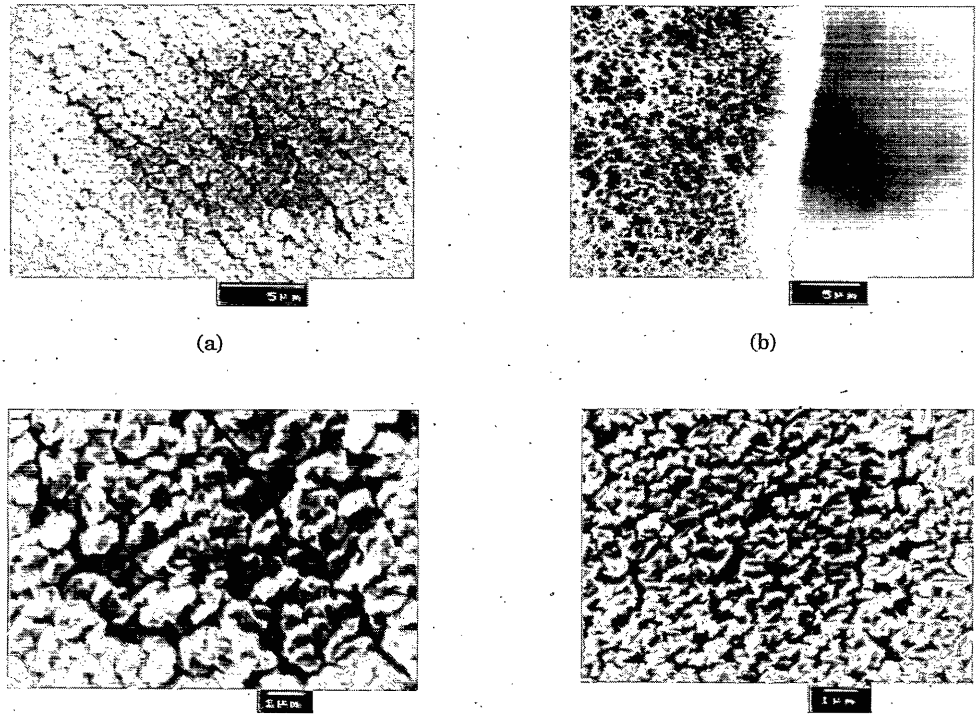


(a) (b)

Figure 4.19. *SEM photographs of Accurel + a toplayer of PIPA and TMCl / IPhCl (0.1 / 0.1) (a) Surface view (3,500x). (b) Cross section (10,000x).*

Figure 4.19 shows SEM pictures of the copolymeric PIPA/TMCl+IPhCl toplayers. Despite the replacement of a part of the TMCl by IPhCl, the surface morphology (figure 4.19a) is the same as for PIPA/TMCl. The toplayer thickness seems to be somewhat lower, although it is difficult to see how far the toplayer has penetrated into the porous support.

The surface texture does not change much when PIPA is replaced by other, similar amines as can be concluded from figure 4.20. In all cases the rippled and folded structure is found. For MPIPA/TMCl, a somewhat finer structure was observed than for DMPIPA/TMCl and AMPIP/TMCl (compare figure 4.20a with 4.20b and c), while the thickness of the toplayer was again in the order of 3-4 μm (4.20b). The very similar surface morphologies found for other amines, might be an indication that polymerizations with TMCl always result in these typical toplayer structures and that the reason for this can be found in the properties of TMCl like the ability to hydrolyse as proposed by Cadotte *et al.* [15].



(a) (b)

(c) (d)

Figure 4.20. *SEM photos of toplayers of TMCl and several amines on Accurel. (a) MPIPA/TMCl, surface (5,000x). (b) MPIPA/TMCl, cross section (3,500x). (c) DMPIPA/TMCl, surface (10,000x). (d) AMPIP/TMCl, surface (10,000x).*

4.4.2 Infrared measurements

In order to elucidate the chemical composition of the toplayers, Attenuated Total Reflectance-FTIR (ATR-FTIR) was used to characterize the composite supports. By means of this technique it was tried to detect chemical differences between PIPA/TMCl coated supports which were prepared with and without the addition of an acid acceptor to the aqueous amine solution. As observed before (figure 4.7), this addition has a large influence on the final nitrate flux and stability of coated SLMs. The most important spectra are given in figure 4.21.

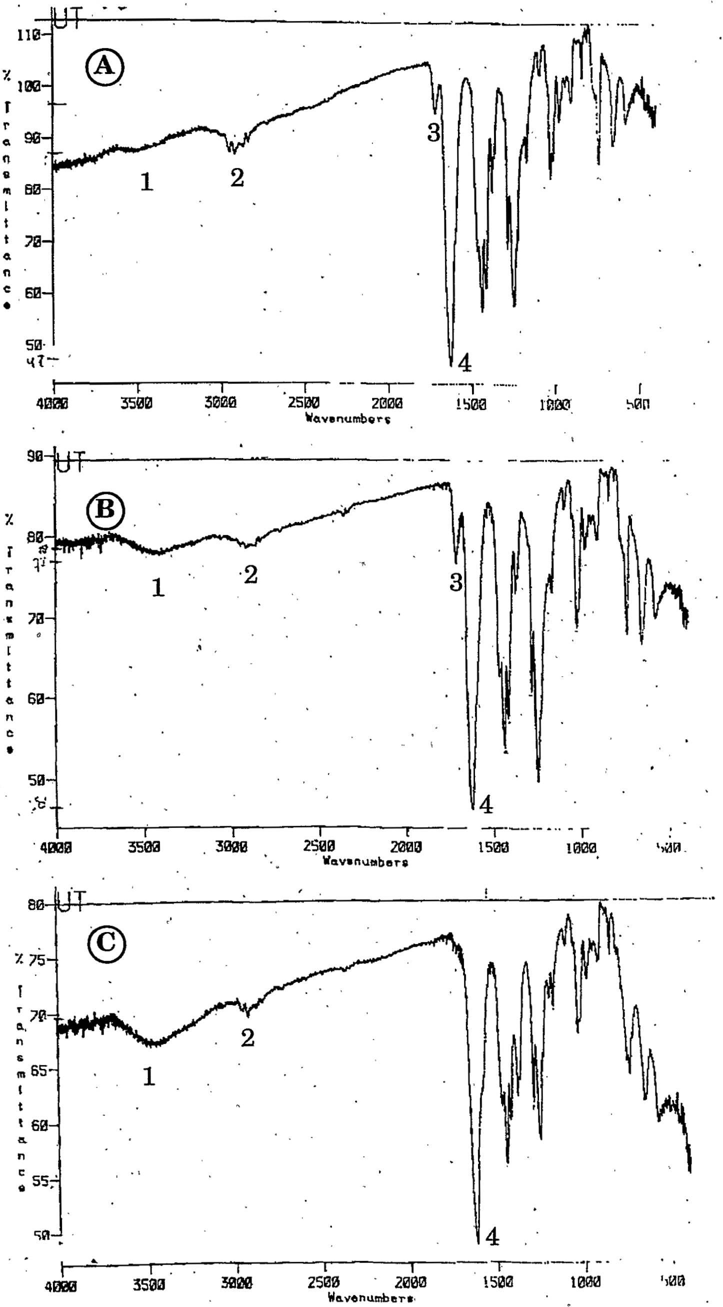


Figure 4.21. *ATR-FTIR spectra of toplayers of PIPA and TMCl on Accurel. (a) No acid acceptor added. (b) 0.10 M NaOH as acid acceptor during polymerization. (c) 0.20 M NaOH as acid acceptor during polymerization.*

In the discussion of the ATR spectra, we restrict ourselves to a qualitative description of a small number of peaks. For wavenumbers smaller than 1500 cm^{-1} the number of peaks is too large to compare the different spectra. The broad band at 3250-3600 cm^{-1} (1) can be subscribed either to the N-H stretch band or to an O-H stretch band. When it is due to the N-H stretch band, this might indicate the presence of amine endgroups. Since the composite is placed against the crystal with the side which has been in contact with the piperazine solution, this is very well possible. This is an experimental confirmation of the ideas of Enkelmann and Wegner: the surface of a nylon-6,10 interfacially polymerized membrane which has been in contact with the water phase consists of amino endgroups [12,24]

The peaks between 2970 and 2750 cm^{-1} (2) are the characteristic C-H stretch vibration bands. The origin of this may be the polypropylene support or the C-H band of the polyamide. The probing depth for the KRS-5 crystal used is in the order of 1-3 μm, depending on the angular setting of the crystal [25], while the toplayer thickness is in the order of 2-5 μm. Probably, the band is due to both materials.

The two interesting peaks are those at 1715 cm^{-1} (3) and 1627 cm^{-1} (4). The first peak at 1715 cm^{-1} is the C=O stretch band, which is most likely associated with a carboxylic acid. The band at 1627 cm^{-1}, the most intensive one, is also the characteristic C=O stretch vibration band, but in this case it is the C=O stretch band from the amide bond, and as a result much more clearly present. The carboxylic acid band was also observed by other authors for several interfacially polymerized membranes. Bartels investigated the FT-30 membrane, a commercially available RO membrane (see chapter 3 of this thesis) prepared with TMCl as one of the monomers, and found a band at 1710 cm^{-1} which was subscribed to carboxylic acid [25]. Indeed, the FT-30 membrane is believed to be mildly anionic in charge due to a partly hydrolysis of the acid chloride groups. Chern *et al.* [19,20] also subscribed the observed band at 1720 cm^{-1} to the C=O stretch band from an acid group for membranes prepared out of 1,2,4,5-benzenetetraacyl chloride and 4,4'-methylenedianiline or ethylenediamine.

The peak at 1720 cm^{-1} (3) is interesting since it disappears when the NaOH concentration during polymerization is higher than 0.20 M. When the band is indeed due to carboxylic acid groups, which are the result from the hydrolysis of acid chloride groups, this would mean that the presence of (high enough concentrations of) acid acceptors decreases the amount of hydrolysed groups. This is in agreement with the results from Chern *et al.* [19,20], who found for their system the intensity of the 1720 cm^{-1} band to be less in the presence of an acid acceptor than without one. Cadotte *et al.*, nevertheless, claimed the opposite for the system PIPA/TMCl: the stronger the acid acceptor, the more severe the hydrolysis of acid chloride groups [15]. No experimental proof was given for this hypothesis, however. The ATR results support the idea that hydrolysis is not the reason for the loss in flux and stability of coated SLMs which were prepared in the presence of an acid acceptor, as the results in table 4.5 already indicated. Still, no explanation is found for these phenomena.

Chern *et al.* also determined quantitatively, *i.e.* in the percents, the hydrolysed groups for their interfacially polymerized films by using the optical density of the FTIR spectra for their calculation [20]. We tried to compare the different spectra by measuring the peak intensities from the base line to the lowest point in the IR spectrum. A calculation of the peak surface was not possible with the software present. However, problems were encountered in the tightening of the membrane sample to the crystal, which is known to be a problem for the reproducibility in ATR measurements [26]. The stronger the membrane sample is pressed onto the crystal, the more deformed the toplayer is, which causes differences in penetration depth of the IR-beam. Furthermore, the place of the membrane on the crystal is of importance, since the intensity of the beam is lower after several reflections in the crystal. Even when care was taken to keep these factors constant, no reproducible quantitative data were obtained. This means no data on absolute or relative amounts of carboxyl groups will be presented here.

4.4.3 X-ray Photoelectron Spectroscopy (XPS) measurements

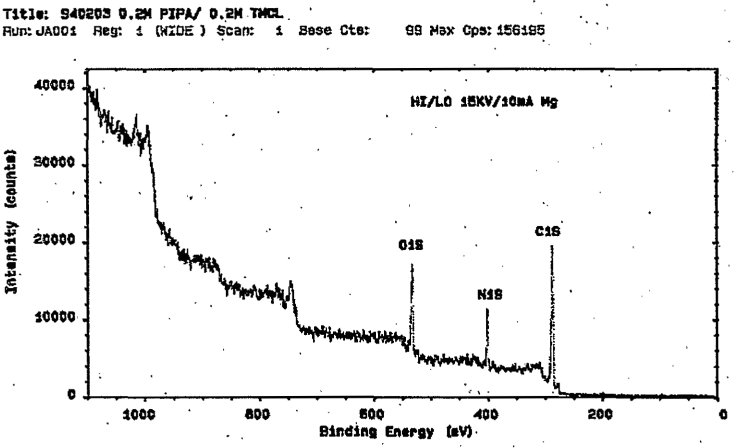


Figure 4.22. *Wide range XPS spectrum of a toplayer of PIPA and TMCl on Accurel. No acid acceptor used during polymerization.*

Another method for obtaining information on the chemical composition of surfaces is XPS. An example of an XPS spectrum as recorded for a toplayer of PIPA and TMCl on Accurel is shown in figure 4.22. All the expected peaks were observed. At a binding energy of 287 eV, the C1s peak is found. The peak at 401 eV is caused by

N1s, while O1s has its peak at 533 eV. Also the Auger bands of oxygen (730 eV) and carbon (950 eV) are present. From the areas under the peaks in the spectra, the atom-percentages of the different elements can be calculated. The results are given in table 4.11. Also the theoretical values are listed, for the cases of no hydrolysis and one hydrolysed group for each TMCl molecule.

Table 4.11. *Results of XPS measurements of Accurel or Accurel with a PIPA/TMCl toplayer. The concentrations are given in atom percentages. Except where indicated, the concentrations of TMCl and PIPA for the polymerization was 0.2 M in dodecane and water, respectively.*

sample	acid acceptor	fraction C [atom %]	fraction O [atom %]	fraction N [atom %]
Accurel PP	-	97.3	2.8	-
PIPA/TMCl	none	70.9	16.3	12.8
PIPA/TMCl	none	71.5	16.5	12.0
PIPA/TMCl*	none	70.9	15.8	13.3
PIPA/TMCl	0.075 M NaOH	70.9	16.3	12.8
PIPA/TMCl	0.2 M NaOH	70.6	15.9	13.5
<u>theoretical</u>				
no hydrolysis	-	63.1	16.8	14.7
1 hydrolysed group per TMCl	-	60.0	24.6	10.7

*: concentration PIPA 0.4 M

It is difficult to draw definite conclusions from the data in table 4.11. This is due to the experimental error in the measured data (maximum error 30 %) and the small differences between the different data. Nevertheless, one can see different effects in table 4.11. When pure Accurel is measured, there is a small amount of oxygen present. Since Accurel is made out of polypropylene which does not contain oxygen, this might be an indication of impurities in the sample (*e.g.* residual water) or of an oxidation of the surface. Since the PIPA/TMCl toplayers are assumed to be hydrophilic, this problem will be more severe and the observed percentages will possibly be somewhat too high. Indeed problems were encountered in obtaining the high vacuum for the XPS measurements. Although the observed amount of nitrogen falls nice in between the calculated extremes, this is not the case for carbon and, to a some degree, for oxygen. Summarizing, XPS does not give any decisive answers whether carboxylic acid groups are present in the top 50 Å of the toplayer sampled by XPS [25].

4.5 Conclusions

The application of interfacially polymerized toplayers of piperazine and trimesoyl chloride on Accurel supports was investigated thoroughly in this chapter. By using a mould during preparation of the toplayer, very promising results were obtained. While an uncoated SLM shows no flux after one day of enhanced degradation, the best coated membranes show no flux decrease after 350 hours of operation. The flux of these modified SLMs is as high as the initial flux of an uncoated membrane. When the toplayer of PIPA and TMCl is applied on top of other SLM-supports, similar stability improvements were observed. Several other, piperazine-like, amines show also an improvement in the SLM stability, sometimes in combination with a remarkable initial flux increase compared to uncoated SLMs.

Different characterization techniques were used to investigate whether differences in chemical composition were responsible for the decrease in both flux and stability when an acid acceptor was used during application of the PIPA/TMCl toplayer. ATR measurements gave an indication of the disappearance of carboxylic acid groups in the polymer, but no definite conclusions could be drawn. XPS was not suitable to detect the small amount of hydrolyzed groups.

Finally, there are still problems with reproducing the results, even when a mould is used for the interfacial polymerization. This might be an indication that the flux measurement method itself causes defects in the toplayer. Experiments which may confirm this hypothesis can be found in chapter 5.

4.6 References

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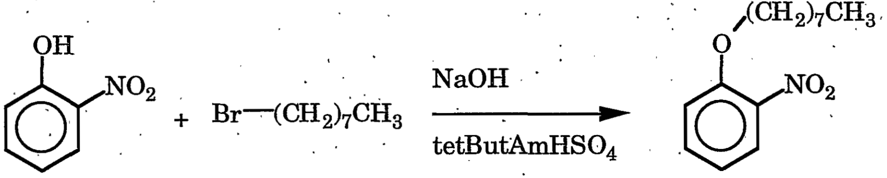
Appendix A to chapter 4

Synthesis of *o*-nitrophenyloctylether (*o*-NPOE)

In literature, no simple recipe was found for the synthesis of *o*-NPOE. Therefore, in corporation with the Laboratory of Organic Chemistry at the University of Twente, a new recipe was developed. The synthesis is based on the following reaction:



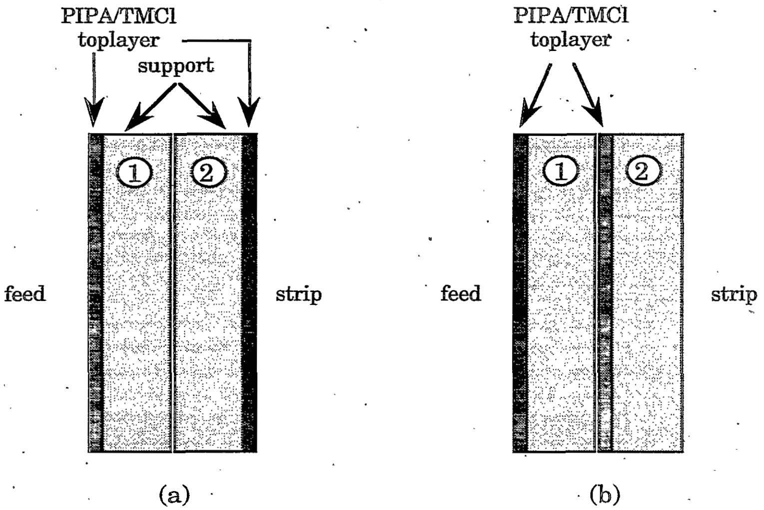
153.64 gr (1.10 moles) of *o*-nitrophenol (Janssen Chimica) and 213.12 gr (1.10 moles) of bromooctane (Janssen Chimica) were added to a 1000 ml three-necked flask. By means of a mechanical stirring device the contents of the flask were gently stirred for three hours. 9.3 gr Tetrabutylammoniumhydrogensulfate (Janssen Chimica) was added. A solution of approximately 220 gr NaOH (Merck) in 440 ml demineralized water was added dropwise to the flask by means of a funnel. The colour became red while the contents of the flask were getting clotty. A reflux condenser was placed on the flask, after which the reaction mixture was heated overnight at 60 °C.

The contents of the flask were transferred to a 4 l separatory funnel and washed two times with ether (app. 2 l the first time, second time less ether was used). The ether phases were added to each other and washed with 2 M NaOH (at least four times) until the NaOH remained colourless. After shaking the ether phase with a saturated NaCl (Merck) solution, 2 spoonfuls of MgSO4 were added per 1 l separatory funnel. The erlenmeyer flasks with the ether/MgSO4 were stirred for about 15 minutes to remove the lasts traces of water. After filtration using filter paper, the ether was evaporated in a film evaporator. Finally, the *o*-NPOE was purified by vacuum distillation. The resulting product (yield approximately 90 %) was a yellow oily liquid with a purity of 99.8 % as revealed by gas chromatography (capillary column type Z5).

Appendix B to chapter 4

Double layer SLMs

In this chapter, it was shown that the application of a single toplayer on the feed side of the membrane could increase the lifetime of SLMs for nitrate transport considerably. Nevertheless, after a while also for the very stable membranes the flux starts to decrease. This is an indication of carrier and/or membrane solvent loss. According to Neplenbroek *et al.*, loss of LM-phase takes place at the feed side of the membrane where the salt concentration is low [1]. To check whether loss to the strip phase is also possible, SLMs with two toplayers were prepared. When a single support has toplayers on each side, it is very difficult to remove residual reactants from the support and to impregnate it with the LM-phase. Furthermore, SEM examination of Accurel revealed a considerable surface roughness on the back side (the 'non-shining' side) of Accurel. Polymerization on this side surely would cause difficulties in obtaining a defect free toplayer in a reproducible way. Therefore, a different approach was chosen. Two SLMs with a toplayer of piperazine and trimesoyl chloride, prepared as described in section 4.2.2 and 4.2.4, were fixed on another in two different ways as shown in figure B1. To obtain a better contact between them, the two coated SLMs were fixed together using a small droplet of LM-phase.



(a) (b)

Figure B1. *Double layer SLMs. (a): one toplayer towards feed, one toplayer towards strip. (b): one toplayer towards feed, one toplayer in the middle of the SLM.*

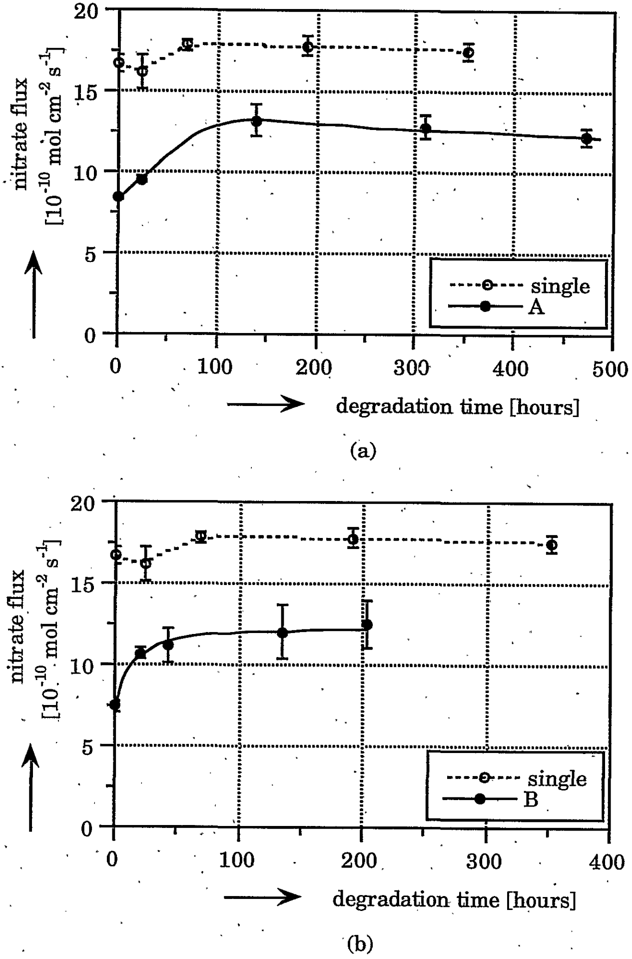


Figure B2. *Nitrate fluxes and stabilities of double layer SLMs. Support: 2 Accurel supports + PIPA/TMCl toplayer. PIPA concentration: 0.2 M in water. TMCl concentration: 0.2 M in dodecane. Reaction time 15 minutes using a mould. LM-phase: 0.2 M TOMA in o-NPOE. a) Toplayers at feed and strip side. b) Toplayers at feed side and in the middle. The values for the single SLM + PIPA/TMCl coating are taken from figure 4.14. The error bars indicate maximum and minimum values obtained in a series of experiments.*

The double layer SLMs were tested on nitrate flux and long term stability. The results are shown in figure B2. Since the double toplayer membranes have thicknesses twice that of a single membrane, it was expected that the fluxes would be halved when the resistance against transport is assumed to be completely in the organic phase. In figure B2 it can be seen that this indeed is the case for the initial fluxes. However, remarkable results on the long term are observed. In both cases, the double layer membranes are stable. Their fluxes *increase* in time to values which are *more than half* that of the 'single' reference membrane, although in situation a) the flux shows a slight decrease later on. An explanation for this remarkable phenomenon has not been found yet. Furthermore, there is no clear difference between the two geometries of the double layer membranes as can be seen when figure B2a and B2b are compared: in both cases, fluxes raise to approximately the same level of 12-13 * 10^{-10} mol cm^{-2} s^{-1}. Since in both cases the stabilities of the double layer SLMs are the same, it is clear that the application of a toplayer at the strip side does not increase the stability. This supports the hypothesis of Neplenbroek *et al.*: loss of LM-phase components takes place at the feed side. The presence of an extra resistance in the middle of the SLM (the toplayer in case B) has no effect on nitrate flux. This indicates that the transport in this toplayer takes place through a layer of LM-phase which has swollen the toplayer. When the LM-components can swell the toplayer, loss of the LM-phase by dissolution still can take place at the feed side of the membrane.

From these experiments with double layer SLMs we can conclude that loss of LM-components will take place at the feed side of the SLM, and that there are indications that the LM-phase can swell the toplayer of PIPA and TMCl.

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5

HOLLOW FIBER SUPPORTED LIQUID MEMBRANES FOR NITRATE REMOVAL

SUMMARY

This chapter describes the development of a hollow fiber supported liquid membrane (HFSLM) for the removal of nitrate ions from water. Two different membrane modules were designed which differed in the length of the fibers. In order to test the HFSLMs on nitrate flux and stability, two set-ups were used: one in which feed and strip were recirculated and one for the continuous removal of nitrate. Furthermore, part of the experiments were carried out using fibers with a toplayer of piperazine and trimesoyl chloride at the lumen side to increase the stability of the HFSLM.

Nitrate fluxes of the HFSLMs were only slightly lower than those of flat sheet SLMs, despite the much larger thickness of the fiber wall. In both set-ups, the nitrate flux decreased in time. By applying a toplayer on the lumen side of the fibers, lifetime of the liquid membrane was raised. SEM observations showed the toplayer, although defect-free, not to be uniform in morphology which resulted in difficulties in reproducibility of the results.

5.1 Introduction

In the chapters 3 and 4, research was focussed on flat sheet SLMs for nitrate removal and their stabilization. In order to obtain economical separations, a large membrane area must be provided for the reactions at feed and strip side. For industrial applications, a hollow fiber geometry is more advantageous due to its high surface area per volume membrane module (1,000 - 10,000 $m^2\ m^{-3}$, values up to 30,000 $m^2\ m^{-3}$ might be obtained [1,2]). The higher the ratio, the lower the costs per installed membrane area.

In this chapter, a start is made with using hollow fibers as support material for liquid membranes for the removal of nitrate from water. Furthermore, part of the experiments is focussed on stabilizing these hollow fiber supported liquid membranes (HFSLMs) by applying a toplayer on the membrane surface by means of an interfacial polymerization reaction as described before in this thesis. Aim of this work is to get more insight and a better feeling for working with HFSLMs and the specific problems in application of the toplayer.

5.2 Experimental

5.2.1 Materials and membranes

Support

Throughout this chapter, only one type of hydrophobic hollow fiber is used, *i.e.* the Q3/2 fiber, which was kindly supplied by Akzo. The fiber has an inside diameter of 600 µm (mean value) and a wall thickness of 200 µm (mean value). The fiber is made out of polypropylene with a nominal pore size of 0.2 µm [3]. The pore structure of the fiber is highly asymmetric. The smallest pores are at the lumen side of the fiber, while the pore size at the shell side is much larger.

Carrier and solvent

In order to be able to compare the results of HFSLMs with those of flat sheet SLMs as described in the chapters 3 and 4, it was chosen to use the same liquid membrane phase. The organic solvent for the carrier was *o*-nitrophenyloctylether, *o*-NPOE, prepared in our laboratories according to the method described in the first appendix in chapter 4 of this thesis. Trioctylmethylammonium chloride (TOMA) was applied as carrier for nitrate transport. It was obtained from Fluka, had a purity of about 97 % (manufacturer's data) and was used without further purification. The carrier was dissolved in *o*-NPOE up to a concentration of 0.2 M.

Interfacial polymerization

Interfacial polymerizations were carried out using piperazine (PIPA) and trimesoylchloride (TMCl) as the monomers, identical to the successful stabilization experiments in chapter 4. PIPA was obtained from Fluka (purity > 99 %) and TMCl from Aldrich (purity 98 %). Both monomers were not further purified before use. Dodecane from Janssen Chimica (purity 99 %) was taken as organic solvent for TMCl, while PIPA was dissolved in Milli-Q water (Milli-Q water is demineralized water purified with a Milli-Q Plus Water Purification System from Millipore®).

5.2.2 Module preparation

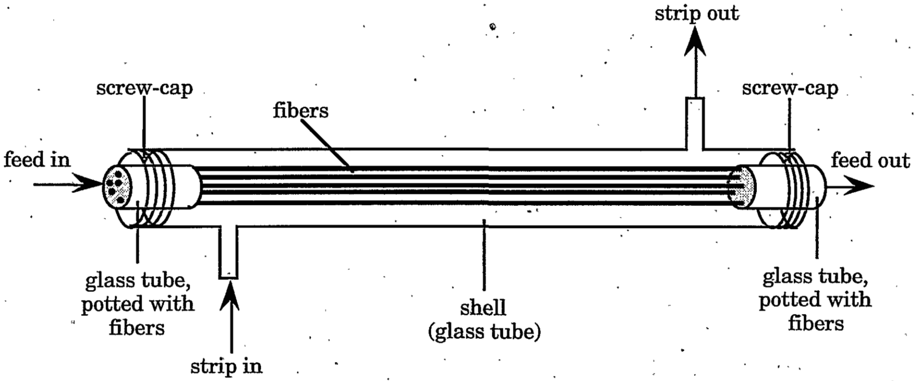


Figure 5.1. *Schematic drawing of the hollow fiber supported liquid membrane module with 5 fibers. Although shown horizontally, the module was placed vertically in the permeation set-up.*

The membrane module as used throughout this chapter is schematically shown in figure 5.1. Modules with 1 and 5 fibers were used. Furthermore, modules with two different dimensions were prepared: one with an effective fiber length of about 17 cm, and a second with an effective fiber length of approximately 38 cm.

The membrane modules were prepared in the following way. Firstly, the fibers were arranged into a bundle and the ends were embedded into a glass tube by means of polyurethane potting material (two components adhesive). When the potting material had hardened, the plug was sliced open at the glass tube end to free the fibers and allow the passage of the aqueous feed phase through the lumen of the fibers. The same was done for the other end of the fibers. In a number of experiments, a toplayer was applied on the lumen side of the fibers (see section

5.2.3) before impregnation of the fibers with liquid membrane phase (section 5.2.4). The bundle of impregnated fibers was inserted into the outer (shell) glass tube. Finally, by means of screw caps, with a rubber ring in the middle, the potted fibers were fixed in the shell.

5.2.3 Application of the toplayer

In several modules, a toplayer was applied at the lumen side of the fibers by an interfacial polymerization reaction. The monomers used (PIPA and TMCl) were also used for the stabilization of flat sheet SLMs as described before in chapter 4. Due to the geometry of the membrane, the application of the toplayer was somewhat different. At the shell side of the fiber the pore size was much larger as revealed by scanning electron microscopy which might cause problems in obtaining a defect free toplayer. Therefore, it was decided to prepare the toplayer at the inside of the fiber, and, consequently, to let the the feed flow through the lumen side of the fiber in all flux and stability experiments.

After potting the fibers in the glass tube, they were impregnated with the TMCl solution in dodecane (0.2 M). This was done by placing the fibers in vertical position and dripping the TMCl solution on the lumen side of the fibers. To prevent organic droplets on the membrane surface at the lumen side, a nitrogen gas stream was flushed slowly through the inside of the fibers. Attached TMCl solution on the outside was removed carefully with a paper tissue. A certain amount of PIPA solution (varying concentrations) in water was allowed to 'flow' through the lumen side of the fiber under gravity. Excess reactants were removed by rinsing the fibers with Milli-Q water and ethanol. The coated fibers were stored in ethanol until further use.

5.2.4 SLM preparation

Before impregnation, the length of the fibers between the two inner glass tubes (see figure 5.1) was measured in order to calculate the membrane area. Uncoated and potted fibers were impregnated by dipping them for a while in a petri-dish containing some LM-phase. Coated fibers were impregnated somewhat differently. The potted fibers were hanged in a vertical position after which the LM-phase was introduced on the outside of the fibers by means of a pipette. In both cases, nitrogen gas was flushed slowly through the lumen of the fibers to prevent as much as possible the formation of LM-phase droplets on the inner membrane wall. When the fibers were completely transparent, they were considered to be impregnated. Excess LM-phase was carefully removed from the outside of the fibers with a tissue. In some cases, membrane modules were re-used. The impregnated LM-phase was removed by washing the fibers with ethanol and ether. After drying, the fibers were re-impregnated and ready for further use.

5.2.5 Permeability and stability measurements

Flux determination

Nitrate fluxes of the hollow fiber SLMs were determined using two different set-ups, schematically drawn in figures 5.2 and 5.3. Set-up 1 is very similar to the flat sheet SLM apparatus described before.

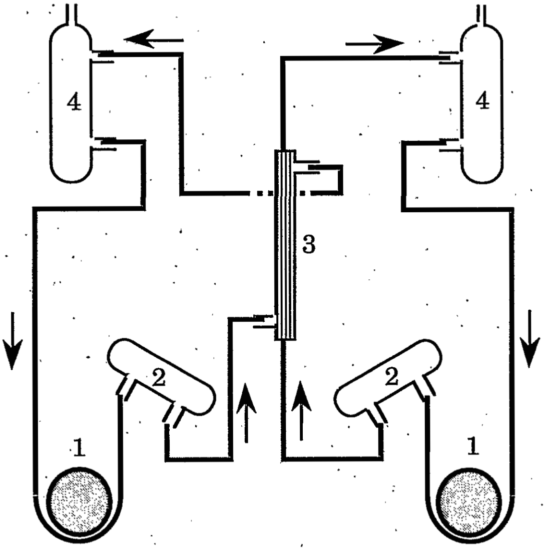


Figure 5.2. *Experimental set-up 1 for testing HFSLMs (1 = peristaltic pump, 2 = accumulator, 3 = membrane module, 4 = thermostated buffer vessel).*

After preparation of the hollow fiber module, it is placed in the set-up. Next, the system is filled with 130 ml 4 * 10^{-3} ml $NaNO_3$ (feed) and 130 ml 4 M NaCl (strip) aqueous solutions. Peristaltic pumps circulated feed and strip around with velocities of 2 ml s^{-1} (feed) and 5 ml s^{-1} (strip). In some experiments, both flow velocities were reduced to 1 ml s^{-1} as will be explained later on in this chapter. Both feed and strip phases flow in a co-current manner through the module, the feed flowing through the lumen side of the fibers, and the strip at the shell side. The buffer vessels were kept at a temperature of 25 °C. Periodically, samples of about 1 ml were taken from the feed solution and analyzed on nitrate and chloride concentration by means of HPLC (Waters IC-PAK™ anion column). From the linear decrease of nitrate concentration in time, the nitrate flux was calculated using equation (1)

$$J = - \frac{d\,[NO_3^-]}{dt}\frac{V}{A}, \qquad (1)$$

where J is the nitrate flux in mol cm^{-2} s^{-1}, $d[NO_3^-]/dt$ the linear decrease of the nitrate feed concentration in time, V the feed volume and A the membrane area in contact with the aqueous feed phase. The feed volume was assumed to be constant. From the length of the impregnated fibers, their inside diameter and the number of fibers, the membrane area at the lumen side was calculated.

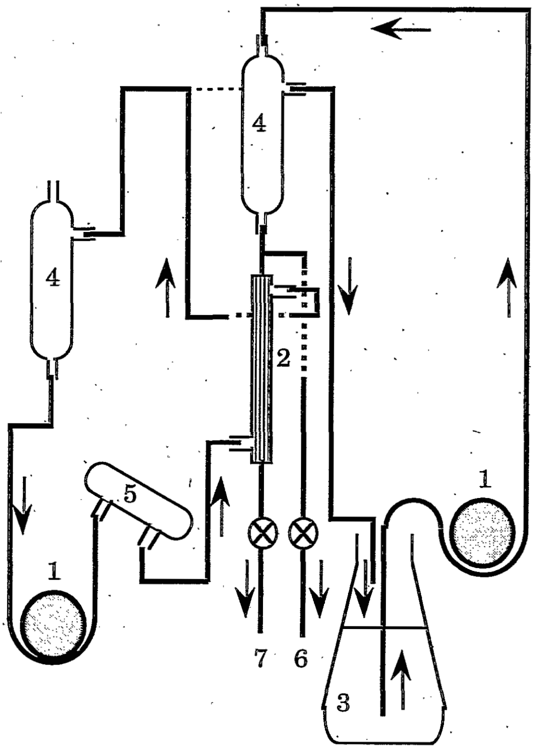


Figure 5.3. *Experimental set-up 2 for testing HFSLMs (1 = peristaltic pump, 2 = membrane module, 3 = stirred feed vessel, 4 = thermostated buffer vessel, 5 = accumulator, 6 = tap feed before module passage, 7 = tap feed after passage).*

For several reasons, discussed later on in this chapter, a second set-up was used which worked somewhat different from that drawn in figure 5.2. The strip circulation side was identical to that of the other setup. However, the feed solution was not pumped through the lumen. By means of a peristaltic pump, feed solution was pumped out of a large feed reservoir (5 l) into a thermostated buffer vessel placed above the membrane module. Part of the feed solution flowed back into the large feed reservoir, so that the feed level in the buffer vessel was kept constant. In the lumen of the fibers there will be a pressure gradient due to the hydrostatic pressure of the feed column. By keeping the strip outlet at the same height as the feed level in the thermostated buffer vessel, pressure differences between lumen and shell side of the fiber are minimized.

Under influence of the gravity, feed will flow through the fibers counter-currently with the strip phase. The flow velocity was regulated with a valve at the lumen outlet. The feed was collected at the outlet of the module and weighted to determine the flow rate assuming a density of 1 g ml^{-1} for the feed phase. By means of a second valve, the feed solution at the entrance of the module could be drained. The composition of the feed before and after passage through the module was determined by HPLC (Waters IC-PAK™ anion column). From the difference in nitrate concentration between feed inlet and outlet $\Delta\,[NO_3^-]$, the nitrate flux J was calculated using equation (2)

$$J = \Delta\,[NO_3^-]\,\frac{\Phi}{A}\,, \qquad (2)$$

where Φ is the volume flow rate and A the effective internal surface area of the fibers. Most experiments were carried out at 25 °C.

Stability measurements

The stability measurements for set-up 1 were carried out analogous to those in chapters 3 and 4. After the initial flux measurements, feed and strip were replaced by a 10^{-4} M NO_3^- solution and a fresh strip solution, respectively. After about 20 hours of enhanced degradation, both phases were replaced by the starting solutions ($4 * 10^{-3}$ M $NaNO_3$ and 4 M NaCl) to determine the nitrate flux again. This cycle of degradation and flux measurements could be repeated several times depending on the observed stability of the HFSLM. The period the liquid membrane was exposed to the degradation liquid was called the degradation time.

For set-up 2, several stability experiments were carried out depending on the experiment. Since the membrane was always exposed to fresh feed solution (the feed is not recirculated as is the case with set-up 1), degradation took place continuously. The stability of the HFSLM could be monitored 'on-line' simply by analyzing the feed before and after passage of the module. In one series of experiments, the feed solution was replaced temporarily by demineralized water ('demiwater') to check its influence on stability. To determine the flux, the membrane was exposed again to the usual $4 * 10^{-3}$ $NaNO_3$ feed solution. For set–up 2, the flux could be measured as a function of the amount of feed passed through the module or the time the experiment was running.

5.2.6 Fiber characterization

The structure of fiber and toplayer were examined with scanning electron microscopy (SEM). Coated fibers could only be characterized after the permeation experiments since the fibers had to be cut out of the module for examination, which destroyed the module. So, after the flux measurements, the remaining LM-phase was removed by ethanol. After drying, a small part of fiber was cut out of the module. The fiber was cut under an angle of about 45 degrees with the length axis. In this way, both shell and lumen (with the toplayer) side of the fiber could be examined. Next, the fiber was glued on a sample holder by means of double-sided adhesive tape. Cross sections were prepared by cryogenic breaking, *i.e.* they were immersed in an ethanol/water mixture and broken in liquid nitrogen. The samples were coated with gold in a Balzer Union SCD 040 sputtering apparatus (3 minutes, 0.1 mbar, 15 mA). A Jeol JSM T 220A scanning electron microscope was used for examination of the fibers (accelerating voltage 20 kV).

5.3 Results and discussion

5.3.1 Membrane modules prepared

Table 5.1. *Overview of the modules used and characteristics of their flux determinations*

code	number of fibers	fiber area* [cm^2]	toplayer	flux set-up	degradation	remarks†
M1	5	14.0	yes	1	10^{-4} M NO_3^-	1
M2	5	16.5	no	1	10^{-4} M NO_3^-	1
M3	5	16.0	no	1	10^{-4} M NO_3^-	1
M4	5	17.0	no	1	10^{-4} M NO_3^-	1
M5	5	15.7	no	1	10^{-4} M NO_3^-	1
M2b	5	16.5	no	1	10^{-4} M NO_3^-	1,3
M4b	5	17.0	yes	1	10^{-4} M NO_3^-	1,3
M5b	5	15.7	yes	1	10^{-4} M NO_3^-	1,3
M23	5	18.7	yes	1	10^{-4} M NO_3^-	1
M9	5	15.5	no	2	$4 * 10^{-3}$ M NO_3^-	1
M13	1	7.2	no	2	$4 * 10^{-3}$ M NO_3^-	2
M14	1	7.1	no	2	$4 * 10^{-3}$ M NO_3^-	2
M13b	1	7.2	no	2	demiwater	2,3
M17	1	7.1	no	2	demiwater	2
M14b	1	7.1	no	2	$4 * 10^{-3}$ M NO_3^-	2
M18	1	7.2	no	2	$4 * 10^{-3}$ M NO_3^-	2,3
M15	1	7.1	yes	2	$4 * 10^{-3}$ M NO_3^-	2
M16	1	7.3	yes	2	$4 * 10^{-3}$ M NO_3^-	2

*: inner area.† remarks: 1 = short module. 2 = long module. 3 = regenerated module, *e.g.* M2b is identical to module M2, after removal of LM-phase and re-impregnation.

In table 5.1, the characteristics of the membrane modules as used in the experiments are given. Table 5.2 provides information on the way the PIPA/TMCl toplayers are applied at the lumen side of the fiber. The exact procedure was given in section 5.2.3.

Table 5.2. *Monomer concentrations and quantities for the application of the toplayer at the lumen side of the fibers.*

code	[TMCl] [M]	[PIPA] [M]	amount of PIPA passed through fibers [ml]
M1	0.20	0.05	40
M4b	0.20	0.05	100
M5b	0.20	0.05	50
M23	0.20	0.05	100
M15	0.20	1.0	20
M16	0.20	0.1	20

5.3.2 Results co-current flux set-up

Uncoated fibers

Firstly, manometers were attached to set-up 1 to determine the pressure drop in the module. Between strip inlet and outlet almost no pressure difference was detected at a volume flow rate of 5 ml s^{-1}. The observed pressure difference between feed inlet and outlet was approximately 0.5-0.6 bar at a feed flow rate of 2 ml s^{-1}. So, the maximum pressure difference between feed and strip over the liquid membrane at these flow rates will be 0.5-0.6 bar. For a cylindrical capillary with a pore radius r the break-through pressure, at which the impregnating phase is displaced out of the pores, can be calculated with the Laplace equation [4]

$$P_c = \frac{2\gamma}{r}\cos\theta\,, \qquad (3)$$

where P_c is the break-through pressure (N m^{-2}), γ the interfacial tension between the aqueous phase and the LM-phase (N m^{-1}), θ the contact angle measured through the impregnating liquid and r the pore radius (m). For a pore radius of 0.1 μm [3] and an interfacial tension of $5.0 * 10^{-3}$ N m^{-1} between water and 0.2 M TOMA in *o*-NPOE [5,6] a break-through pressure of 1 bar is calculated, which is higher than the maximum obtained pressure difference.

The flow velocity in the fibers is quite high: for the 5 fiber modules and an overall feed volume flow rate of 2 ml s^{-1}, the flow rate in each fiber is 140 cm s^{-1}. Such high flow velocities undoubtedly will promote degradation of the membrane by emulsion formation due to a large deformation of the LM-meniscus [5,7]. This is one reason for building set-up 2 as will be discussed in section 5.3.3.

Table 5.3. *Nitrate fluxes of uncoated HFSLMs tested with set-up 1.*

code	initial flux, 1st run [10^{-10} mol cm^{-2} s^{-1}]	initial flux, 2nd run [10^{-10} mol cm^{-2} s^{-1}]	flux after 1 day [10^{-10} mol cm^{-2} s^{-1}]
M2	13.8	11.9	2.3
M3	12.9	12.1	1.8
M4	11.6	10.6	4.0
M5	11.5	10.6	3.5

The results for membrane modules M2, M3, M4 and M5 are shown in table 5.3. Directly after the first flux measurement was completed, the feed was replaced by a fresh feed solution for a second determination of the 'initial' nitrate flux. It is clear from the data in table 5.3 that replacement of feed induced degradation of the liquid membrane since the nitrate flux decreased. In each flux measurement the decrease in nitrate concentration in time was still linear, so it can not be concluded that degradation of the membrane took already place during the flux measurement.

The data in table 5.3 can be compared with those of flat sheet SLMs in table 3.5. For uncoated SLMs with TOMA as carrier, fluxes between $17 * 10^{-10}$ and $19 * 10^{-10}$ mol cm^{-2} s^{-1} were measured. The thickness of the flat sheet SLM is about 95 μm while the wall thickness of the fibers is approximately 200 μm. So, the nitrate flux through the fibers is clearly more than half the flux across a flat sheet SLM. Differences in membrane morphology, pore size (distribution), surface porosity and the completely different measurement conditions might cause this difference. It is therefore difficult to compare the flat sheet and hollow fiber results directly.

Coated membranes

Figure 5.4 shows the effect of a toplayer at the lumen side of the fibers on the long term stability of HFSLMs. The modules M2b, M4b, M5b and M23 were tested at lower feed and strip flow velocities of 1 ml s^{-1} compared to modules M1 and M10 (feed 2 ml s^{-1} and strip 5 ml s^{-1}) to minimize the influence of the pressure drop across the module on the stability. Several conclusions can be drawn from figure 5.4 which are quite similar to those observed for flat sheet SLMs with a

PIPA/TMCl toplayer as described in chapter 4. The initial fluxes of coated and uncoated membranes are almost equal, indicating a low resistance of the toplayer. The lowering of feed and strip flow velocities has no influence on the initial flux. Due to the small diameter of the fibers, the velocity of the feed in the lumen of the fiber is still high enough to minimize the aqueous boundary layer resistance at the feed side. Apparently, the same is valid for the resistance of the boundary layer at the strip side of the fibers. Furthermore, the coated membranes all retain their flux longer than the ones without a toplayer: application of a toplayer raises the lifetime of HFSLMs.

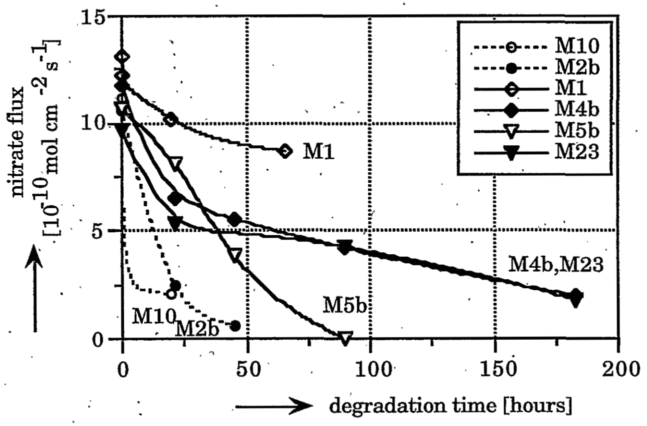


Figure 5.4. *Nitrate flux and stability of hollow fiber SLMs. Support: Accurel Q3/2 capillary membrane or Accurel Q3/2 + PIPA/TMCl toplayer. LM-phase: 0.2 M TOMA in o–NPOE.*

The differences between the several coated fibers are sometimes hard to explain. The modules M4b and M23 are prepared in the same way (see table 5.2) and show almost identical flux-time curves. Module M1 is prepared using the same concentration of PIPA as M4b and M23, but a smaller amount of solution passed through the fiber. It was expected that the toplayer would be thinner since less reactant was supplied and therefore the flux of module M1 should be higher. Indeed this was observed. However, the stability of M1 was better than that of M4b and M23 despite the (probably) thinner layer. Furthermore, module M5b reveals a lower flux than M4b and M23, while in this case less reactant passed the fibers.

The results given above in figure 5.4 show that the stability of HFSLMs can be improved by applying a toplayer of PIPA and TMCl on the lumen side of the fibers. When the results are compared with the best results obtained with flat sheet SLMs, it is clear that the application of the toplayer still has to be improved since with the coated flat sheet SLMs reasonable nitrate fluxes could be maintained for a much longer period. Besides, with several modules it was observed by SEM examination of the fibers that some of them in one and the same module did not contain a toplayer while others in the same module did. In other cases, the fibers were almost blocked by the toplayer, indicated by a large pressure build-up and slipping of the tubes connected to the module in the flux set-up. So, the toplayer could not be applied in an homogeneous and reproducible way.

5.3.3 Results set-up for continuous removal of nitrate

For several reasons, a flux set-up in which the feed *and* strip are pumped across the fibers has some disadvantages. The pumping will cause vibrations of the fibers. Furthermore, due to the high feed flow velocity inside the fibers, a pressure drop is generated of about 0.6 bar for uncoated fibers (at 2 ml s^{-1}), which will be even higher for coated fibers due to the extra hydrodynamic resistance. These two factors will certainly affect membrane stability, but its exact effects are unknown. For a good investigation of HFSLM instability effects this is unwanted. Another problem was the application of the toplayer at the inside of the 5 fibers in one module. After impregnation of the fibers with the organic TMCl solution, a known quantity of PIPA solution was flown through the lumen of the fibers by gravitation. It is doubtful whether all reactant will flow through the 5 fibers with the same velocity and thus whether the reaction conditions in all 5 fibers are identical. SEM observations confirmed this suspicion. Better reproducible coatings might be expected when the modules contained only one fiber. Such modules are difficult to test when the feed is pumped through the fiber since the flow velocity will be relatively high (promoting instability) and the membrane area is low. To increase the membrane area, modules with a longer fiber length can be applied, but this will also increase the pressure drop. Finally, in practical applications the feed will not be circulated through the set-up, but pass the module only once and nitrate will be continuously removed from the feed. This is different from the 'classical' set-up used before for hollow fibers and flat sheet SLMs, where the nitrate is removed batch-wise. A continuous removal also has the advantage of continuously monitoring membrane stability, because the composition of feed before and after passage of the module easily can be determined at every moment. For these reasons, a new set-up was built as shown in figure 5.3.

Uncoated membranes

Preliminary experiments with module M9 (5 short fibers, see table 5.1) revealed several characteristics of the new set-up. Directly after starting the experiment at a flow velocity of 10 cm s^{-1}, results of determinations of the nitrate concentration at the module outlet were quite scattered. Probably, at the beginning still some LM-phase is attached to the membrane wall at the lumen side which is removed by the flow of the feed. When the feed velocity was lowered to 2-3 cm s^{-1} after two hours, the determined nitrate concentrations were much better reproducible. Therefore, in all experiments with this set-up during the first 1-2 hours the feed was allowed to flow through the fiber at a somewhat higher flow rate before flux measurements started. The maximum overall flow rate in this set-up was around 20 cm s^{-1}. For most flux measurements flow rates of approximately 5 cm s^{-1} (unless mentioned differently) were satisfactory to obtain reproducible results. It was however difficult to regulate the feed flow rate precisely at a constant value with the simple type of valves used. The feed flow velocities given are therefore approximate values (± 0.3 cm s^{-1}).

The flux results are shown in figure 5.5. A remarkable result is the high nitrate flux measured. Despite the low feed velocity (2-3 cm s^{-1} while in the other setup the feed was pumped through the lumen with 140 cm s^{-1}), nitrate fluxes are almost equal. The degradation of the hollow fiber module is clear. As more feed has passed the module, the nitrate flux decreased. At the end of the experiment after 73 hours, about 9 liters of feed had passed the 5 fibers. Degradation of the module seems to be somewhat slower than with set-up 1 (see table 5.3 and figure 5.4), but it must be emphasized that in module M9 no special destabilization feed (10^{-4} M NO_3^-, see table 5.1) was used.

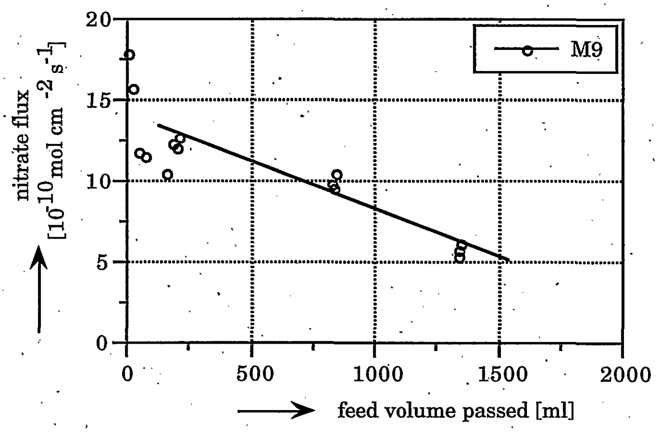


Figure 5.5. *Nitrate flux as a function of the amount of feed passed through module M9 (5 fibers, short module). Support: Accurel Q3/2. LM-phase: 0.2 M TOMA in o-NPOE.*

Flux decrease in time for two long one-fiber modules (M13 and M14) are given in figure 5.6. After starting at an initially higher feed flow rate of 17-18 cm s^{-1} for 1.5 hours, the flow rate was decreased to about 5 cm s^{-1} (about 1 ml min^{-1}) and fluxes were determined as a function of the amount of feed passed through the fiber. Initially, the nitrate flux was in the order of 10-11 * 10^{-10} mol cm^{-2} s^{-1}, slightly lower than the five-fibers module M9 in figure 5.5. Furthermore, the decrease of nitrate flux is less for the one fiber modules. Differences with module M9 are the lower membrane area and the higher flow rate in the case of modules M13 and M13. The latter implies that a certain amount of feed has passed modules M13 and M14 in a shorter time period than in module M9. Consequently, figures 5.5 and 5.6 might not be compared directly. Compared with flat sheet SLMs in which the feed and strip were pumped around with a velocity of 5.5 *ml* s^{-1}, the flux is only slightly lower for the one fiber module. The very low feed flow rate does not result in a dramatic decrease of the nitrate flux.

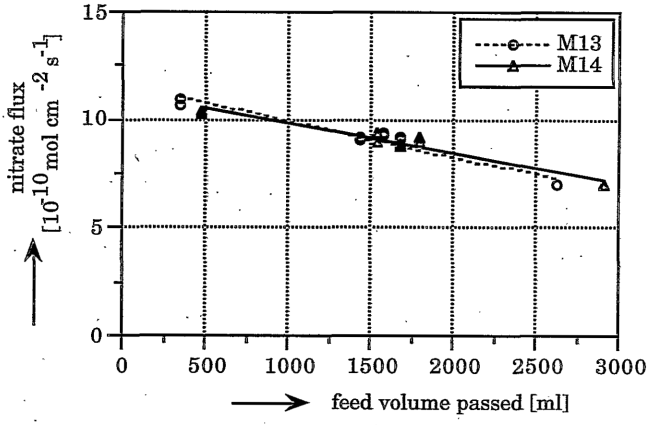


Figure 5.6. *Nitrate flux as a function of the amount of feed passed through modules M13 and M14 (one fiber, long modules). Support: Accurel Q3/2. LM-phase: 0.2 M TOMA in o–NPOE.*

Four uncoated modules were prepared to elucidate the effect of the degradation step on membrane stability. After 45 minutes at a higher feed flow velocity, the flow rate was decreases to approximately 5 ml s^{-1} for determination of the nitrate flux. Next, the fibers were degraded by allowing the feed (modules M14b and M18) or pure demiwater (modules M13b and M17) to flow through the fibers at an elevated feed flow velocity. The exact degradation conditions are given in table 5.4. After degradation, fluxes were determined again. All the permeation results are given in table 5.4.

Table 5.4. *Nitrate fluxes and stabilities (in duplicate) of the modules used for the degradation experiments. Support: Accurel Q3/2. LM-phase: 0.2 M TOMA in o-NPOE.*

code	flux before degradation [10^{-10} mol cm^{-2} s^{-1}]	flux after degradation [10^{-10} mol cm^{-2} s^{-1}]	amount of liquid for degradation [ml]	flow rate during degradation [cm s^{-1}]
M13b	13.6	≈ 0	1500	± 9
	14.0	≈ 0		
M17	14.0	≈ 0	1100	± 7
	13.8	≈ 0		
M14b	13.4	10.5	1300	± 8
	13.3	10.3		
M18	12.6	10.6	1600	± 10
	13.0	10.6		

In table 5.4, the effect of the two degradation methods on the flux is obvious. When demineralized water is used for degradation, no flux can be detected anymore after 1 night. Possibly, the modules are degraded even earlier but the flux was not monitored continuously. On the other hand, when the feed solution of 4 * 10^{-3} M $NaNO_3$ was used, the flux decrease was small. The observations are in agreement with those of Neplenbroek *et al.* for flat sheet SLMs: the lower the salt content of the aqueous phase, the higher the carrier loss and the lower the SLM stability [5,7].

Coated membranes

Two one fiber modules, M15 and M16, were prepared with a polymeric toplayer of PIPA and TMCl at the lumen side of the fiber. The only difference between the two fibers is the concentration of the PIPA solution which passed the fiber (see table 5.2): 1.0 M for M15 and 0.1 M for M16. Firstly, the nitrate flux was determined as a function of the flow velocity to elucidate below which velocity aqueous boundary layer resistances start to play a role. Results are shown in figure 5.7a and 5.7b. The fluxes were measured on two separate days (M15-1/M16-1 and M15-2/M16-2, respectively) in between which the flowing of feed and strip in the set-up was shut down. For module M15, the flux shows a small decrease when the feed velocity is below 2 cm s^{-1}, for module M16 no decrease in flux was found. Possibly, its limit is even below 2 cm s^{-1}. The data measured on two different days show no difference: apparently the modules are quite stable. For further experiments with module M16, a feed velocity of 5 cm s^{-1} was used.

Strange enough, the module prepared with the lowest concentration PIPA (module M 16) showed the lowest nitrate flux. The opposite should be expected: the lower the concentration ratio between amine and acid chloride, the less polymer is expected to be formed [8] and the thinner or less tight the toplayer should be, resulting in a higher nitrate flux. However, the nitrate flux of module M16 is almost halve that of module M15 and the uncoated membranes (figure 5.6). SEM did not show any noticeable differences between the two toplayers in the two modules. No explanation for this result is found yet.

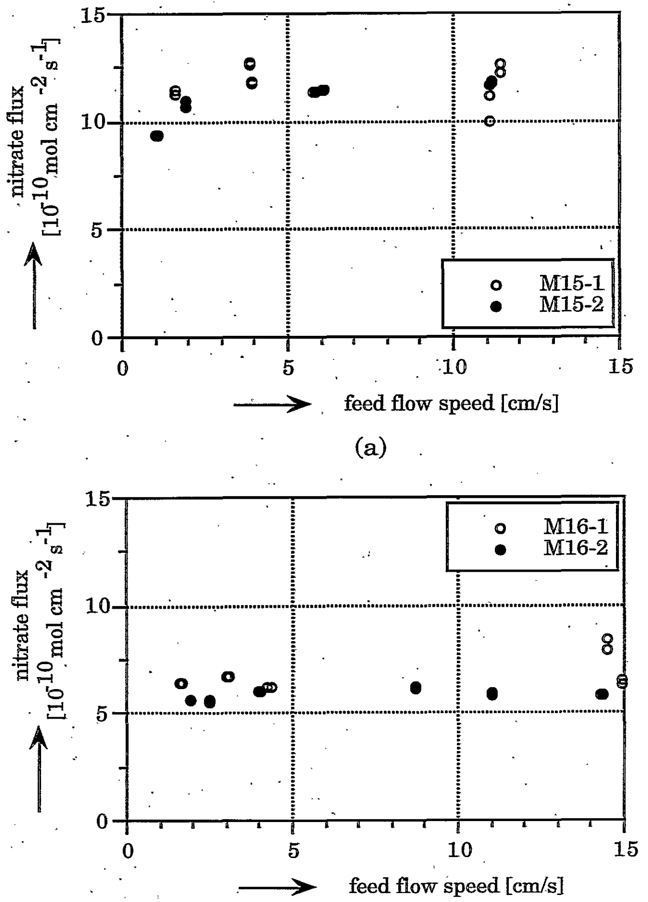


Figure 5.7. *Influence of feed flow rate on nitrate flux for (a) module M15 and (b) module M16 measured on two different days (suffix -1 and -2). Support: Accurel Q3/2 + PIPA/TMCl toplayer. LM-phase: 0.2 M TOMA in o–NPOE.*

Several additional experiments were carried out with module M16. Firstly, in a period of 8 days feed of 4 * 10^{-3} M $NaNO_3$ was allowed to flow through the lumen side of the fibers at a velocity of about 2.5 cm s^{-1} (about 5000 ml of feed solution passed the fiber). Next, the flux was determined again, which was *still* approximately 6 * 10^{-10} mol cm^{-2} s^{-1}. The module indeed is very stable due to the application of the toplayer, although the absolute flux value is lower than that of an uncoated hollow fiber SLM as presented in figure 5.6. The toplayer seems to hinder the transport of the ions. Identical measurements with module M15 gave the same promising results: no flux decrease after 8 days flowing of feed through the fibers.

Module M16 was used to investigate the stability of coated hollow fiber SLMs at elevated temperatures. It might be expected that an increase in temperature raises instability phenomena such as solubility of the LM-components in the aqueous phases. During three days, temperature experiments were carried out. In between the first and second day, feed solution passed the fibers at 25 °C. Then the fluxes at several temperatures on the second day were determined. Next, during the night feed solution at a temperature of 45 °C was used to destabilize the module. On the third day, finally, again the nitrate fluxes were determined at room- and elevated temperatures. Flow rates used were all between 4 and 6 cm s^{-1}. The results are given in figure 5.8.

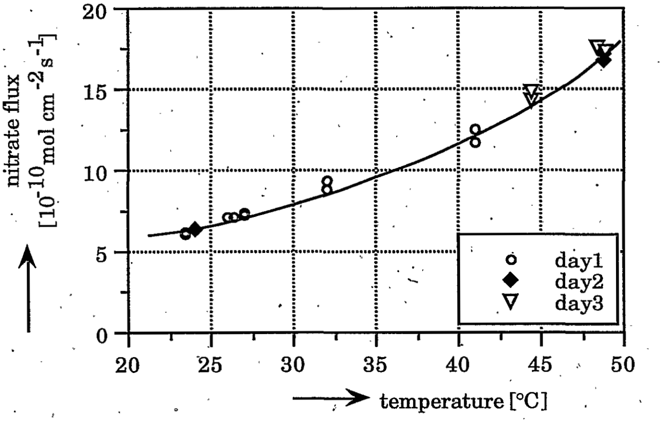
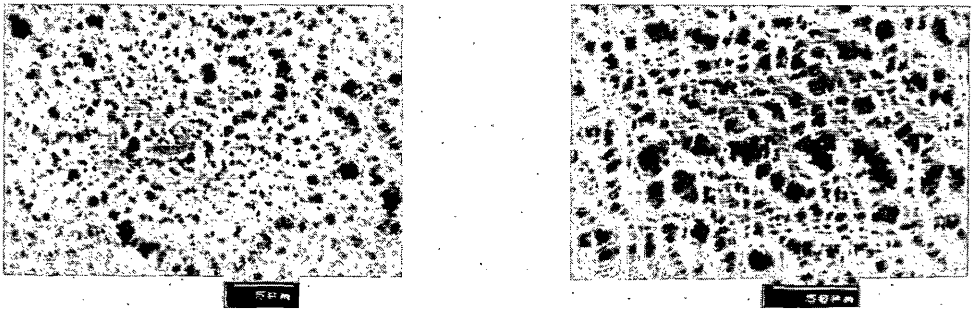


Figure 5.8. Influence of the temperature on nitrate flux and stability of module M16. Support: Accurel Q3/2 + PIPA/TMCl toplayer. LM-phase: 0.2 M TOMA in o-NPOE.

Figure 5.8 clearly shows the stability of the coated membrane. In spite of the increase in temperature and the degradation with feed solution during the night, fluxes on the three days are identical. Although no data of uncoated membranes are available for comparison, module M16 reveals a stable operation. Furthermore, with increasing temperature, the flux increases. Since the diffusion coefficient of the carrier-nitrate complex increases with temperature, and the viscosity of the LM-phase decreases with temperature, the nitrate flux will increase with increasing temperature.

5.3.4 SEM characterization

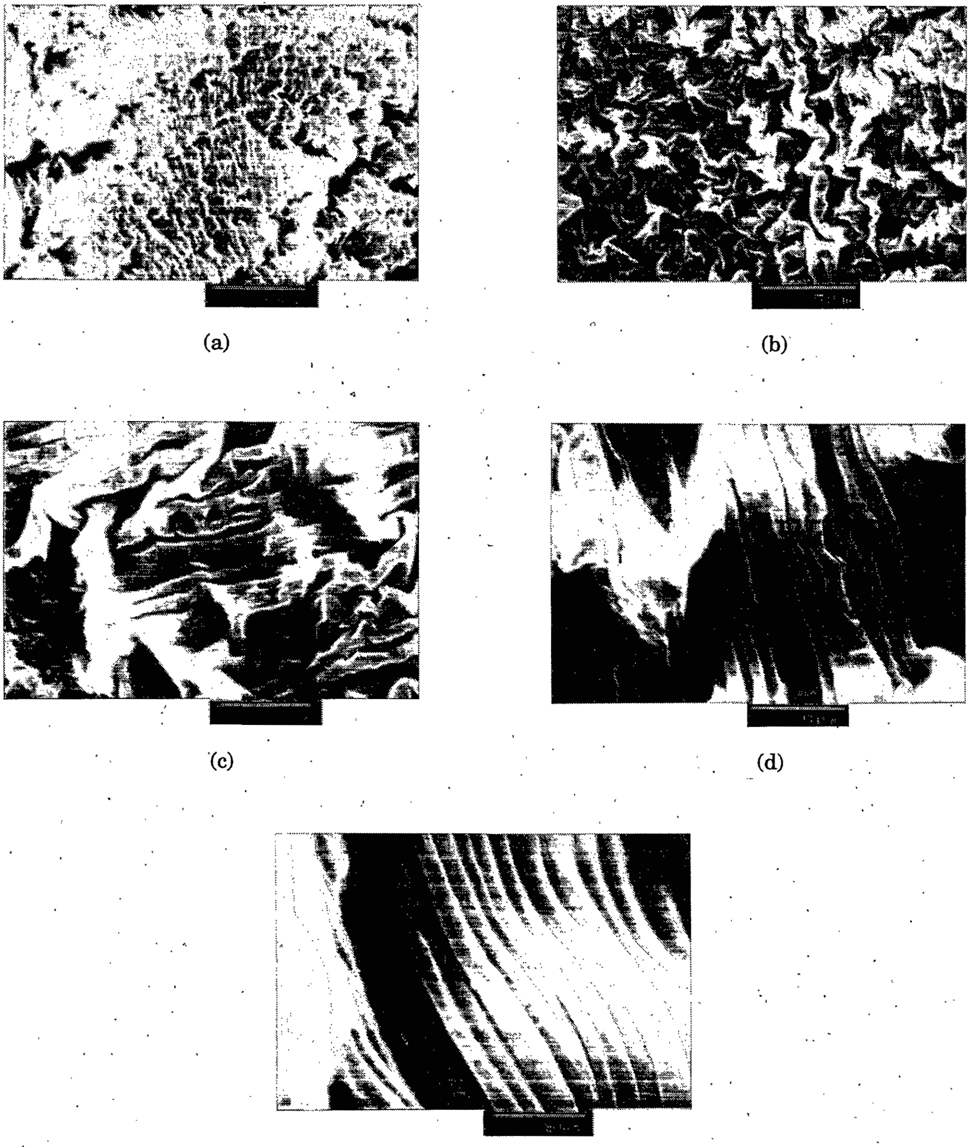
By means of scanning electron microscopy, it was tried to obtain knowledge on the uniformity of the applied toplayers. Figure 5.9 contains SEM-photographs of shell and lumen sides of uncoated fibers (take care of the different magnifications!). The lumen side of Accurel Q3/2 fibers (figure 5.9a) looks much similar to flat sheet Accurel 1E-PP as shown in figure 3.6. At the shell side however, pore sizes are much larger (up to 50 μm). The fibers are asymmetrical and coating the shell side of the fiber will be difficult.



(a) (b)

Figure 5.9. *SEM photographs of the surface of an Accurel Q3/2 capillary membrane. a) Lumen side of the fiber (3,500x). b) Shell side (500x).*

An example of the morphology of a toplayer applied at the lumen side of a fiber after the flux determinations is shown in figure 5.10. The photographs are taken from fiber samples at different distances from the 'origin' of the potted fiber (the origin is located at the top of the module where the fiber comes out of the potting material and thus where the PIPA solution is introduced into the fiber). It is clear from the photographs that the morphology of the toplayer changes over the length axis of the fiber. At the top of the fiber, where the amine concentration is the highest, the toplayer has a cake-layer like structure. At 8 cm from the top (figure 5.10b), the typical 'hill and valley' structure observed before for coated flat sheet Accurel membranes is observed (see *e.g.* figure 4.14). Going further down the fiber, the 'folds' in the layer get bigger. Especially further down the fiber, the folds are all in the direction in which the PIPA solution flowed during polymerization. On the cross sectional photographs the toplayer was difficult to see, but over the whole length of the fiber its thickness was approximately 1 μm. The toplayer in module



(a)

(b)

(c)

(d)

(e)

Figure 5.10. *SEM photographs of the toplayer in module M15 at several distances from the top of the module: a) 0 cm, b) 8 cm, c) 16 cm, d) 24 cm, e) 32 cm. All photographs at a magnification of 5,000x. The direction of the length axis of the fiber is from left to right for photograph c) and from up to down for d) and e).*

M16 showed the same morphology and thickness. From these photographs it can be concluded that it is difficult to apply a uniform toplayer at the lumen side of hollow fibers by an interfacial polymerization reaction.

5.4 Conclusions

A start was made with the preparation of supported liquid membranes using hollow fibers as support (HFSLMs). Two experimental set-ups to determine the nitrate fluxes and stabilities of the HFSLMs were designed: one in which both feed and strip were pumped co-currently through the membrane module and one in which the feed continuously passed the module counter-currently with the strip solution under influence of gravity. Disadvantage of the last set-up is its low feed flow rate.

The nitrate fluxes of uncoated HFSLMs were only slightly lower than the fluxes in flat sheet SLMs. In both set-ups, the application of a toplayer of piperazine and trimesoylchloride on the lumen side of the fiber by means of an interfacial polymerization reaction resulted in a significant increase in membrane stability. However, application of a uniform toplayer on the fiber is quite difficult as revealed by the scattering in flux data of these coated membranes and by scanning electron microscopy investigations.

5.5 References

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6

STABILIZATION OF SUPPORTED LIQUID MEMBRANES BY GELATION

Tested on an instable system

SUMMARY

This chapter describes the gelation of SLMs for nitrate removal which use TOMA-Cl as carrier. Uncoated SLMs with this carrier are very instable. To improve their stability, the LM-phase was gelated with polyvinylchloride as gel forming polymer. Both homogeneous gelations of the LM-phase, as well as the application of an interfacial gel toplayer are described.

In all cases, no improvement of the stability could be observed. For both types of gelation, the initial nitrate flux decreased while the flux after 1 day of degradation was almost zero. The flux decrease is the result of a decrease of the the diffusion rate of carrier complex due to the gel network and to the thickness of the applied gel layer. The absence of any stability improvement might indicate that loss of LM-phase from these membranes is not due to emulsion formation only.

6.1 Introduction

The stability of supported liquid membranes can be improved by gelation of the liquid membrane phase as has been shown by Neplenbroek *et al.* [1-3] and as was described in chapter 2 of this thesis. Gels, either natural or artificial, are present everywhere. The membranes of blood vessels and kidneys are also composed of gel type structures and play a fundamental role in the transport of oxygen, nutrients and other molecules [4].

A polymer gel can be defined as a crosslinked polymer network, swollen in a liquid medium [5]. The polymer network is prevented from collapsing into a compact mass by the liquid, while the liquid is prevented from flowing away by the network. However, not all polymers have the ability to form gel-type networks. A schematic drawing of a polymer gel is shown in figure 6.1. The crosslinks drawn can be either physical (reversible gels) or chemical (irreversible gels) [6]. Physically crosslinked gels can be formed by dissolving a gel-forming polymer in a solvent at elevated temperatures and subsequently cooling down of the mixture, during which the gel is formed. Another possibility is the use of a suitable volatile second solvent. The polymer and the solvent are dissolved in the second solvent. Gelation occurs during evaporation of this second solvent. When the gel-forming polymer contains specific chemical groups, an additional chemical crosslinking might be carried out using specific crosslinking agents.

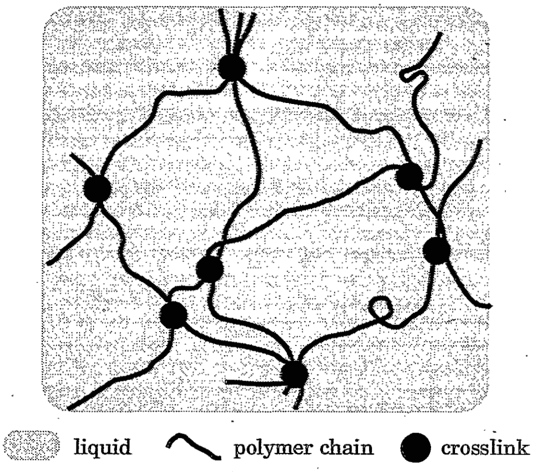

Figure 6.1. *Schematic drawing of a polymeric gel.*

From the definition of a polymer gel given above, it might be clear that the nature of the liquid itself is not changed, but there are polymer chains ('barriers') present in the liquid. For carrier mediated transport membranes, this enables one to make use of gelation for embedding the solvent in a polymer matrix while the carrier molecules, necessary for transport, are still dissolved in the liquid. The only drawback will be the kinetics of transport inside the carrier mediated transport membrane. This will depend on the amount of barriers (the polymer concentration in the gel) and the crosslink density. The principle of gelation has been used by other researchers for different membrane applications.

Bloch *et al.* were the first who used so called 'solvent membranes' for the selective transport of metal ions [7]. These solvent membranes were made of polyvinylchloride (PVC), plasticized with phosphate esters like tributylphosphate (TBP), cresyldibutylphosphate (CDBP) or dicresylbutylphosphate (DCBP). The phosphates could act as an extracting agent for the separation of uranium from aqueous solutions. However, the lifetime of these membranes was insufficient due to loss of plasticizer resulting in completely impermeable, hard PVC films. The plasticizing power of the phosphate ester used, was thought to have a large influence on membrane lifetime. Vofsi *et al.* extended research on solvent membranes to other systems and to the use of this type of membranes as ion-selective electrodes [8-10]. The combination of polymer films and plasticizers was also investigated by Sugiara *et al.* for the transport of picrate or metal ions [11–14]. Due to the thickness and high polymer concentrations of these 'solvent polymeric membranes', necessary for a sufficient mechanical strength, fluxes were up to a factor 100 lower than described throughout this thesis. Gankema prepared solvent polymeric membranes by gel casting of solutions of ultra-high molecular weight polyethylene (UHMW-PE) and a carrier solution [6]. After uniaxial and biaxial stretching of the resulting membranes, sodium and potassium fluxes were measured. By using polymethacrylate bound calix(4)arenes or siloxane copolymers as carrier in the above mentioned solvent polymeric membranes, it was claimed that the stability of these systems could be improved by changing the drawing ratio. Sakahora *et al.* prepared acrylamide gels in the pores of silica-alumina membranes for the pervaporation of organic/water mixtures [15]. Membrane performance did not change significantly for a period of three months. In a patent by Matson *et al.*, the application of a thin gel layer on top of a microporous polymeric support was reported for the scrubbing of acid gases [16].

The idea of improving the stability of SLMs by an homogeneous gelation in the pores of the support was first suggested by Neplenbroek *et al.* [1,2,3]. The support improved the mechanical strength of the gel, while the presence of the gel could prevent loss of the membrane phase, as was expected by the authors. Indeed, promising results were obtained using PVC as polymer and tetraoctyl-ammoniumbromide TeOA (which already gave fairly stable SLMs without gelation) as carrier. However, the best results were obtained when the gel was applied as a thin layer (< 2 μm) on the feed side of the SLM and chemically crosslinked after preparation. In this way, the resistance towards transport due to gelation was minimized as a result of the low thickness of the gel layer. Secondly, emulsion formation of the LM-phase, according to the authors the main reason of SLM instability in their system, could be suppressed more effectively since the polymer concentration could be high without any flux reduction. Two months experiments were carried out under circumstances which enhanced significantly the degradation of the SLM. A membrane lifetime over two years under normal circumstances was predicted by the authors.

Other research on gelled SLMs, based on Neplenbroek's promising results, was carried out by Bromberg *et al.* [17] and Levin *et al.* [18]. The transport of several metal ions (Ag^+, Hg^{2+}, Cd^+, Fe^{3+}, Zn^{2+} and Ni^{2+}) through homogeneously gelled SLMs was studied by Bromberg *et al.* The LM-phase was composed of PVC, *o*–NPOE as plasticizer and di(2-ethylhexyl)dithiophosphoric acid as carrier. Fluxes decreased as PVC concentrations increased due to a decrease of the effective diffusion coefficient. No data on the stability were given. Levin *et al.* prepared gelled membranes by using a plasticized polymer (PVC with substituted dioctyldithiocarbamate groups), which was capable of complexing certain ions together with a carrier for silver, mercury and other ions. However, because of the high polymer concentration of the gel, fluxes were all in the order of 10^{-10}–10^{-11} mol cm^{-2} s^{-1}, which is a factor 10-100 lower than the gelled membranes of Neplenbroek. Also here, no data on membrane lifetime were presented.

In the previous chapters, it was shown that interfacial polymerization is a successful method for the stabilization of supported liquid membranes for the system investigated. As has been indicated above, gelation of supported liquid membranes also is a useful method for stabilization. Therefore, it would be useful to compare the results of gelation and interfacial polymerization on the same system. However, Neplenbroek *et al.* did only present a few data on long term stability of gelled membranes using instable SLMs with TOMA-Cl as carrier. Therefore, in this chapter the preparation and characterization of homogeneously gelled SLMs and SLMs with a gelled toplayer is described. The results will be compared with interfacially polymerized SLMs. Such a comparison is necessary, because not only the flux but also the stability of the liquid membranes is of importance. Neplenbroek *et al.* used their gelation to study the instability phenomena of SLMs and to stabilize their membranes. For industrial applications however, the way stabilized SLMs can be prepared is also of interest. The method used by Neplenbroek *et al.* [1,3] for the preparation of a thin gel layer, *i.e.* spreading the gel layer with a tissue as smoothly as possible over the membrane surface, is not suitable for large scale production, in contrast to the interfacial polymerization described in the chapters 3, 4 and 5 of this thesis. In our work, the stabilization of hollow fiber SLMs, which is most likely the membrane configuration to be used in industry, has been studied in a number of experiments described in chapter 5.

The gels described in this chapter are all prepared using polyvinylchloride (PVC) as polymer. The motivations for the use of this polymer are the following. The material is hydrophobic, and the LM-phase can be used as solvent for the gel forming polymer since o-NPOE is known to be a plasticizer for PVC [19]. It is possible to obtain a gelled phase already at low polymer concentrations (2 to 3 wt% for PVC / di-2-ethylhexylphthalate) [20]. Furthermore, in related systems like ion selective electrodes, this polymer is most frequently applied [19] and superior in stability and sensitivity to polyurethane [21,22], polymethylmethacrylate, polystyrene and silicone rubber [21] membranes. Finally, by using the same type of PVC as gel forming polymer, the data can be compared easily with those of Neplenbroek *et al.*

The preparation of physically and chemically crosslinked gels is described in this chapter. The mechanism of PVC gel formation and its structure is still not fully understood [23-26]. Most widely accepted is the hypothesis that the physical crosslink points in the gel are 'microcrystalline regions, resulting from short syndiotactic, regular runs in a predominantly atactic structure' [23]. One important property of this gel type is the thermo-reversibility of the physical crosslinks.

Physically crosslinked gels are prepared either by the temperature method (see before) or by evaporation of tetrahydrofuran (THF), added as a third component. To obtain a shorter mesh size and a stiffer structure, apart from the physical crosslinking the gel also can be crosslinked chemically. When PVC with carboxylic acid side groups is used, crosslinking can take place according to the general scheme in figure 6.2. The first step is the activation of the carboxylated PVC by a di-imide compound [27,28]. In the following reaction, the anhydride formed in step 1 reacts with a diamine and, via the carboxylic side groups, a chemical crosslink between two PVC chains is formed [28]. The physical crosslinks are reversible while the chemical crosslinks are irreversible. It might be expected therefore that the structure of a microscopic gel is less susceptible to changes in time and that its properties are more constant. This is an additional advantage of chemically crosslinked gels in this case.

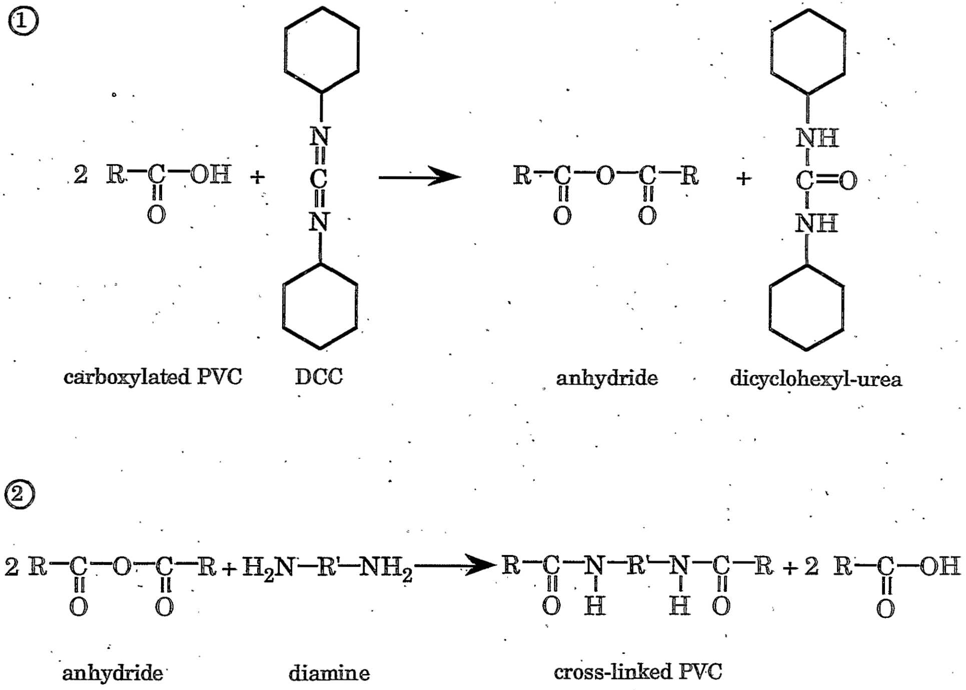

Figure 6.2. *Chemical crosslinking of carboxylated PVC. 1: The PVC is activated by dicyclohexylcarbodiimide (DCC). 2: Two coupled PVC-chains react with a diamine.*

6.2 Experimental

6.2.1 Materials and membranes

Support

Throughout this chapter, two different flat sheet supports were used. Accurel® 1E–PP was obtained from Akzo. It is made from polypropylene, has a nominal pore diameter of 0.2 µm, an overall porosity of 69 % (Akzo specifications) and a thickness of approximately 100 µm (measured with a Mitutoyo digital micrometer). Durapore GVHP (Millipore) is a hydrophobic PVDF membrane with a pore size of 0.22 µm, a thickness of 80 µm and 75 % overall porosity (data from Millipore).

Carrier and solvent

In all cases, *o*-nitrophenyloctylether (*o*-NPOE) was used as membrane solvent for the quaternary ammonium salts used as carriers. The *o*-NPOE was synthesized in our laboratories by the method described in appendix A of chapter 4. As carrier, both trioctylmethylammoniumchloride (TOMA) and tetraoctylammoniumbromide (TeOA) were applied. The carriers were obtained from Fluka and used without further purification. Carrier concentration in the LM-phase was always 0.2 M. The TOMA/*o*-NPOE mixture had to be heated slightly to dissolve all the carrier.

Gelation

Polyvinylchloride (PVC) was used for the gelation of the LM-phase. PVC-HMW ('high molecular weight') and PVC-LMW ('low molecular weight') were obtained from Fluka. The molecular weight of PVC-LMW was 48,000 g mol^{-1} (suppliers data), the Mw value for PVC-HMW as determined by gel permeation chromatography was 91,000 g mol^{-1} [1,3]. For the chemically crosslinked gels, carboxylated PVC (PVC-carb) from Janssen Chimica was used. Its molecular weight was 200,000 g mol^{-1}, with 1.8 wt % carboxyl groups. For PVC-degradation experiments, also PVC-vHMW ('very high Mw', two different batches from Aldrich and one from Janssen Chimica) were tested. As activator for the crosslinking reaction, N,N'-dicyclohexylcarbodiimide (DCC) from Janssen Chimica was used. 1,4-Phenylenediamine, PDA, (Fluka) or 1,12 diaminododecane, DDDA, (Janssen Chimica) were chosen as crosslinking agents. The volatile solvent for the gel preparation by the evaporation method was tetrahydrofuran (THF) from Merck. All these chemicals were used as received without further purification. PVC-HMW, the activator DCC and both crosslinkers had the same product specifications as those used by Neplenbroek *et al.* [1,3]. The PVC-carb used in this work contained a slightly higher amount of carboxyl groups than that applied by Neplenbroek *et al.* [1,3].

6.2.2 Membrane preparation

Homogeneous gelation

Homogeneously gelled SLMs were prepared in two different ways: (1) by the volatile solvent method and (2) by a temperature method as has been described in the introduction. For the volatile solvent method, the desired amount of PVC was dissolved in the LM-phase (0.2 M TOMA in *o*-NPOE). To this mixture, a certain amount of THF was added (see table 6.1). The amount of THF depended on the polymer concentration. When the polymer concentration was higher, more THF should be used since otherwise the PVC-LM-phase-THF mixture became too viscous and the support would not be fully impregnated later on. The THF, polymer and LM-phase were stirred together until a homogeneous mixture was formed. This solution was poured out in a petri-dish. A circular piece of LM-support (diameter 74 mm) was weighted and placed in the solution. After one day of drying under nitrogen, all THF was evaporated. Residual gel substance was carefully removed from the surface of the membrane by gently wiping with a paper tissue. In all cases, PVC-HMW was used as polymer for homogeneous gelations.

Table 6.1. *Amount of THF added to the different amounts of PVC/LM-phase mixtures for the preparation of homogeneously gelled SLMs.*

wt% PVC	ml THF/g mixture
2.5	5.0
5.0	7.5
7.5	10.0
10.0	12.5

When the temperature method was used for the gel preparation, the desired amounts of PVC and LM-phase were put in a petri-dish. The dish was placed in an oven (120 °C) under nitrogen for half an hour and stirred from time to time, after which the support (diameter 74 mm) was placed in the homogeneous mixture. After 3 minutes, the impregnated support was removed from the dish and remaining gel substance at the surface was wiped off quickly with a tissue. The different actions outside the oven had to be carried out quickly, since immediately after removing the membrane from the oven gel formation started and as a result remaining gel could not be removed anymore.

Interfacial gel layers

A rectangular piece of support (dimensions approximately 14 x 23 cm) was cut out of a roll and impregnated with the LM-phase. Excess LM-phase was removed using a paper tissue. PVC/LM-phase mixtures were prepared using the desired weight fractions. Different types of PVC were used in this case. Depending on the quantity of polymer in the mixture, a certain amount of THF was added to this mixture (see table 6.2) and stirred until the solution was homogenous. To this solution activator and crosslinker, if used, could be added shortly before preparation of the gel layer. Directly after addition of crosslinker and/or activator, the homogeneous solution was spread on the impregnated support, which was placed on a horizontal glass plate. By means of casting knives of 50 or 100 µm, the solution was spread as a thin layer of uniform thickness on top of the impregnated support. The membranes were stored under nitrogen for at least three days before use. The thickness of the gel layers was measured with a digital Mitutoyo micrometer. By means of this technique, developed in our laboratories [29], the layers were much more uniform in thickness than those prepared by the method of Neplenbroek using a tissue [1,3].

Table 6.2. *Amount of THF added to the different amounts of PVC/LM-phase mixture for the preparation of thin gel layers.*

wt% PVC	ml THF/g mixture
40	5.0
50	6.0
70	6.0
100	7.0

6.2.3 Permeability measurements

SLM preparation

Supported liquid membranes which were not gelated, were prepared as described before in the chapters 3 and 4. LM-phase was spread on the bottom of a petri-dish, in which a circular support (diameter 74 mm) was placed. After an impregnation time of at least 15 minutes, the supports were completely transparent and removed from the dish. Attached membrane phase was carefully wiped from the surface of the SLM. The preparation of homogeneously gelled SLMs was described in section 6.2.2. From the sheet SLM with an interfacial gel layer, a circular piece (diameter 74 mm) was carefully cut out using a scalpel. In some cases, SLMs with a toplayer on both sides of the membrane were used. They were prepared using two SLMs with one toplayer each, which were 'glued' together using a droplet of LM-phase.

Flux determination

In all cases, the flux was determined in the same way as described in section 3.3.3 and figure 3.5b [30]. The SLM was clamped in between the two cell halves which were placed in the set-up. The toplayer was directed towards the feed side. The feed consisted of 130 ml 4 * 10^{-3} M $NaNO_3$ (Merck) solution in water, the strip phase consisted of 130 ml 4 M NaCl (Merck). Both phases were pumped around with a velocity of 5.5 ml s^{-1}. By observing the concentration of nitrate and chloride in the feed phase in time (HPLC, Waters IC-PAK™ anion column), the nitrate flux was calculated.

6.2.4 Stability measurements

In between two flux measurements, the feed phase was replaced by a 10^{-4} M $NaNO_3$ solution. A lower salt concentration enhances degradation of the membrane as was observed by Neplenbroek *et al.* [1,31]. After approximately

20–21 hours of 'degradation', both feed and strip were refreshed with the original solutions for a new determination of the nitrate flux. In chapter 3 it was shown that in this way an uncoated membrane, with TOMA as carrier, showed no nitrate transport after 1 day of degradation. In several cases, long-term experiments were carried out over a period up to 7 days. The masses of the SLMs before and after the flux measurements were determined using an analytical balance to obtain the LM-phase loss.

6.2.5 Characterization

SLMs with an interfacial gel layer were examined by scanning electron microscopy (SEM) to investigate the uniformity of the toplayer thickness and the texture of the toplayer. A slightly different preparation method has been applied to prepare the SEM samples compared to the method used in chapters 3 and 4 for supports with a toplayer prepared by an interfacial polymerization reaction. Cross-sections were prepared by breaking small sections of the gelated membrane in liquid nitrogen after which they were placed in a sample holder. Surface-samples were simply cut out of the membrane and glued on a sample holder by means of double-sided adhesive tape. The samples were not immersed in ethanol/water before breaking, as was done for interfacially polymerized membranes [30,32,33], since in that case the gel would be removed from the support. The samples were sputtered with gold to make them conductive using a Balzer Union SCD 040 sputtering apparatus (sputtering time 3 minutes at 15 mA). SEM investigations were carried out on a Jeol JSM T 220A scanning electron microscope at 20 kV. Despite the presence of gelled LM-phase, no problems were met in obtaining the high vacuum necessary in the apparatus.

6.3 Gelation results

6.3.1 Homogeneous gelation

Temperature method

Serious problems were met when homogeneously gelled SLMs were prepared by the temperature method at 120 °C. A colour change of the PVC-LM-phase mixture was observed 10-15 minutes after the mixture was placed in the oven. The colour changed from yellow via red to dark, almost black. The colour change was not observed when the polymer concentration was 0 wt%. This might indicate a degradation of the PVC. It is known that the PVC polymers are easily thermally and photochemically degradated [34]. To investigate whether the degradation was due to the high temperature, the presence of carrier and organic solvent or a combination of these possibilities, several experiments were carried out. In an oven, small amounts of PVC (PVC-HMW, PVC-LMW, PVC-vHMW and PVC–carb), PVC + *o*-NPOE, PVC + TOMA-Cl/TeOA-Br, *o*-NPOE and carrier were placed and heated under nitrogen at 120 °C for half an hour. Only the PVC/carrier mixtures showed a change in colour. This is an indication that the presence of carrier enhances degradation of the PVC.

The main reason for the degradation of PVC is the dehydrochlorination of the polymer chains [34], schematically shown in figure 6.3. This reaction occurs at elevated temperatures (above 100 °C). It can be initialized, and is therefore catalyzed, by the presence of HCl (autocatalysis) and other strong acids [34], but in the gelation as carried out here no acids are present. The colour change of PVC is believed to be the result of the formation of polyene sequences (double bonds in the chain) or the presence of coloured carbonium salt complexes in PVC. The last reaction is believed to occur by a mechanism in which ions play a role [35]. Maybe, the presence of the carrier in combination with the elevated temperature catalyses the latter reaction. Neplenbroek *et al.* encountered also these PVC-degradation problems with PVC from Fluka, which were not found when PVC from BASF was used [1,3]. This might be explained by the presence of stabilizers in the PVC-BASF, which are usually added to commercial PVC in order to minimize degradation of the polymer.

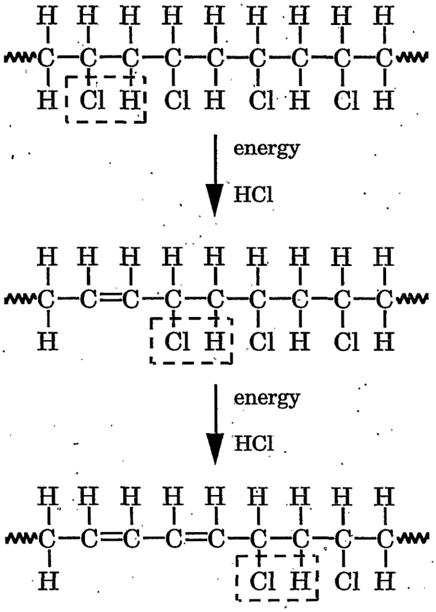

Figure 6.3. *Dehydrochlorination of PVC at elevated temperatures. Adapted from Titow [34].*

Table 6.3. *Nitrate fluxes and stability of homogeneously gelled PVC SLMs. Support: Accurel. Carrier: TOMA-Cl. Gelation at 120 °C.*

PVC content [wt %]	PVC type	initial flux [10^{-10} mol cm^{-2} s^{-1}]	flux after 1 day [10^{-10} mol cm^{-2} s^{-1}]	LM-loss [wt %]
0	-	15.6	1.7	5.6
0	-	17.8	1.4	6.5
2.5	PVC-HMW	14.7	1.4	6.1
2.5	PVC-HMW	15.3	1.5	6.3
2.5	PVC-LMW	14.3	1.3	5.7
2.5	PVC-LMW	14.7	1.1	5.2

Despite the PVC degradation problems, these homogeneously gelled SLMs were tested on nitrate flux and stability as described in section 6.2.3. The results are given in table 6.3. The 0 wt% PVC membranes were prepared in the oven to investigate the effect of the heat treatment on nitrate flux and SLM stability. No difference is found with the values for the ordinary reference membranes (see *e.g.* chapter 3 of this thesis). Addition of PVC to the membrane phase results in only a marginal decrease of the initial nitrate flux since the microscopic viscosity influencing the diffusion rate of the carrier-ion complex remains nearly constant. No improvement in SLM stability was observed: in all cases, the flux after 1 day was nearly zero and the LM-loss did not differ from that of the reference membranes. The use of different types of PVC did not give differences in nitrate fluxes.

Volatile solvent method

Homogeneously gelled SLMs using THF as volatile third component, were prepared as described in section 6.2.2. It was observed that the use of 5 ml THF per gram PVC/LM-phase mixture as used by Neplenbroek *et al.* [1,3] was not satisfactory. The viscosity of the gel was soon too high before the support was fully impregnated. Therefore, more THF was used. However, the attached gel on the surface of the 10 wt% PVC membranes was far too viscous to be removed using a tissue. So, these membranes were not tested on nitrate transport since difficulties in reproducibility of the results were expected.

In figure 6.4, the results of the measurements are plotted. The 0 wt % PVC membranes are obtained by adding 5 ml THF to 1 gram of LM-phase. Subsequently, the support was placed in an excess of this mixture in a petri-dish. After impregnation of the support and complete evaporation the THF, the nitrate flux and stability were measured. The flux for an uncoated 0.2 M TOMA SLM is in the order of 16-19 * 10^{-10} mol cm^{-2} s^{-1}. So, addition of THF to the LM-phase has no influence on the initial nitrate flux. It is clear that addition of PVC to the LM-phase results in a decrease of the initial nitrate flux. Despite the increase of the macroscopic viscosity as observed during membrane preparation, the flux decrease is relatively small indicating that the diffusion rate through the membrane is determined by the microscopic viscosity. The lower fluxes are due to the fact that the carrier complexes have to travel around the polymer chains in the membrane, resulting in an increase in tortuosity.

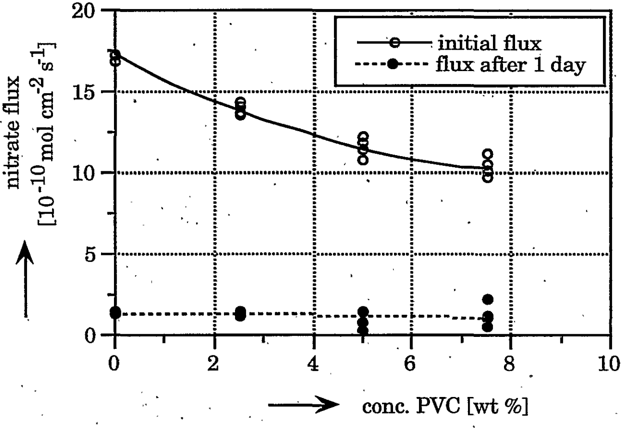

Figure 6.4. *Nitrate fluxes and stability of homogeneously gelled PVC SLMs. Support: Accurel. Carrier: TOMA-Cl. Gelation by evaporation of THF.*

As already revealed by the homogeneously gelled SLMs by the temperature method (table 6.3), no improvement in stability could be observed for all PVC concentrations investigated. In all cases, the flux after 1 day was nearly zero, while LM-losses (not presented here) were all in the order of 14-30 mg. It is expected that when emulsion formation is the main reason for the instability of TOMA-SLMs, gelation will increase the stability. However, for SLMs containing TOMA-Cl as carrier a gelation of the LM-phase in the pores, although increasing its macroscopic viscosity, does not result in a decrease of carrier loss. This remarkable result will be discussed in more detail in chapter 7.

In table 6.4, similar trends can be seen for homogeneously gelled SLMs using Durapore as support. By increasing the polymer content, nitrate flux decreases. The initial fluxes are smaller than those in figure 6.4, an effect already observed in chapter 4 [32]. Again, just like the Accurel SLMs, no improvement of the stability was observed. LM-losses were in general equal or a few percent higher than the reference membrane in table 6.4 (these 0 wt % membranes results were not obtained by the volatile solvent method, but as was mentioned before, there was no influence of THF on the initial nitrate flux).

Table 6.4. *Nitrate fluxes and stability of homogeneously gelled PVC SLMs. Support: Durapore 0.22. Carrier: TOMA-Cl. Gelation by evaporation of THF.*

PVC content [wt %]	initial flux [10^{-10} mol cm^{-2} s^{-1}]	flux after 1 day [10^{-10} mol cm^{-2} s^{-1}]	LM-loss [mg]
0	11.0	1.1	4.8
0	11.8	1.1	5.5
2.5	8.3	1.1	5.9
2.5	7.5	1.8	8.3
7.5	6.2	0.7	5.8
7.5	6.2	0.5	5.1

6.3.2 Gel layers

Gel layers without chemical crosslinking

Firstly, interfacial gel layers were prepared without a chemical crosslinking. The results are given in table 6.5.

Table 6.5. *Nitrate fluxes and stability of SLMs with a PVC gel layer. Support: Accurel. Carrier: TOMA-Cl. Gelation by evaporation of THF. Casting knife thickness 100 μm.*

PVC content* [wt %]	PVC-type	initial flux [10^{-10} mol cm^{-2} s^{-1}]	flux after 1 day [10^{-10} mol cm^{-2} s^{-1}]	LM-loss [mg]
0	-	15.9	1.3	19.7 (7.0%)
0	-	15.1	1.0	18.2 (6.3%)
40	PVC-HMW	10.7	1.3	21.3
40	PVC-HMW	11.0	2.7	13.3
40	PVC-HMW	11.2	2.3	11.3
40	PVC-carb	10.8	2.5	11.6
40	PVC-carb	10.8	2.3	10.1
40	PVC-carb	10.1	0.5	10.3
40	PVC-carb	8.7	0.7	8.7
100	PVC-carb	9.4	0.7	3.4 increase
100	PVC-carb	9.5	0.7	5.5 increase

*: the PVC content is the amount of PVC in the LM-phase/PVC mixture used to cast the toplayer

The decrease of the initial nitrate flux with roughly one third, due to the application of the toplayer, is clear from table 6.5. The volume ratio THF to LM-phase is, for the 40 % membranes, 5 to 1. This means that the film roughly shrinks to one-sixth of its original thickness during evaporation of THF. Casting with a 100 μm knife should therefore give a final toplayer thickness of about 17 μm. SEM observations showed a somewhat lower thickness (10 μm), possibly due to a collapse of the gel network in the vacuum of the microscope. This layer thickness is higher than that calculated by Neplenbroek *et al.* [1,3] who report values of less than 2 μm obtained with their method. In combination with the high polymer concentration, perhaps our layers are too thick, to obtain nitrate fluxes equal to those of uncoated SLMs. The gel network will therefore hinder the transport of the carrier complexes too much, resulting in a flux decrease. Layers consisting of 100 wt% PVC show nevertheless a nitrate flux. This might mean that the layer is permeable to nitrate and chloride, but it might also be an indication of a transfer of LM-phase from the support to the PVC, thereby plasticizing the PVC. This plasticization, or the uptake of LM-phase, might be a necessary condition for transport of nitrate by the carrier.

In table 6.5, also the nitrate fluxes after one day of degradation are given. In all cases, these fluxes are very low. So, despite the presence of the PVC toplayer, carrier is lost from the liquid membrane to the aqueous phases. These uncrosslinked PVC gel networks are not able to suppress the loss of the surface-active carrier TOMA, whose use results in instable SLMs as explained in chapter 2 [36]. This is contrary to the results of Neplenbroek *et al.* where, with these layers and TeOA as carrier, already an improvement of stability could be detected [1,3]. The absolute mass losses show a tendency to be somewhat lower than those of uncoated membranes. However, the increase in weight measured for layers of 100 wt% PVC are not understood. Finally, it must be mentioned that the experiments with the different types of PVC show no differences in initial flux and SLM-stability.

Gel layers with chemical crosslinking

Since uncrosslinked PVC gel layers were not effective in decreasing loss of carrier by emulsion formation, it was tried to shorten the mesh size of the gels by a chemical crosslinking. The amounts of crosslinker and activator were taken from Neplenbroek *et al.* [1,3]. Due to a change in the amount of carboxylgroups in our PVC compared to their PVC-carb, the amounts were somewhat lower. Nevertheless, a chemical crosslinking took place, indicated by the rapid visual increase in viscosity, and solidification after a while, of the PVC/LM-phase mixture when DCC and amine were added.

Table 6.6. *Nitrate fluxes and stability SLMs with a chemically crosslinked PVC gel layer. Support: Accurel. Carrier: TOMA-Cl. Polymer concentration in toplayer: 40 wt%. Gelation by evaporation of THF. Eq DCC, PDA and DDDA to carboxyl groups. Fluxes in 10^{-10} mol cm^{-2} s^{-1}.*

eq DCC	eq PDA	eq DDDA	casting knife* [µm]	initial flux	flux after 1 day	LM-loss [mg]
0.82	-	0.82	100	14.2	0.8	14.0
0.82	-	-	100	11.8	0.8	12.8
0.82	-	-	100	11.7	0.6	13.2
4.1	0.82	-	100	11.5	0.9	10.1
4.1	0.82	-	100	10.2	0.5	15.8
0.82	-	-	50	13.9	0.9	13.3
0.82	-	-	50	14.1	1.0	13.4
4.1	0.82	-	50	13.4	1.1	13.7
4.1	0.82	-	50	13.1	0.8	12.9

*: original thickness casting knife used.

Table 6.7. *Nitrate fluxes and stability SLMs with a chemically crosslinked PVC gel layer. Support: Accurel. Carrier: TOMA-Cl. Polymer concentration in toplayer: 50 wt%. Gelation by evaporation of THF. Eq DCC, PDA and DDDA to carboxyl groups. Fluxes in 10^{-10} mol cm^{-2} s^{-1}.*

eq DCC	eq PDA	eq DDDA	casting knife* [µm]	flux initial	flux after 1 day	LM-loss [mg]
4.1	0.82	-	100	10.2	0.9	19.7
4.1	0.82	-	100	9.8	0.5	17.3
0.82	-	-	100	12.2	0.8	19.1
0.82	-	-	100	12.5	0.7	16.7
0.82	-	-	100	12.4	0.6	11.8
0.82	-	-	100	12.5	0.8	12.3
0.82	-	0.82	100	12.8	0.8	11.7
0.82	-	0.82	100	12.8	0.9	n.d.
0.82	-	0.82	50	13.7	0.8	14.3
0.82	-	0.82	50	14.3	0.9	13.8

*: original thickness of casting knife used; n.d.: not determined

Results concerning the chemically crosslinked membranes are shown in the tables 6.6 and 6.7 for two PVC concentrations investigated (40 wt% and 50 wt % PVC–carb, respectively). Much higher PVC concentrations were very difficult to achieve due to the high viscosity of the mixture and the resulting difficulties in obtaining an uniform toplayer. The thickness mentioned in table 6.6 and 6.7 are the values of the casting knife thickness, and thus the initial thickness of the toplayer. After evaporation and crosslinking the thicknesses are most likely smaller.

The tables 6.5, 6.6 and 6.7 demonstrate the small decrease in initial flux due to the resistance of the toplayer. The thickness of the layer is still too high to obtain the same initial flux as for an uncoated SLM as observed by Neplenbroek *et al.* for gelated SLMs using TeOA-Br as carrier [1,3]. When the crosslinking is carried out using DDDA as crosslinking agent, fluxes are slightly higher than for PDA, both for 40 wt% and 50 wt% PVC. This might be due to the larger length of the crosslinking agent resulting in a somewhat 'opener' structure. The use of a casting knife of 50 µm thickness results in a small increase in initial flux compared to the 100 µm knife. The lower the thickness of the toplayer, the lower the resistance and the higher the initial flux. SEM observations and thickness measurements with a micrometer confirmed the decrease in thickness.

It is clear from tables 6.6. and 6.7 that a chemical crosslinking of the PVC during gelation does not result in an improvement of SLM stability. In all cases, the flux after one day is very low compared to the initial flux, and the absolute LM-losses are almost the same as for uncoated SLMs (table 6.5). In case emulsion formation of the LM-phase is possible and it is the only or most important cause of the instability of TOMA-SLMs, gelation should have resulted in a stability improvement. This is not observed. Apparently, either the emulsion formation hypothesis of Neplenbroek *et al.* [1,3] is incorrect or there are other mechanisms responsible for the degradation of TOMA-SLMs.

When systems using TOMA as carrier are very instable, it might be possible that the stabilizing effect of an interfacial gel layer is masked when in both cases (with and without layer) the flux after one day of degradation is very low. Therefore, a number of experiments were carried out without a degradation step in between the two flux measurements, *i.e.* after measuring the initial flux the feed solution is only replaced by a fresh $4 * 10^{-3}$ M $NaNO_3$ solution when the flux after one day had to be determined. The results are summarized in table 6.8. Despite the low flux after one day, the LM-losses show a tendency to decrease with increasing PVC content in the toplayer. Due to the relatively large thickness of the toplayer, initial fluxes are lowered compared to uncoated SLMs. Comparing the tables 6.5-6.8, fluxes after 1 day without degradation are slightly higher than with degradation. The absolute LM-losses seem to decrease when no degradation step is carried out, although the differences are marginal for 0 wt% and 40 wt% PVC. Only in the 70 wt% case, the determined mass decrease is somewhat lower. Nevertheless, also here the flux after one day is almost zero, which is an indication for a large loss of carrier.

Table 6.8. *Nitrate fluxes and stability of SLMs with a PVC gel layer. Support: Accurel. Carrier: TOMA-Cl. PVC: PVC-carboxylated. Gelation by evaporation of THF. Casting knife 100 μm. No degradation step between the flux measurements.*

PVC content [wt %]	DDC/PDA [eq]*	flux initial [10^{-10} mol cm^{-2} s^{-1}]	flux after 1 day [10^{-10} mol cm^{-2} s^{-1}]	LM-loss [mg]
0	0/0	16.1	2.9	12.2 (4.3%)
0	0/0	16.1	3.1	13.9 (4.9%)
40	4.1/0.82	9.6	1.6	10.3
40	4.1/0.82	9.9	1.9	10.0
70	4.1/0.82	11.3	1.9	4.7
70	4.1/0.82	10.2	1.8	5.0

*: equivalents to carboxyl groups in PVC.

To check whether loss of carrier also takes place at the strip side of the membrane, a double layer membrane was prepared, analogous to the double layer membranes in appendix B to chapter 4 [32], but now with two gel layers on each side of the SLM. Due to the gel layer preparation method, it is difficult to apply the second layer on one and the same membrane without damaging the first layer. Apart from this, the other side of the SLM is usually not flat and this might cause problems in preparing an uniform gel layer. For these reasons, two SLMs with a single, chemically crosslinked gel layer were attached to one another, the layers facing to feed and strip side. Results are given in table 6.9.

Table 6.9. *Results of permeability measurements of two-layered, double SLMs. Support: Accurel. Carrier: TOMA-Cl. Toplayer: PVC-carb (40 wt%), 4.1 eq. DCC, 0.82 eq. PDA. Gelation by evaporation of THF. Casting knife thickness 100 μm.*

membrane	flux initial [10^{-10} mol cm^{-2} s^{-1}]	flux after 1 day [10^{-10} mol cm^{-2} s^{-1}]	flux after 4 days [10^{-10} mol cm^{-2} s^{-1}]
1	6.2	0.3	0.1
2	6.1	0.5	0.2

Table 6.9 demonstrates the reduction of the flux by a factor two, when these data are compared to those in table 6.6. Since the thickness of the double layer membrane is twice that of the usual one-layer SLM, only half of the flux was expected when the two membranes were well sticked together. This is a striking difference with the double layer experiments in chapter 4 [32]. There, double SLMs with two interfacially polymerized toplayers of piperazine and trimesoyl chloride, resulted in a flux which was higher than half the flux of a single SLM with only one

toplayer.

Again the stability of these membranes is not increased. Therefore, these experiments do not give any definitive answer to the question whether carrier is lost also to the strip phase. It is nevertheless remarkable that double layer membranes do not show any flux after 1 day of degradation, which means there is no carrier available anymore for transport. Whether this is due to a complete loss of carrier into the aqueous phases, or to an absence of carrier in the gel layer, not supplied from the LM-phase in the pores of the support resulting in an impermeable barrier, can not be said. Carrier determinations carried out by Neplenbroek *et al.* [1,31,37] were tried earlier in the project for SLMs with an interfacially polymerized toplayer, but did not give conclusive and reproducible results.

TeOA as carrier

Finally, the most successful experiment of Neplenbroek *et al.* was repeated with our test setups and chemicals to see whether stable SLMs were obtained. The results are shown in figure 6.5. A few differences with the results of Neplenbroeks are clear [1,3]. Firstly, the initial flux for for the coated membranes is lower than that of the uncoated reference membrane, while Neplenbroek did not find a difference. This is possibly due to the larger thickness of the toplayers compared to the layers of Neplenbroek *et al.* Furthermore, also with a gel layer hardly any improvement of the stability was observed for TeOA-SLMs. Both for uncoated SLMs as for SLMs with a chemically crosslinked toplayer the fluxes decrease in time. Neplenbroek *et al.* did not find a flux decrease after 80 hours of degradation for the same membrane [1,3]. These remarkable differences of our results with those of Neplenbroek are difficult to explain. One difference is the use of a 10^{-4} M $NaNO_3$ aqueous phase for degradation, while Neplenbroek used a 10^{-4} M NaCl solution, but in both cases the flux for uncoated TOMA SLMs is nihil after 1 day so the difference is not that severe. Furthermore, maybe no or not a complete chemical crosslinking has taken place, but also this seems not the case since after addition of DCC and PDA the LM-phase/PVC mixture started so solidify, indicating that the crosslinking reaction took place. It must be said clearly that the experiments with TeOA were only carried out in duplicate, but the difference between our data and those of Neplenbroek is still quite astonishing then. The idea of gelation works for TeOA-SLMs as Neplenbroek *et al.* have shown [1,3] but when our gelation method and test set-ups are used, there are problems in reproducing their results. Whether this is due to minor differences in properties of the chemicals (different batch numbers) used, the way of gelation or the flux and stability measurements is still an unanswered question.

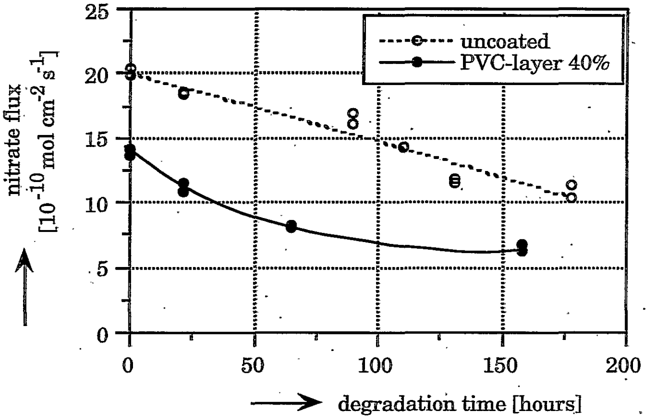

Figure 6.5. *Simulated long term stability of TeOA-SLMs with an interfacial toplayer. Support: Accurel. Carrier: TeOA. PVC concentration in toplayer: 40 wt%. crosslinking with 4.1 eq DCC and 0.82 eq PDA. Gelation by evaporation of THF. Casting knife thickness 100 μm.*

6.4 General discussion

The results in section 6.3 show that gelation of the LM-phase, either homogeneous in the pores of the support or an interfacial gel layer on the feed side, is not able to improve the stability of SLMs used in this study when *TOMA-Cl* is used as carrier. This result is opposite to measurements by Neplenbroek *et al.* [1,3], who found very promising results using a very similar carrier, *TeOA-Br*. The only difference between these two carriers is the replacement of one octyl group from TeOA-Br by a methyl group. This results in a carrier which is much more surface active than TeOA-Cl, and the use of TOMA-Cl therefore results in SLMs which are much more instable when no stabilizing precautions are undertaken. The stabilizing effect of gelation seems to be dependent on the LM-phase used: already fairly stable systems can be stabilized as shown by Neplenbroek *et al.*, but no effect is seen when the SLM is too instable *e.g.* with TOMA-Cl as carrier. Obviously, the mechanism for degradation of SLMs with these carriers is different. TeOA-SLMs might degradate mainly by an emulsion formation process, which can be suppressed by gelation. On the other hand, other mechanisms might be responsible for the instability of TOMA-SLMs which are not minimized by gelation.

Although the gelation was carried out in a way very similar to that of Neplenbroek *et al.*, the experiments with TeOA showed striking differences. This might indicate that the idea of gelation itself works, but that the minor differences between our experiments and theirs causes the discrepancies. Firstly, the chemicals used by Neplenbroek *et al.* and ours may differ. However, care was taken in using exactly the same chemicals (PVC, activator, diamine, carrier) and support material (Accurel), with identical product specifications. Nevertheless, batch numbers might differ, and as a result there might be minor differences in their properties. Although the amount of carboxyl groups for our PVC-carb was somewhat higher than that used by Neplenbroek (1.8 wt% and 1.4 wt%, respectively) and the amounts of activator and crosslinker somewhat lower, we don't believe this can explain the instability of both TOMA and TeOA SLMs with an interfacial gel toplayer. Further, the toplayers were applied by means of a casting knife and not by spreading the gel with a tissue on the support. The casting knife method is considered to give a more uniform toplayer thickness than the tissue method. Another difference is the set-up used for the flux measurements. Although some instability is introduced by replacing feed and strip in between the flux measurements as mentioned in chapter 4 [32], this is also the case in the measurements of Neplenbroek. Besides, in our set-up accumulators were incorporated, which damped the pulsations of the pump and minimized vibrations of the SLM. These accumulators were not present in their setup.

It might be assumed that chemicals and working method used are not mainly responsible for the fact that no stability improvements are observed with gelated SLMs. The whole idea of gelation was based on the assumption that SLM instability in the system is caused mainly by an emulsion formation of the LM-phase [1,3,17,31]. Preventing the LM-meniscus from deformation would lead to an increase in stability, since emulsion formation was suppressed and thus a more stable SLM would be the result. No effect on the stability at all was seen for SLMs with TOMA as carrier when the LM-interface was gelated either homogeneously or by means of an interfacial gel layer. By this gelation the macroscopic viscosity of the LM-phase was increased, and thus the emulsion formation should be reduced. Since no effect on stability was observed, there might be additional factors causing loss of carrier and solvent from the liquid membrane. Such factors might be found on a molecular level, *e.g.* dissolution of carrier or membrane solvent in the aqueous phases. Such factors might explain why interfacially polymerized layers can improve the stability of TOMA-SLMs as presented in chapter 4 [32]. These layers have a high degree of crosslinking due to the use of the trifunctional TMCl as one of the monomers. This might result in layers with a very small 'mesh-size' which can decrease the loss of LM-phase by dissolution. In chapter 7 of this thesis, the gelation results presented here will be discussed further.

6.5 Conclusions

In contrast to the results of Neplenbroek *et al.* [1,3], gelation of the LM-phase when TOMA-Cl is used as carrier, is not effective in improving the stability of relatively instable SLMs. By homogeneous gelation, the initial nitrate flux decreases due to the decrease in diffusion rate of the carrier complex with increasing polymer content. Due to the large thickness of the interfacial gel layers, also the nitrate flux decreased in this case. In both types of gelation, the flux after 1 day of degradation was almost zero. This might be an indication of other, additional causes of SLM instability when TOMA is used as carrier.

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7

SLM DEGRADATION

A review on emulsion formation and other mechanisms

SUMMARY

In the first part of this chapter the theoretical background of emulsion formation is discussed. The general theories on hydrodynamic instabilities and droplet shredding are applied to the supported liquid membranes used in this thesis with the objective to calculate whether emulsification of the LM-phase is possible or not. Then, several other possible causes of SLM instabilities are discussed in an attempt to rationalize some of the experimental observations.

Calculations on hydrodynamical instabilities and general rules used in emulsification processes give no rise to an emulsification of the LM-phase in SLMs for nitrate removal. However, the calculations are very rough, and nothing can be said about the effect of interfacial tension gradients. Additional mechanisms like solubility of the LM-components also seem to play a role in the degradation of SLMs with trioctylmethylammonium chloride as carrier.

7.1 Introduction

In the previous chapters it was shown that interfacial polymerization can be an effective technique for the stabilization of supported liquid membranes [1-3]. However, when an attempt was made to increase the lifetime of relatively instable SLMs with trioctylmethylammonium chloride (TOMA) as carrier by gelation with PVC, no improvement was observed [4]. This was different from the results of Neplenbroek *et al.* [5-7], who observed a clear stability improvement applying the same gelation method on similar SLMs, but with tetraoctylammonium bromide (TeOA) as carrier. This might indicate that in our case other mechanisms for degradation are more important than in their system or that emulsion formation is much more severe for their SLMs.

This chapter will start with a closer look at the backgrounds of emulsion formation in general and in the case of our supported liquid membranes in particular. Furthermore, other possible causes for SLM instability, as presented before in chapter 2 [8] will be applied to our system in order to explain why gelation might not work when TOMA is applied as carrier.

7.2 Emulsion formation

7.2.1 General backgrounds

What is an emulsion?

An emulsion is a disperse system consisting of two (or more) mutually insoluble or sparingly soluble liquids. The liquid usually present in excess is called the *continuous* or *external phase*, while the liquid dispersed in it is named the *dispersed* or *internal* phase. If the continuous phase consists of water and the dispersed phase of an organic liquid, we have an 'oil in water' (o/w) emulsion. When the water is finely dispersed in the oil phase it is called an 'water in oil' (w/o) emulsion. Both types of emulsions are schematically shown in figure 7.1. Other possibilities, but less often occurring, are 'oil in oil' (o/o) and 'water in water' (w/w) emulsions. A daily example of an o/w emulsion is cow's milk (ca 3.5 % fat dispersed in the aqueous phase), while butter is a typical example of a w/o emulsion (up to 20 % water in the dispersion) [9].

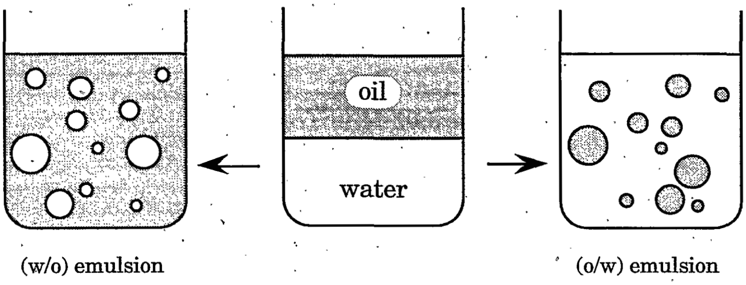

Figure 7.1. *Schematic drawing of types of emulsions in aqueous systems.*

Properties of emulsions

Emulsions with a mean particle diameter between 10^{-4} - 10^{-6} m usually have a turbid and milky appearance. With a mean diameter of 10^{-6} - 10^{-8} m, they have the typical appearance of colloidal solutions. Emulsions with a droplet diameter below 10^{-8} m do not exist [9]. To prevent the droplets from coalescence after formation, usually emulsifiers are added which build energy barriers preventing the droplets from fusing when they collide. Polar emulsifier molecules usually accumulate at the interface between continuous and disperse phase in such a way that their hydrophilic groups project into the water and their hydrophobic groups project into the organic phase.

The stability of emulsions

An emulsion can be regarded as stable when fusion of the droplets is prevented by a sufficiently high energy barrier built up, *e.g.* by the presence of an emulsifier. Emulsions are irreversible colloidal systems: due to the large energy barrier they are more or less stable. The emulsifier can be ionic or nonionic of nature. In the case of ionic emulsifiers, the accumulation of ionic surfactant (emulsifier) molecules in the droplet surface charges the drops. The charged groups of the emulsifier are fixed on the oil/water surface of the droplet. Due to the charging of the droplets, the counterions are attracted to the surface by electrical forces and by an entropic force to distribute themselves over the continuous phase. As a result, the Helmholtz electrical double layer is formed. This electric double layer stabilizes the emulsion. Addition of electrolyte to the continuous phase causes a reduction of the electric double-layer potential, whereas the Van der Waals attraction potential remains essentially unchanged. As a result, with increasing electrolyte concentration the reduced electric double layer potential causes a reduction of the total potential (attraction + repulsion) and at a certain electrolyte concentration the maximum barrier height is reduced to a level at which the stability of the emulsion is lost, depending on the absolute potential values [10]. This is not only valid for the stability of emulsions, but for all colloidal systems. Friberg *et al.* state that o/w emulsions can be stabilized by electric repulsion if the aqueous phase contains monovalent counterions at a concentration less than 0.1 M, divalent ones at less than 0.01 M or trivalent ones at less than 0.001 M [10]. In those cases, the zeta potential is 40 mV or higher, but this is only valid for a certain surface potential of the emulsion droplet which is not given by the authors. For higher electrolyte concentrations or for w/o emulsions, the zeta potential has no importance for stability and other stabilizing agents must be found, *e.g.* by adsorption of polymers (steric hindrance). When emulsions are not stable, they will coalesce [11].

The role of the surfactant in the emulsification mechanism

The question is how an emulsion droplet is formed. For the production of a stable emulsion a suitable surfactant is necessary [12]. By its presence, the surfactant or emulsifier will lower the interfacial tension and consequently the Laplace pressure in the droplet will decrease. Disruption of the droplet will become easier. In order for the surfactant to be active, it must be transported from the bulk liquid to the interface of the film as fast as possible (diffusion effect), where it is adsorbed and forms a surface layer reducing interfacial tension as much as possible (adsorption effect). Apart from this diffusional surface adsorption, the Marangoni effect is also of importance. Due to local differences in the interfacial tension, the part of the interface with the higher interfacial tension will be contracted while the interface with low γ will be extended. As a result, the droplet will be disrupted into two smaller ones. Both processes are schematically drawn in figure 7.2. This smoothening of the interfacial tension takes place more rapidly as the diffusion or spreading rate is larger.

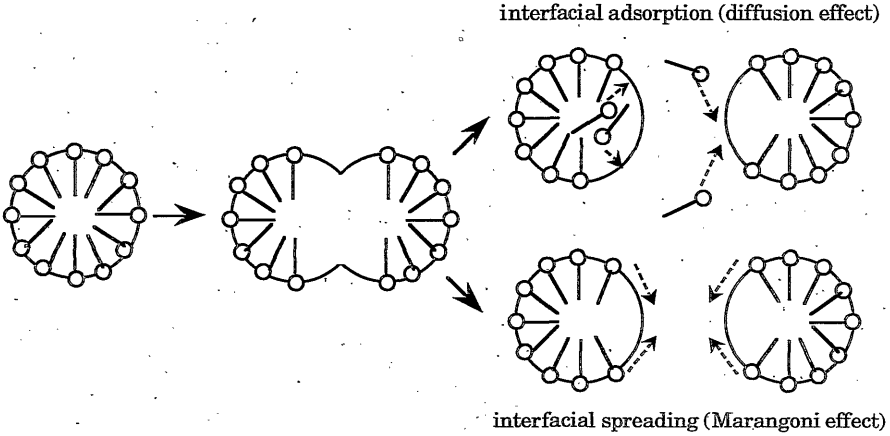

Figure 7.2. *Schematical representation of emulsification mechanisms [9].*

Apart from the lowering of the interfacial tension, addition of surfactant has several other effects [12]. Coalescence of newly formed drops is slowed down due to the Gibbs-Marangoni effect. Suppose we have two droplets approaching each other. During emulsification, adsorption of surfactant is usually incomplete. The interfacial tension will be the highest where the film is the thinnest since the Gibbs elasticity is the highest there. The Gibbs elasticity equals twice the surface dilational modulus, which gives the extent to which the interfacial tension γ is different from its equilibrium value ($= d\gamma/d(\ln A)$, where A is the surface area) [12]. An interfacial tension gradient will develop, causing surfactant molecules to move in the interface in the direction of higher γ, dragging liquid along with it (Marangoni effect). The liquid of the continuous phase forces its way into the gap between the two droplets, pushing them apart and thus stabilizing the emulsion. This is only valid when the surfactant is in the continuous phase. If it is in the disperse phase, no liquid streaming will take place since there are no γ gradients and the droplets are not stabilized by this mechanism. Another effect of interfacial tension gradients might be that they cause such strong Marangoni effects that the surface might be so deformed as to shred droplets.

It was mentioned above that only in the case the surfactant is soluble in the continuous phase, interfacial tension gradient might prevent re-coalescence of *formed* emulsion droplets. This rule is known as *Bancroft's rule* [9,12,13]: the continuous phase is usually the one in which the surfactant is more soluble. The rule is only of importance in emulsification technology, where emulsions with a small emulsion droplet size are desired sometimes. Several explanations can be found for this rule. When the surfactant is in the dispersed phase, droplets are very instable to coalescence or films lacking surfactant can not be made [12].

7.2.2 Emulsification

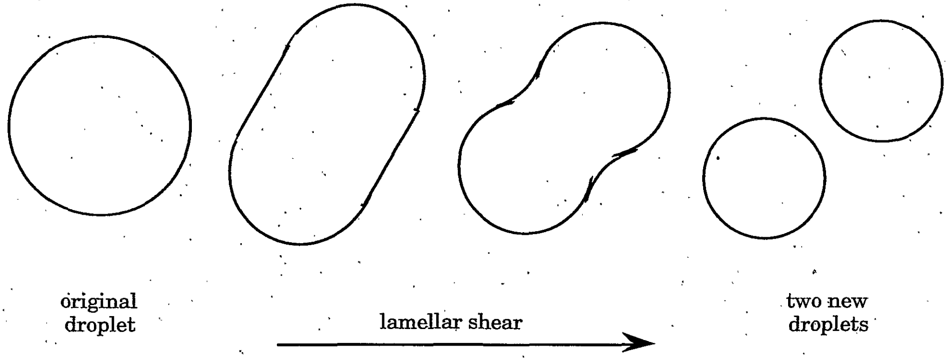

Figure 7.3. *Breakage of an emulsion droplet into two new ones in lamellar shear [10].*

For the formation of emulsion out of two immiscible liquids, mechanical energy is necessary. Firstly, the interface between the two phases (the film) has to be deformed to such an extent that droplet formation takes place (see section 7.2.3). Next, these droplets are broken up or disrupted into smaller ones due to shear forces [12]. This disruption of the droplets, schematically drawn in figure 7.3, is a critical step in the preparation of emulsions with a small droplet diameter [13].

The droplets have to be deformed to achieve their disruption. This deformation is opposed by the Laplace pressure. For a spherical droplet with radius r, the Laplace pressure is equal to the left-hand side of equation (1) [12], which was already mentioned in chapter 2:

$$\Delta P = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \frac{2\gamma}{r}, \qquad (1)$$

where ΔP is the pressure difference between the convex and concave side of the droplet, γ is the interfacial tension between the two phases and R_1 and R_2 are the two radii of curvature. Any deformation of the droplet will result in a pressure difference ΔP, which has to be applied over a distance r to disrupt the droplet. The droplets can also be deformed by shear stress due to an applied velocity gradient, resulting in viscous forces exerting on the droplets by the surrounding liquid. The ratio between these viscous forces and the Laplace force is called the Weber number, defined by equation (2) [10]

$$We = \frac{\eta_c G r}{\gamma}. \qquad (2)$$

In equation (2), We is the Weber number, η_c the (dynamic) viscosity of the continuous phase, G the velocity gradient, r the radius of the emulsion droplet and γ the interfacial tension between the two phases. For elongational flow (*i.e.* flow with a velocity gradient in the direction of flow), G is equal to dv_x/dx. [12]. The Weber number is only of importance for the final diameter of the emulsion droplets formed. It shows that when the interfacial tension γ is higher, the emulsion droplet size will be larger when η_c and G are constant. For viscosity ratios of the dispersed phase to the continuous phase of less than approximately five, a rule of thumb is that the Weber number should be larger than one [10]. Higher viscosity ratios might lead to rotation of the droplets rather than to breakage of the droplet.

7.2.3 Film deformation

At the onset of emulsion formation, there are often two bulk phases. Because of the presence of surfactant, an interfacial tension gradient $d\gamma/dz$ might be present generated *e.g.* by shear stresses as a result of streaming. This implies that the interface is locally expanded or compressed, and surfactant molecules will diffuse towards the interface to lower the interfacial tension (see figure 7.2). The interfacial tension gradients are essential for emulsion formation. When the surfactant concentration is not too small, adsorption of surfactant is fast enough to keep up with the formation of new interface. Droplet formation may take place due to several mechanisms which were already mentioned in chapter two of this thesis [8] and reviewed by several other authors in literature dealing with emulsions in general [12-14]. Suppose we have two phases with densities ρ_1 and ρ_2, where $\rho_1 \geq \rho_2$, and viscosities η_1 and η_2. Droplet formation might take place by the following mechanisms:

(a) *Turbulence.* Turbulent eddies disrupt the interface when the Reynolds number exceeds a certain value and fluid flow gets irregular. The Reynolds number is given by equation (3):

$$\mathrm{Re} = \frac{\rho\, v\, d}{\eta}, \tag{3}$$

where ρ is the density, v the flow velocity, d is a characteristic length and η the viscosity of the fluid. Approximate calculations show this type of hydrodynamic instabilities do not cause disruption of the interface unless γ is very low [12].

(b) *Capillary ripples.* Surface waves ('ripples') are developed by any disturbance of the interface. This might lead to shredding of droplets. Usually, these waves are damped (*e.g.* by the presence of surfactant or the viscosity of the liquids), but when an external source keeps acting at a suitable frequency, standing waves are formed and the amplitude will increase till disruption of the interface occurs. Large γ gradients also cause interfacial turbulence and possible droplet shredding.

(c) *The Rayleigh-Taylor instability.* This type of hydrodynamic instability occurs when the interface between two phases is accelerated perpendicular to its plane and directed from the lighter into the heavier phase, where acceleration due to gravity must be taken into account. For the preparation of emulsions by shaking this mechanism is of importance, but in other situations the importance of the Rayleigh-Taylor instability is doubtful [12].

(d) *The Kelvin-Helmholtz instability.* When two phases move with different velocities u_1 and u_2 parallel to the interface, instabilities will arise. The development of waves on the water surface due to blowing of the wind is an example of this type of instability. Chandrasekhar derived several equations which must be fulfilled otherwise surface forces will damp the waves [12,14]. For the case of two uniform liquids in relative horizontal motion, separated by a horizontal boundary, any perturbation will be enhanced when for constant γ [12]

$$k > \frac{a\left(\rho_1^2 - \rho_2^2\right)}{\rho_1 \rho_2 (u_1 - u_2)^2} \tag{4}$$

and

$$(u_1 - u_2)^2 > 2(\rho_1 - \rho_2)\frac{\sqrt{[a\,\gamma(\rho_1 - \rho_2)]}}{\rho_1 \rho_2}, \tag{5}$$

where k = wave number = $2\pi/\lambda$ [m^{-1}];
λ = wavelength [m];
a = acceleration (= the acceleration due to gravity = g = 9.81 m s^{-2}).

When the actual velocity difference (u_1-u_2) is larger than the one calculated with equation (5), waves will not be damped by surface forces. Whether this will lead to shredding of droplets is not certain.

(5) *Other instabilities.* Several other instabilities are known which might cause interfacial instabilities. For instance, the Benard instability is due to density differences and might occur in homogeneous liquids too (unlike Kelvin-Helmholtz or Rayleigh-Taylor instabilities). As a result of temperature or concentration gradients, heavier particles might be above lighter ones in a gravitational field. This situation tends to redistribute itself which is only possible when buoyancy forces exceed the viscous resistance by a certain amount [13].

In general, it is difficult to deduce which from the above mentioned mechanisms will be mainly responsible for droplet formation since it will depend on the conditions. Most likely, a combination of several effects seems most reasonable. It is known, for instance, that on large ripples caused by Rayleigh-Taylor instabilities, Kelvin-Helmholtz instabilities can develop.

7.2.4 Emulsification in SLMs

In the forthcoming section, physical properties of the liquid membrane system as used in the previous chapters will be used to analyze roughly whether emulsification of the LM-phase is possible with these SLMs and which hydrodynamical instabilities might be responsible for droplet formation. One must bear in mind however, that much of the knowledge concerning emulsion formation is ‘still of a cookbook nature’ as Walstra pointed out [12].

The rule of Bancroft can not be used to decide whether emulsion formation can take place in SLMs or not. The solubility of TOMA-Cl and TeOA-Br in water is lower (see table 7.3) than in the LM-solvent [15,16]. Then, the rule of Bancroft only tells us that the coalescence of *already formed* o/w emulsions of the LM-phase in water will not be prevented by interfacial tension gradients. For the destabilization of SLM by emulsion formation it is only necessary that an emulsion droplet is formed and split off from the LM-meniscus. For that reason, the effect of hydrodynamic instabilities on emulsion formation are interesting and this will be discussed next.

Physical properties of the solutions and the membrane

For calculations, knowledge of the physical properties of the aqueous feed and strip phases and the different LM-phases are necessary. These are listed in tables 7.1 and 7.2, respectively. Note that the properties of the aqueous phases are measured at 20 °C and those of the LM-components and LM-phases at 25 °C. No salt solution data at 25 °C were found. For the LM-solutions, a density of 1.03 * 10^3 kg m^{-3} was used [5,17]. For *o*-NPOE, a density of 1.04 * 10^3 kg m^{-3} is found in literature [18].

Table 7.1. *Physical properties of aqueous phases at 20 °C [19].*

aqueous phase	solute	density [10^3 kg m^{-3}]	absolute viscosity [cP]
water	-	0.9982	1.002
feed	$4*10^{-3}$ M $NaNO_3$	0.9987	1.003
strip	4 M NaCl	1.1500	1.585

Table 7.2. *Physical properties of LM-systems at 25 °C [5,20].*

			interfacial tension	
solvent	carrier (0.2 M)	viscosity [cP]	water [10^{-3} N m^{-1}]	4.0 M NaCl [10^{-3} N m^{-1}]
o-NPOE	-	12.3	27.9	35.0
o-NPOE	TeOA	21.0	16.4	17.3
o-NPOE	TOMA	17.1	5.0	7.3

Firstly, it is tried to calculate whether the flow pattern in the membrane module is laminar or turbulent, where we restrict ourselves in this discussion to the *flat sheet* module used most frequently throughout this thesis. In the case of turbulent flow and a low viscosity of the continuous phase η_c, inertial (ΔP) forces are usually predominant for droplet disruption, contrary to laminar flow [12]. Theories for droplet disruption are different in the two cases. However, in the membrane module the flow pattern of the aqueous phases is not well defined. At the inlet of the module, the tube has a diameter between 3 and 5 mm, depending on the module used. At a volume flow of 5.5 ml s^{-1} as always used in the experiments, the mean velocity of the fluid can be calculated with equation (6):

$$\phi = v\,A, \tag{6}$$

where ϕ is the volume flow rate, v the mean velocity and A the cross sectional area of the tube. By using equation (3), it can be calculated that the Reynolds number for the feed phase lies between 1400 and 2300, while for the strip these values are 1000 and 1700, respectively. Generally, for fluids in a tube the flow pattern changes from laminar to turbulent at a Reynolds number of approximately 2100 [21]. This means that at the inlet of the cell the transition of laminar flow to turbulent flow has just started. In the membrane module itself, the situation is much more complicated. For non-circular geometries a hydraulic diameter has to be used, which is defined as four times the cross-sectional flow area divided by the appropriate flow perimeter [21]. For a rectangular pipe with height H and width W, the hydraulic diameter d_h can be calculated using

$$d_h = \frac{2\,H\,W}{H + B}. \tag{7}$$

The membrane module is of circular shape (see figure 4.3), but in the middle one might consider the cross-section, perpendicular to the membrane, as a rectangular pipe for rough calculations. By replacing the diameter in equation (3) by the hydraulic diameter calculated with equation (7) using 48 mm and 18 mm as width and height, respectively, the Reynolds number would be approximately 170 (feed) and 120 (strip), clearly in the laminar regime. However, these are very rough estimates. As already mentioned, the flow patterns are not well defined in this module. Furthermore, several inlet and outlet effects take place. At the module inlet, the fluid flows as a jet and gradually expands to fill the module with a recirculation flow outside the jet [21]. At the outlet, we have a sudden contraction of the flow. The flow pattern there is different from the inlet. Nevertheless, we assume for the forthcoming analysis that the flow throughout the cell is mainly laminar, apart from a very small region around the inlet of the membrane module, but one must bear in mind that there is no certainty about it.

In section 7.2.3 several possible hydrodynamical instabilities were mentioned. Not all of them might play a role when emulsification of SLMs really takes place. Interfacial turbulence will only play a role when the interfacial tension γ between

LM-phase and the aqueous phase is extremely low. As can be seen in table 7.2, interfacial tensions are not extremely low so turbulence is excluded. Capillary ripples are caused by any disturbances of the interface in SLMs, like vibrations of the membrane due to pumping of the aqueous phases across its surface. Its effect might be damped by γ gradients, but nothing is known about these gradients for our system. Nevertheless, when vibrations of the membrane are severe, the formed ripples might finally lead to shredding of droplets. The Rayleigh-Taylor instabilities are only of importance when the acceleration of the lighter into the heavier phase is very high, taking the gravitational acceleration into account. At the feed side, the aqueous phase density is lower than that of the organic solution, so acceleration of the LM-phase into the feed phase might enhance interfacial instabilities. The opposite is the case for the strip phase since its density is higher than that of the LM-phase.

Most likely as main cause of local deformations in SLM systems seem to be the Kelvin-Helmholtz instabilities. By using equation (5), it is possible to estimate roughly whether any perturbations of the meniscus will be enhanced or not. The calculation, however, is only valid at the inlet of the module, since nothing is known about the velocities of the aqueous phases in the module. Densities and interfacial tensions were taken from tables 7.1 and 7.2. It is assumed that the interfacial tension between the feed containing $4 * 10^{-3}$ M $NaNO_3$ and LM-phase is the same as that between pure water and LM-phase as given in table 7.2. It can be calculated then that for TeOA, the velocity difference between the aqueous phases and LM-phase should be larger than 9.4 cm s^{-1} (feed) and 12.9 cm s^{-1} (strip). For TOMA, these velocity differences are 7.0 and 10.4 cm s^{-1} for feed and strip side, respectively. At the inlet of the membrane module, the mean velocities are 78 cm s^{-1} for the 3 mm inlet and 28 cm s^{-1} for the 5 mm inlet. The velocity of the LM-phase is zero due to the immobilization in the pores. This means that *at the inlet* of the module, the condition in equation (5) is fulfilled and any disturbance of the interface will be enhanced. In other parts of the module nothing is known about the velocity of the aqueous phases. The crosssectional area perpendicular to the membrane is considerably larger, and therefore the mean flow velocity is smaller and can drop easily below the critical values calculated before. So, it seems not likely that everywhere in the module Kelvin-Helmholtz instabilities cause emulsion droplet shredding. However, this is not necessary for SLM degradation: when only at the inlet of the module emulsification of LM-phase is possible, the membrane might also be regarded as being instable. Even when the velocity is high enough, nothing is known about the effects of γ gradients and viscosities of the phases on the effect of the Kelvin-Helmholtz instabilities. On this basis, it can therefore not be concluded that the LM-meniscus will be deformed to such an extent that droplets are formed.

Once emulsion droplets have been formed or are almost split off the LM-meniscus, they can bounce back to the LM-phase in the membrane pores or be broken up by shear forces into smaller ones. Whether the droplets can coalesce with the remaining LM-phase in the pores is influenced by their stability. The stability on the other hand is largely influenced *e.g.* by surfactant type, electrolyte concentration and flow velocity. Neplenbroek *et al.* indeed showed these variables to be of importance on emulsion stability and SLM instability [5,17]. Zha criticized the light transmission measurements carried out by Neplenbroek *et al.* who used it as a as criterion for emulsion stability. Droplet size distribution measurements as a function of process and product variables for n-decanol in different aqueous solutions were therefore carried out by Zha [22]. It was found that with increasing salt concentration in the aqueous solution it was more difficult to form o/w emulsions and the formed emulsions were less stable.

It is not easy to predict whether droplet break up by shear forces occurs due to the irregular and unknown flow pattern in our membrane module. In equation (2) the Weber number was mentioned. However, nothing is known about the velocity gradient G at the membrane surface in the module, so the Weber number can not be calculated. Since the velocity in the module is very low (mean flow velocity in the middle is 0.64 cm s^{-1}), it is expected that the gradient is also low and We will be <<1. A rule of thumb was that We should be in excess of one for droplet break up when viscosity ratios of dispersed to continuous phase is smaller than 5 [10]. The ratio is larger than five as can be concluded from tables 7.1 and 7.2. Nevertheless, the very low Weber number is indicating that break up of droplets will not take place in the membrane module. The droplets, when present, will rotate rather than break due to the high ratio η_d/η_c [10,12,13]

At this moment, it might be concluded that several rules of thumb and rough calculations presented above show that the *formation* of emulsion droplets in SLMs as used throughout this thesis by hydrodynamic forces alone in the *whole* membrane module is not very likely (but also not necessary!). The energy applied by streaming of aqueous phases across the liquid membrane seems not enough to cause sufficient hydrodynamic instabilities. However, since interfacial tension gradients play a very important role in emulsification and nothing is known about these gradients, emulsion formation can still take place. A strong point in favor of the emulsification hypothesis is that all observations (influence of salt type and concentration, flow velocity, carrier structure) can be explained well in that context.

7.3 Other causes of SLM instability

Neplenbroek *et al.* also showed that the application of an interfacial, chemically crosslinked PVC gel layer at the feed side of the SLM could prevent loss of LM-phase [7]. Similar experiments with TOMA as carrier and a PVC gel toplayer described in chapter 6 of this thesis did not show any stability improvement. In case emulsion formation is also the most important mechanism for degradation of our membranes, gelation should improve the stability. Gelation of the LM-phase will decrease the deformation of the LM-meniscus. As a result, emulsification will be suppressed and the membrane should become more stable. The fact that this is not observed experimentally, indicates that other mechanisms of SLM degradation are playing a more important role in TOMA-SLMs, on which gelation has no or only minor influence. In this section, an attempt is made to explain these instability phenomena.

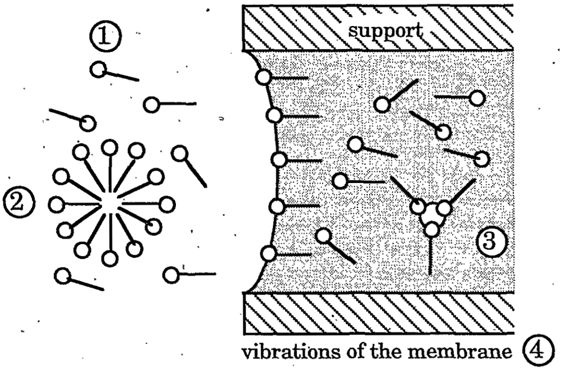

Figure 7.4. *Several mechanisms for SLM degradation. 1: Dissolution of carrier. 2: Aggregate formation (micelles). 3: Reversed micelles. 4: Vibrations of the membrane.*

In figure 7.4, several mechanisms for SLM degradation are depicted. Firstly, the dissolution of carrier and/or solvent into the adjacent aqueous phases might play a role. Neplenbroek *et al.* pre-saturated the aqueous phases with the organic LM-solvent (decanol or dibutylphthalate), but still found for their a considerable amount of solvent removed from the SLM [5,17]. However, no saturation experiments with the LM-phase (both solvent *and* carrier) were carried out or described in their work. So, solubility effects still might play a role for gelated TOMA-SLMs. Throughout this thesis, mainly SLMs consisting of *o*-NPOE and TOMA-Cl were used. The solubility data for this carrier and solvent are given in table 7.3, together with the values for several TeOA salts.

In table 7.3, one can see that the solubility of *o*-NPOE in water is very low, so the loss of *o*-NPOE by dissolution in our system will be much smaller than the loss of carrier by dissolution. With the data given in table 4.1 for Accurel supports (porosity and thickness) and the diameter of the membrane module (74 mm), a total pore volume of 0.2819 ml can be calculated. The aqueous feed volume is 130 ml during SLM flux measurements, being much larger than the volume of LM-phase in the support. The carrier concentration is always 0.2 M at the beginning of the experiment. Suppose all carrier is lost to one aqueous phase, then the maximum carrier concentration in the aqueous phase would be $4.34 * 10^{-4}$ M. It is clear from table 7.3 that this can be reached easily for TOMA-Cl since the maximum solubility in water is higher. Furthermore, for every flux or stability measurement both phases are replaced by fresh ones. Every time a phase is replaced by a fresh one, loss of carrier to the aqueous phase by dissolution might continue until all carrier is lost and no flux can be detected anymore. However, care must be taken in the interpretation of the maximum solubility data since these data are of the pure components, and in the SLM we have a combination of organic solvent (*o*-NPOE) and carrier. In fact, knowledge of the distribution coefficient of carrier between the aqueous phase and *o*-NPOE is needed, but this is unknown.

Table 7.3. *Solubilities of SLM components (carrier and organic solvent) in pure water. All data at 25 °C, except TOMA-Cl at 30 °C.*

component	solubility in H_2O [g/l]	solubility in H_2O [mol/l]	H_2O solubility [g/l]	reference
o-NPOE	$0.16 * 10^{-3}$	$6.4 * 10^{-7}$	0.98	18
TeOA-Br	0.049	$9.00 * 10^{-5}$		15
TeOA-NO_3	0.0295	$5.58 * 10^{-5}$		15
TeOA-Cl†	0.29	$5.70 * 10^{-4}$		15
TeOA-ClO_4	0.00244	$4.31 * 10^{-6}$		15
TOMA-Cl*	4.04	10^{-2}		16
	0.404	10^{-3}		

†: Forms a two liquid phase system in which a fairly dilute aqueous solution is in equilibrium with a fairly concentrated solution. The solubility given is the maximum concentration in the dilute aqueous phase.

*: Only a solubility range (between 10^{-2}-10^{-3} M) was found in literature. Nothing was mentioned about the purity of the used TOMA-Cl.

When solubility plays a major role in degradation of the SLMs used in this thesis, we have to show why loss of carrier takes place to the aqueous phase since it was shown by Neplenbroek *et al.* that the amount of TOMA removed from the SLM was lower when the salt concentration was higher [5,17]. The solubilities in table 7.3 are all in pure water. When salt is added, the solubility of the carrier will decrease. The solubility product is constant, and when the anion concentration increases this implies that the amount of carrier cation which can dissolve in the aqueous phase should decrease. The high salt concentration at the strip side might explain why loss of carrier only occurs at the feed side where the salt concentration is low.

Solubility effects as an additional mechanism, next to emulsion formation, for TOMA-SLM degradation might explain the gelation results presented before in chapter 6. It was observed that the application of a thin, chemically crosslinked PVC gel layer at the feed side of the membrane did not stabilize the SLM [4], different from the promising gelation results of Neplenbroek when TeOA was used as carrier [5,7]. Gelation will suppress deformations of the LM-meniscus and prevent the formation of emulsion droplets, assuming emulsification is possible in SLMs. When using gelled TOMA-SLMs, emulsification might very well be prevented. However, the gel network might still be so open that the carrier can dissolve in the adjacent aqueous phase. In that case the solubility effect is the predominant mechanism for TOMA-SLM degradation and the stability of TOMA-SLMs will not increase as a result of the application of a gel toplayer. For TeOA-SLMs, the solubility might be of minor importance, and gelation in order to prevent membrane degradation by emulsion formation will be more effective.

Hollow fiber results in chapter 5 showed a clear influence of the aqueous feed composition during degradation on the nitrate flux after a large amount of fresh aqueous phase has been passed through the fiber [3]. When the usual feed solution of $4 * 10^{-3}$ M $NaNO_3$ was used in between two flux measurements, a reasonable flux was still present. After passing pure water through the lumen, no flux could be detected anymore. Both emulsification and solubility effects can explain these results. Suppose enough energy has been supplied to the system to emulsify the LM-phase. An increase in salt concentration will decrease the emulsion stability. According to the emulsion formation hypothesis of Neplenbroek *et al.* [5,17], SLM stability will increase with increasing salt concentration, which is in accordance with our results. The presence of salt will also influence the solubility of LM components as already mentioned before. Although the effect seems to be quite drastic for this low salt concentration, it fits in the picture: the higher the salt concentration, the lower the loss by dissolution and the more stable the membrane. Calculation of the amount of carrier dissolved into the aqueous phase, however, is not possible due to the lack in knowledge of the partition coefficient of the carrier between *o*–NPOE and feed phase.

Solubility on a molecular scale alone however fails to explain the high loss of *o*–NPOE when either both carrier and solvent or solvent alone are present in the SLM. The solubility of *o*-NPOE in pure water is very low, 0.16 mg l^{-1}, as can be seen in table 7.3. However, in chapter 3 table 3.5, it was reported that the loss of *o*-NPOE after 1 day was in the order of 10-15 mg in absence of carrier and in between 11-20 mg when carrier (TOMA or TeOA) was present [1]. Although feed and strip phases were replaced for enhanced degradation purposes and some of the LM-phase might simple be pressed out of the support due to the way the two cell halves were squeezed together, resulting in an inaccurate LM-loss measurement, this loss of 11-20 mg of solvent is still high. Emulsification of the LM-phase can explain this high loss, but solubility effects hardly can. Therefore, for TOMA-SLMs without a gel or polymeric toplayer, emulsification of the LM-phase as instability mechanism can not be excluded.

In figure 7.4, several other additional mechanisms for TOMA-SLM degradation were suggested. In case the amount of carrier dissolved in the aqueous phase is above the so called critical micelle concentration (cmc), micelles or aggregates of TOMA in water might be formed. When micelles of TOMA in the aqueous phase can be formed, additional TOMA can dissolve. An increase in salt concentration tends to decrease the cmc [23]. For TeOA, no data on micelle formation were found and it is not likely that symmetrical tetraalkylammonium salts form micelles [24] Okahata *et al.* measured a 'cmc' in water for TOMA-Cl by surface tension measurements [16]. According to the authors, TOMA-Cl forms aggregates at very low concentrations (in between 10^{-4} and 10^{-5} M), but no data on the purity of the carrier were given. Furthermore, although the determined 'cmc' for CTAB (cetyltrimethylammonium bromide, a cationic surfactant) agreed well with literature data, the surface tension of CTAB in water as measured was always higher than that of TOMA-Cl in water, which might indicate that the TOMA-Cl used had a low purity. Therefore, the 'cmc' data are considered to be rather doubtful Kunitake *et al.* [25], from the same group as Okahata, reported identical measurements on the critical micelle (aggregate) concentration of CTAB and TOMA-Cl. The 'cmc' was determined by a dye method and found to be ca. $3 * 10^{-4}$ mol l^{-1}. By means of a laser light scattering method, the aggregate weight was measured. TOMA had an aggregate weight of lower than 10^4 g mol^{-1}, indicating a small and tight aggregate. Due to the small size of the micelles and the question whether the concentration of TOMA in water can reach the 'cmc' in actual SLM processes, micelle formation is not thought be an additional cause of SLM instability in our system.

On the other hand, TOMA-Cl is used for the reversed micellar extraction of proteins (for a review article see Sebba [26]). As organic solvents for reversed micelles of TOMA or Aliquat 336 (a mixture of several trialkylmethylammonium compounds with TOMA as one of the main components) cyclohexane and isooctane are reported [26,27]. By means of reversed micelles, where the 'continuous' phase is an oil phase and the reversed micelle interior consist of water, the aqueous feed and strip phases might be introduced into the SLM (figure 7.4). However, it is unknown whether TOMA can form reversed micelles in *o*-NPOE, and what their size is. For TOMA–NO_3 in xylene, it was found that for the extraction of rare earth elements eight water molecules were associated with four TOMA molecules [28]. It seems unlikely that such small micelles can introduce a significantly large amount of water into the SLM to replace the organic phase and to degradate the SLM. Furthermore the effect of salt concentration in the *aqueous phases* on SLM stability can not be explained with reversed micelle formation.

Finally, as mentioned before, vibrations of the membrane can be a cause of SLM instability. It may enhance emulsion formation by causing capillary ripples to develop on the LM-meniscus [12]. Furthermore, in combination with small pressure gradients LM-phase might be pressed out of the support.

7.4 Conclusions

In this chapter the emulsion formation hypothesis of Neplenbroek *et al.* as main mechanism of LM degradation was reviewed. By means of several rough calculations on hydrodynamic instabilities it was shown that for the flat sheet SLMs as used throughout this thesis, it is doubtful whether enough energy can be supplied to the interface for droplet shredding throughout the whole membrane module. However, nothing could be said about the effect of interfacial tension gradients on emulsion formation. Furthermore, with emulsion formation most experimental results can be explained. Dissolution of the LM-components in the adjacent aqueous phases might be an additional cause for the instability of TOMA-SLMs in order to explain the gelation data in chapter 6. Most likely, the mechanism most important for the the instability effects of an SLM are dependent on the type of membrane and experimental procedures.

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SUMMARY

Membrane processes provide a relatively new and economically attractive separation technique. One type of membrane processes, *i.e.* the use of facilitated transport in liquid membranes, is particularly attractive. Compared to other membrane processes, liquid membranes show high selectivities, high diffusion rates through the liquid and provide the possibility of concentrating species by means of a coupled transport process. The work described in this thesis is focussed on supported liquid membranes (SLMs), in which an organic solvent containing a selective carrier is immobilized in the pores of a microfiltration membrane. In spite of their clear advantages are SLMs not used on an industrial scale nowadays. The main reason for this is their lack of stability and subsequently short lifetime. In this thesis, a new method is presented to stabilize SLMs: the precipitation of a polymeric toplayer on the macroporous support by an interfacial polymerization which decreases the loss of the membrane liquid to the adjacent aqueous phases.

In chapter 1 a general introduction on membrane technology is given. Special attention is paid to two types of liquid membranes, *i.e.* the emulsion liquid membrane and the supported liquid membrane.

The major problem concerning SLMs is their instability. Due to the loss of carrier and/or solvent from the pores of the support, both selectivity and flux are lost after some time. In literature, several mechanisms are proposed with which the authors try to explain the degradation of an SLM. In chapter 2 an overview is given on these mechanisms. Most likely, the solubility of carrier and membrane solvent in the adjacent feed and strip solutions, and an emulsification of the LM-phase in water induced by lateral shear forces are the main reasons for SLM degradation. In this chapter also several suggestions for SLM lifetime improvement are critically reviewed. Although new liquid membrane configurations seem to be very stable, modifications of the LM-phase by adding a gel forming polymer is a simple and promising technique.

In literature the application of a thin, chemically crosslinked PVC toplayer on one side of the SLM in order to improve the lifetime of SLMs for nitrate removal is described. Based on this earlier work, polymeric toplayers were deposited on SLM supports by means of an interfacial polymerization reaction. This technique is well known for the preparation of composite membranes, as is described in chapter 3. From literature references, several monomers were chosen and polymerized on top of microfiltration membranes. These composite membranes were used as support for SLMs for the removal of nitrate ions from water. The objective of this study

was to find suitable toplayers for the stabilization of SLMs, without a significant reduction in nitrate flux. Most of the applied toplayers did not hinder the transport of nitrate, but only a few of them could increase the stability of the SLM. The best results were obtained when piperazine (PIPA) and trimesoylchloride (TMCl) were used as monomers.

There are many factors which influence the final properties of polymers if prepared by an interfacial polymerization reaction. Some of these factors were systematically varied in order to elucidate their influence on the stabilizing effects of PIPA/TMCl toplayers. Furthermore, the application of the toplayer is optimized. The results are described in chapter 4. Very promising results for relatively instable SLMs were obtained when a mould was used for the preparation of the toplayer on the support and when the toplayer was kept in the wet state after polymerization. Several other, piperazine-like monomers were also able to increase the lifetime of SLMs, sometimes even with a clear increase in initial nitrate flux compared to uncoated SLMs. Different characterization techniques were used to investigate the structure and chemical composition of the toplayers. These techniques could not explain the nitrate flux decrease and instability of SLMs with a PIPA/TMCl toplayer when an acid acceptor was added during polymerization. In the second appendix to this chapter, results are presented which might be an indication that the LM-phase can swell the PIPA/TMCl toplayer.

For the industrial application of SLMs and from an economical point of view, a hollow fiber configuration is more attractive than flat sheet membranes. In chapter 5 results are presented on hollow fiber SLMs for nitrate removal. Two different set-ups were designed to test the fibers: one which worked batch-wise and one in which nitrate was continuously removed from the feed solution. After coating the lumen side of the fibers with a toplayer of PIPA and TMCl by means of an interfacial polymerization reaction, fluxes and stabilities of the fibers were compared to those of uncoated fibers. It was observed that the application of the toplayer increased the life-time of the hollow fiber SLM. However, the application of an uniform toplayer on the fiber is not easy, as was revealed by the scattering in flux data and by structural investigations using scanning electron microscopy.

From literature it is known that gelation of the LM-phase results in more stable SLMs. To compare both techniques the results of gelation experiments with our nitrate removal system are presented in chapter 6. Polyvinylchloride (PVC) was used as gel forming polymer, and either the whole LM-phase was gelated, or a chemically crosslinked gel layer was applied on top of the SLM. In all cases, gelation did not result in an increase of the stability. The results indicate that an emulsification of the LM-phase is not the only mechanism for degradation of our SLMs.

The results obtained in this thesis gave rise to a critical look at the emulsion formation hypothesis and other mechanisms for SLM degradation. In chapter 7, calculations on hydrodynamic instabilities and some general rules on emulsion formation showed that only in a very small part of the membrane module emulsification of the LM-phase is probable for our system. However, the effect of interfacial tension gradients was not taken into consideration. Additional mechanisms like the solubility of carrier and organic solvent in the adjacent aqueous phases also seem to be important.

SAMENVATTING

Membraanprocessen bieden een relatief nieuwe en ekonomisch aantrekkelijke scheidingstechniek. Eén soort membraanproces, het gebruik van gefaciliteerd transport in vloeistofmembranen, is bijzonder aantrekkelijk. Vergeleken met andere processen, hebben vloeistofmembranen een hoge selektiviteit en een hoge diffusiesnelheid door de vloeistof en bieden ze de mogelijkheid deeltjes te koncentreren door middel van een gekoppeld transport. Het werk, zoals beschreven in dit proefschrift, heeft betrekking op geïmmobiliseerde vloeistofmembranen (supported liquid membranes: SLMs), waarin een organisch oplosmiddel met een 'carrier' is geïmmobiliseerd in de poriën van een microfiltratiemembraan. Ondanks de voordelen die SLMs bieden, worden ze vandaag de dag niet toegepast op industriële schaal. De belangrijkste reden hiervoor is het gebrek aan stabiliteit en de daaruit volgende korte levensduur. In dit proefschrift wordt een nieuwe methode beschreven om SLMs te stabiliseren: het aanbrengen van een toplaag op de macroporeuze drager door middel van een grensvlakpolymerisatie, die het verlies van de membraanvloeistof naar de aangrenzende waterige fasen vermindert.

In hoofdstuk 1 wordt een algemene inleiding op het gebied van membranen gegeven. De aandacht gaat speciaal uit naar twee soorten vloeistofmembranen: het geëmulgeerd vloeistofmembraan en het geïmmobiliseerd vloeistofmembraan.

Het belangrijkste probleem betreffende SLMs is hun instabiliteit. Vanwege het verlies van carrier en/of oplosmiddel uit de poriën van de drager, veranderen selektiviteit en flux na enige tijd. In de literatuur worden verschillende mechanismen voorgesteld, waarmee de auteurs de degradatie van SLMs proberen te verklaren. In hoofdstuk 2 wordt een overzicht gegeven van deze mechanismen. De oplosbaarheid van carrier en oplosmiddel in de aangrenzende waterfasen, en een emulsificatie van de vloeistofmembraanfase (LM-fase) in water als gevolg van afschuifkrachten lijken de belangrijkste oorzaken van SLM degradatie. In dit hoofdstuk worden ook verschillende suggesties voor het verhogen van de levensduur van SLMs kritisch bekeken. Alhoewel nieuwe uitvoeringsvormen voor vloeistofmembranen stabiel lijken te zijn, is een modificatie van de LM-fase door het toevoegen van een gel-vormend polymeer een simpeler en veelbelovende techniek.

In de literatuur is het aanbrengen van een dunne, chemisch gecrosslinkte PVC gellaag, om zo de levensduur van SLMs voor nitraatverwijdering te verbeteren, beschreven. Gebaseerd op dit idee zijn polymere toplagen op dragers voor SLMs aangebracht door middel van een grensvlakpolymerisatie. Zoals beschreven in hoofdstuk 3, is dit een bekende techniek voor het maken van komposietmembranen. Uit literatuurreferenties werden verschillende monomeren gekozen en gepolymeriseerd op microfiltratiemembranen. Deze komposietmembranen werden gebruikt als drager voor SLMs voor de verwijdering van nitraationen uit water. Het doel van deze studie was het vinden van een geschikte toplaag voor de stabilisering van SLMs zonder een noemenswaardige afname van de nitraatflux. De meeste aangebrachte toplagen hinderden het transport van nitraat niet, maar slechts enkelen konden de stabiliteit van het SLM verhogen. De beste resultaten werden verkregen met piperazine (PIPA) en trimesoylchloride (TMCl) als monomeren.

De uiteindelijke eigenschappen van polymeren, gemaakt via een grensvlakpolymerisatie reaktie, worden beïnvloed door vele faktoren. Een aantal van deze faktoren zijn systematisch gevariëerd om hun invloed op de stabiliserende werking van PIPA/TMCl toplagen te bekijken. Vervolgens is het aanbrengen van de toplaag geoptimaliseerd. De resultaten staan beschreven in hoofdstuk 4. Voor relatief instabiele SLMs werden veelbelovende resultaten verkregen wanneer voor het aanbrengen van de toplaag op de drager een mal werd gebruikt en de toplaag in de natte toestand werd gehouden na de polymerisatie. Verschillende andere, piperazine-achtige monomeren waren ook in staat de levensduur van de SLMs te verbeteren, soms zelfs met een duidelijke toename in initiële nitraatflux vergeleken met ongecoate SLMs. Verschillende karakteriseringstechnieken werden gebruikt om de struktuur en chemische samenstelling van de toplagen te onderzoeken. Met deze technieken kon de daling van de nitraatflux en de instabiliteit van SLMs met een PIPA/TMCl toplaag, gepolymeriseerd met toevoeging van een zuuracceptor, niet worden verklaard. In de tweede appendix bij dit hoofdstuk zijn resultaten gepresenteerd die een indikatie kunnen zijn voor het zwellen van de PIPA/TMCl toplaag door de LM-fase.

Voor de industriële toepassing van SLMs en uit ekonomisch oogpunt lijkt een konfiguratie met holle vezels aantrekkelijker dan één met vlakke membranen. Resultaten voor nitraatverwijdering met holle vezel-SLMs staan beschreven in hoofdstuk 5. Twee verschillende opstellingen zijn ontworpen om de vezels te testen: één die batchgewijs werkt en één die nitraat kontinu uit de voeding haalt. Nadat de lumenzijde van de vezels van een PIPA/TMCl toplaag was voorzien met behulp van een grensvlakpolymerisatie reaktie, zijn de flux en stabiliteit van de gecoate vezel vergeleken met die van ongecoate vezels. Het aanbrengen van de toplaag resulteerde in een langere levensduur van het holle vezel-SLM. Het aanbrengen van een uniforme toplaag op de vezel was echter niet gemakkelijk, hetgeen de spreiding van de fluxen en de met raster elektronen mikroskopie onderzochte struktuur van de laagjes lieten zien.

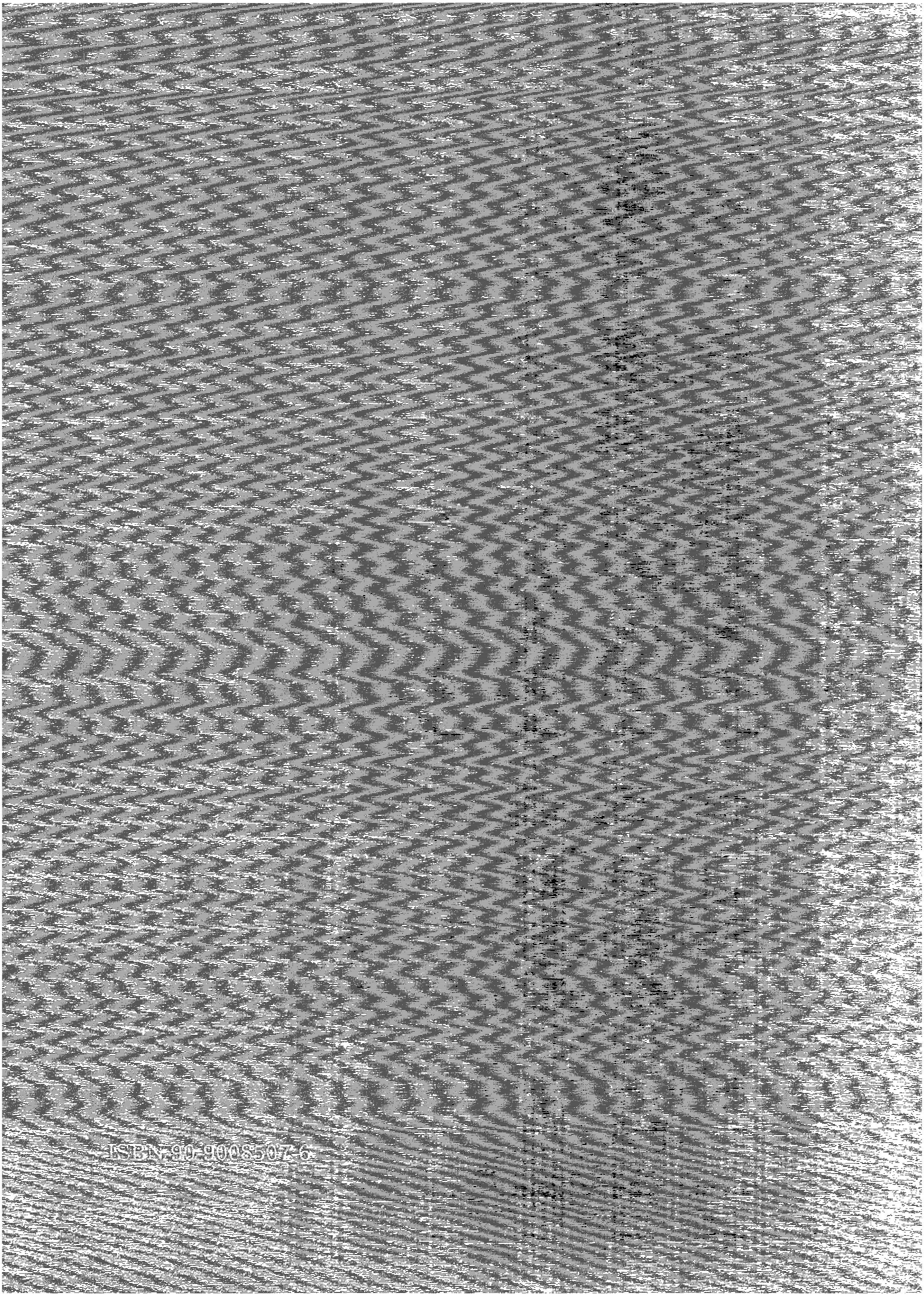
Uit de literatuur is bekend dat een gelering van de LM-fase stabielere SLMs oplevert. Om beide technieken te kunnen vergelijken, staan in hoofdstuk 6 resultaten van geleringsexperimenten met ons SLM systeem beschreven. Polyvinylchloride (PVC) werd gebruikt als gel-vormend polymeer: of de gehele LM fase werd gegeleerd, of een chemisch gecrosslinkte gellaag werd op het SLM aangebracht. In alle gevallen werd geen verbetering van de stabiliteit door gelering waargenomen. De resultaten geven een indikatie dat emulsievorming van de LM-fase niet het enigste mechanisme voor de gebruikte SLMs is.

De resultaten verkregen in dit proefschrift gaven aanleiding de emulsievormings-hypothese en andere mechanismen voor SLM degradatie kritisch te bekijken. In hoofdstuk 7 laten berekeningen over hydrodynamische instabiliteiten en een aantal algemene regels omtrent emulsievorming zien dat slechts in een klein deel van de membraanmodule een emulsificatie van de LM-fase mogelijk is voor ons systeem. Het effekt van grensvlakspanningsgradiënten is echter niet in beschouwing genomen. Aanvullende mechanismen zoals de oplosbaarheid van carrier en oplosmiddel in de aangrenzende waterfasen lijken ook belangrijk te zijn.

LEVENSLOOP

Antoine Kemperman werd op 27 april 1968 geboren te Arnhem. In dezelfde stad behaalde hij in 1986 zijn VWO diploma aan het Thomas à Kempis College, waarna hij begon aan zijn studie Chemische Technologie aan de Technische Hogeschool Twente (later Universiteit Twente). Tijdens zijn studie liep hij drie maanden stage bij Akzo Research Laboratories Arnhem (ARLA) waar onderzoek gedaan werd naar de bereiding, zuivering en karakterisering van core-shell latices ten behoeve van affiniteits cross-flow filtratie. De afstudeeropdracht werd uitgevoerd in de onderzoekgroep Membraantechnologie (vakgroep Grensvlak- en Scheidingstechnologie) van prof.dr. C.A. Smolders en had als titel 'Zeolite filled polymeric membranes for gas separation'. In augustus 1991 behaalde hij zijn ingenieursdiploma.

Per 1 september 1991 begon hij als assistent in opleiding (AIO) aan het in dit proefschrift beschreven onderzoek. Het onderzoek werd verricht binnen de vakgroep Membraantechnologie onder leiding van prof.dr.ing. H. Strathmann. In de periode april-juni 1994 was hij tijdelijk gastmedewerker aan het Dalian Institute of Chemical Physics te Dalian, China, en werkte daar aan de scheiding van cobalt en nikkel middels vloeistof/vloeistof - en membraan extractie in de afdeling Membrane Processes van prof. Jian.



ISBN 90-9008507-6