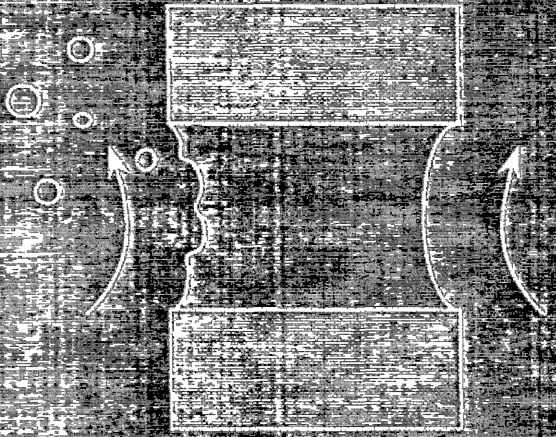
STABILITY OF SUPPORTED LIQUID MEMBRANES



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Tommy Neplenbroek

STABILITY OF
SUPPORTED LIQUID MEMBRANES

PROEFSCHRIFT

ter verkrijging van
de graad van doctor aan de Universiteit Twente,
op gezag van de rector magnificus
prof. dr. ir. J.H.A. de Smit,
volgens besluit van het College van Dekanen
in het openbaar te verdedigen
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ANTONIUS MARIA NEPLENBROEK
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Dit proefschrift is goedgekeurd door de promotor: prof. dr. C.A. Smolders
Assistent promotor: dr. D. Bargeman
Referent: dr. J. Lucassen

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On the eighth day God created liquid membranes,
and he saw that they were *almost* perfect ......

VOORWOORD

Gedurende de afgelopen 4 jaar hebben we ons bezig gehouden met de ontwikkeling van een nieuwe scheidingstechniek van gebruik in het laboratorium naar toepassing in de praktijk. In tegenstelling tot de ervaring van een expert op dit gebied (P.R. Danesi) werd dit geen frustrerend maar juist een motiverend onderzoek, wat wellicht werd bepaald door de stimulerende vorderingen die behaald werden.

Deze resultaten werden in de eerste plaats vergaard door de technische assistenten Clemens Padberg, Zandrie Borneman en Peter Schwering. Daarnaast was er, in de vorm van een stage of afstudeeropdracht, de enthousiaste medewerking van de volgende studenten: Rudy Visscher, Gert Nijman, Henk Schonewille, Gea Spijkerman, Herbert van der Hoek, Claudia Kokkeler en Hans ter Steege.

De vakgroep Membraantechnologie, met zijn diversiteit aan theoretisch en praktisch ingestelde onderzoekers, is een goede voedingsbodem voor het uitbroeden en realiseren van nieuwe ideeën. Niet in de laatste plaats is de uiteindelijk richting van het project bepaald door de vele discussies en besprekingen zowel binnen de vakgroep als daarbuiten. Bij de voltooiing van het proefschrift wil ik dan ook een ieder danken die een bijdrage heeft geleverd aan de totstandkoming ervan.

Een speciaal woord van dank gaat uit naar Dick Bargeman wiens begeleiding ertoe leidde dat vele kwalitatieve gedachten werden omgezet in meetbare grootheden. Tenslotte wist Kees Smolders telkens de krenten in de pap aan te wijzen zodat het vertrouwen is gegroeid dat de geïmmobiliseerde vloeistof membranen inderdaad hun weg naar toepassing in de praktijk zullen vinden.

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Chapter 1

Introduction

1.1. Membrane processes

"What is a membrane?" With this question and the complexity of the answer given by Lonsdale (1) it is illustrated how difficult it is to give a fairly rigorous definition of a membrane. But for the purpose of this thesis one of his older definitions satisfies: "A membrane is a thin, usually polymeric, film that exhibits permselectivity". Here permselectivity is " the property of a membrane characterized by exhibiting a much higher permeability to one species than to another or other species."

The most important membranes are situated in the human body. These biological membranes function as a very selective permeable boundary which allows water and certain nutrients to pass but forms a barrier for other substances. The biological membrane contains about 40 % of bipolar lipids, which are believed to be arranged in bilayers, and about 60 % of proteins, which have penetrated partially or completely into the lipid bilayer (2).

People started to imitate nature and attempted to execute separations with the use of membranes also. At first materials like fish-skins and pig's-bladders were used for the separations of all kinds of mixtures. Later on these bio-materials were replaced by synthetic materials, especially nitrocellulose (3). From these experiments membrane technology was born; a rather young science which passed through enormous developments during the last decades. A hugh diversity of membranes and membrane processes were developed for the separation of components from mixtures varying from drinking water or industrial products to waste streams. The most important advantages of these processes as compared to other separation techniques can be that better separations are possible with the use of less energy and under gentle conditions.

Some of the most well-known processes in this area are:

- micro filtration, ultra filtration and reverse osmosis; for these membrane filtration processes a hydrostatic pressure difference is the driving force for the separation, which is based on a sieving effect or on affinity differences. The diameter of the pores in the membrane is tuned to the dimensions of the particles to be separated and varies from ± 1.000 nm for microfiltration (e.g. removal of bacteria from water streams) to ± 10 nm for ultrafilltration (e.g. the recovery of proteins from milk) to some tenths of a nanometer for reverse osmosis (like the desalination of sea-water).
- dialysis; in this process diffusive transport of small molecules takes place through a porous membrane as a consequence of a concentration gradient. A well-known example is hemodialysis (artificial kidney).
- electro dialysis; this is the only membrane separation process in which an electrical field is used as a driving force. Electrically charged species are removed selectively from a solution by using an ion exchange membrane (e.g. for the recovery of valuable components from a waste stream).
- gas separation; a gas mixture can be separated by a hydrostatic pressure difference or a concentration gradient through homogeneous membranes. An application of this process is e.g. the removal of acid components out of natural gas.
- pervaporation; this membrane separation process can be used to separate liquid mixtures (e.g. ethanol-water). After diffusion of components through the homogeneous membrane, as a consequence of a concentration gradient, the permeate is collected as a vapour, which usually is condensed afterwards to obtain a permeate in liquid form.

A totally different type of membrane process, which is at such an early stage of development that it is not even mentioned in many surveys in the field of membranes, is a separation-technique making use of liquid membranes. In contrast to the processes mentioned above, in which the membrane material is usually a polymer, the membrane phase here consists of a liquid. So "a liquid membrane consists of a thin liquid film which generally separates two miscible liquids or gases and which controls the mass transfer between these two phases" (4). The mass transfer can be governed by passive, diffusive transport phenomena, but it can also be facilitated by adding to the liquid membrane phase a special component exerting a "carrier" function.

Despite the fact that this process of separation using a liquid membrane is hardly in operation, there is an enormous quantity of literature published on this subject during the past decade. This large interest is most likely connected on the fascinating properties and the highly promising perspectives which are ascribed to these high-performance membranes.

By adding a carrier to the membrane phase, i.e. a complexing agent which acts as a shuttle to carry specific ions through the membrane, one is able to obtain an excellent membrane selectivity with a high permeability. This is the dream of every membrane technologist because these properties of flux and selectivity are usually inversely coupled to each other in other membrane separation processes.

The separation mechanism of facilitated transport approaches the working principle of biological membranes as is illustrated in figure 1.1 In this system carriers in the liquid membrane act as selective transport media for components between the two phases. When more than one component is being transferred simultaneously (either in co-current or counter-current mode) one uses the term coupled transport.

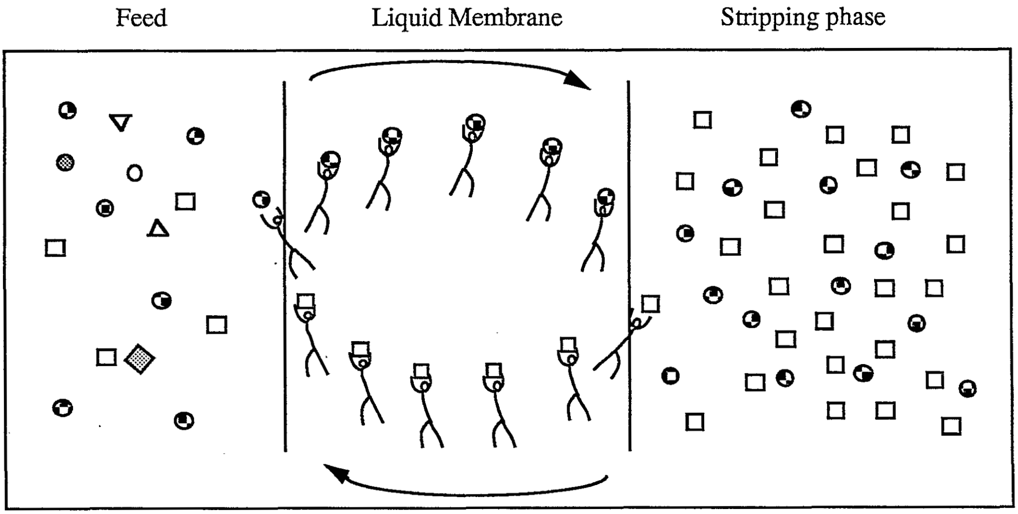


Figure 1.1. Facilitated transport by means of selective carriers

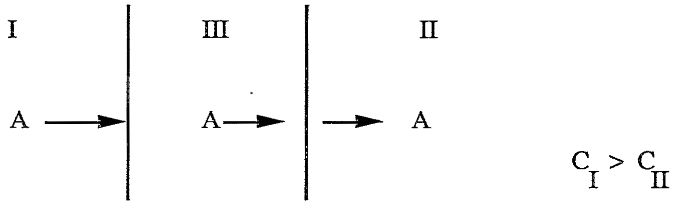
1.2. Liquid membranes

A description of the historical development of coupled transport is given in ref. 5. This process originated in early experiments of biologists using natural carriers contained in cell walls. As early as 1890, Pfeffer postulated selective transport properties in membranes using carriers (6). Perhaps the first coupled transport experiment was performed by Osterhout, who studied the transport of ammonia across algae cell walls (7). By the 1950s the carrier concept was well developed, and workers began to develop synthetic biomembrane analogues of the natural systems. For example, in the mid-1960s, Sollner and Shean (8) studied a number of coupled transport systems using inverted U-tubes. The technique of emulsion type liquid membranes was exposed and developed by Li and his coworkers at Exxon (9, 10) and the first patent was awarded in 1968. The first patent on supported liquid membranes was awarded to Miyauchi (11) in 1977 and this technique was further developed by among others Baker et al. (12).

1.2.1. Transport mechanisms

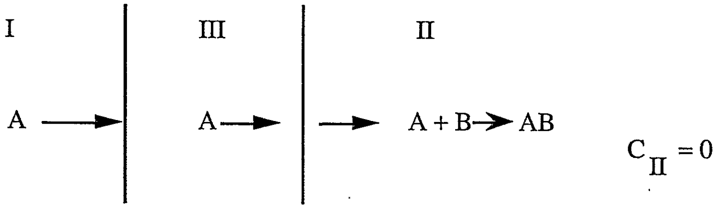
Transport of component A from phase I to phase II through a liquid membrane (phase III) can take place in several ways. Schematically the following transport mechanisms can be distinguished from literature data:

a; simple permeation of a species A



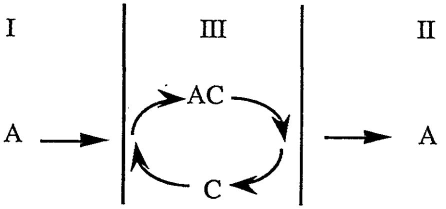
Species A permeates from the high concentration side (phase I) through the liquid membrane to the second phase. In case of multicomponent systems the products of the diffusion coefficient and the solubility of the various permeants in the membrane phase determine the selectivity of the mass transfer process, whereas the mass transfer rates are determined by the diffusion coefficients of the permeants in the membrane, the concentration differences of the various components and the membrane thickness.

b; simple permeation of A aided by chemical reaction of the permeant in phase II



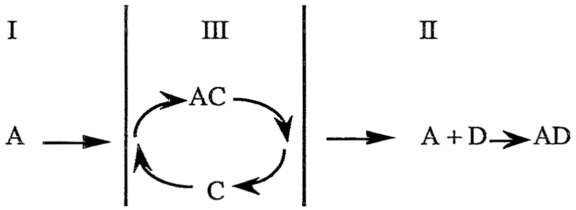
The effectivity of the transport is enhanced, when the concentration of the permeating species in phase II stays low by a chemical reaction. A well-known example of this mechanism is the phenol extraction process from waste water by aqueous caustic soda solutions using the liquid membrane process (13)

c; simple carrier facilitated transport



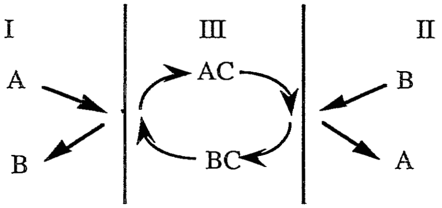
The selectivity and transport rate of a liquid membrane can be increased in comparison with the case of simple permeation if a specific carrier is active in the membrane phase. The permeant forms a complex with the carrier C at the high concentration boundary. Following the concentration gradient of the complex AC, this complex diffuses through the membrane to the membrane-phase II boundary, where the complex breaks up.The free carrier diffuses back to the opposite phase boundary as a result of its concentration gradient. The increase in mass transfer rate results from a higher solubility of the permeant in the membrane phase through complex formation with the carrier C. This increases the concentration gradient across the membrane compared to simple permeation. Also the selectivity of the mass transfer process increases since the complex formation reaction of the permeant is a very specific one. An example of this type of process is the transport of O_2 with hemoglobin as the carrier (14).

d; carrier facilitated transport including a chemical reaction in phase II



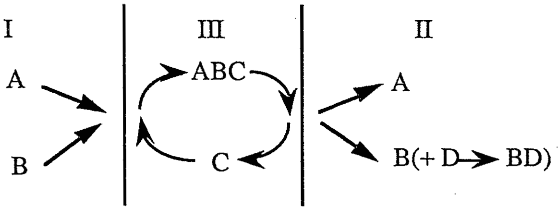
The effectiveness of the system is enhanced since the concentration of the permeant in phase II is small through the chemical reaction with species D; the concentration gradient of the permeating species across the membrane phase is as high as possible.

e; Counter transport



In this case the transport of the selected ion A is coupled with a transport process of an ion B with the same total charge in the opposite direction. When the driving force for the counter-transport is high enough it is even possible to transfer the desired component against its concentration gradient. Numerous examples of this type of mechanism have been published in literature in which metal ions are removed from water by a countertransport of protons. The experiments described in this thesis also deal with this transport mechanism. Nitrate ions are completely removed from a waterphase by a countertransport of chloride ions using a quaternary ammonium salt as carrier in the liquid membrane phase.

f; co-transport



The component to be collected A is transported together with a second component B by the carrier through the membrane. Even when the concentration of A in phase II is large compared with the concentration of A in phase I it can be transported against its concentration gradient provided that the concentration difference of component B is large. It is possible to remove component A quantitatively from phase I when component B reacts chemically in phase II, yielding an effective concentration of zero for B. An example of this type of transport mechanism is the removal of nitrate ions from water with protons as co-ions and with the use of a basic carrier in the liquid membrane (15). Nitrate ions can be concentrated in this process because of the high pH in phase II.

g; active transport

This type of transport gives also the possibility of "up hill" diffusion, but contrary to coupled transport the energy source is now a chemical reaction. An example of this type of transport is the photo induced carrier mediated transport of alkali metal salts (16).

The distinct steps in which the permeation process of a permeant in a liquid membrane can be subdivided will be discussed in Chapter 2.

1.2.2. Types of LMs

Usually two types of LMs are distinguished (4):

1. The emulsion type of liquid membrane (ELM); this type is also called "liquid surfactant membrane" and was first described by Li (17). These membranes are formed by making an emulsion of two immiscible phases. The continuous phase of the emulsion forms the liquid membrane and the dispersed droplets in the emulsion form the so-called "inner phase". The emulsion can be either oil-in- water or water-in-oil. The liquid membrane phase normally contains surfactants and additives, which are used to control the stability, the permeability and selectivity of the membrane. The emulsion is then dispersed in the form of droplets in a third phase (the continuous outer phase), which is normally miscible with the inner phase. Figure 1.2 gives a schematic representation of this type of liquid membrane.

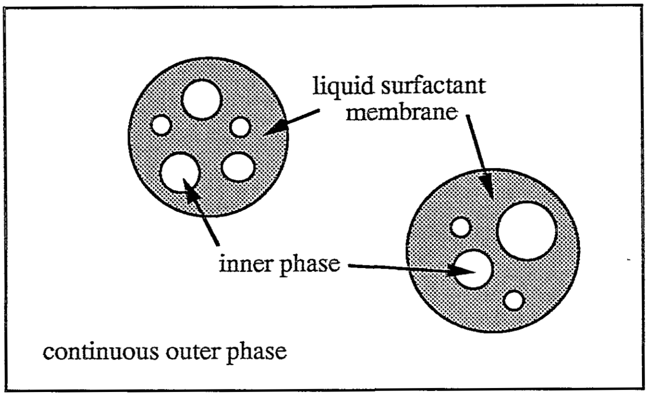


Figure 1.2. Emulsion liquid membrane (ELM)

After the transport of components through the membrane from the continuous outer phase to the inner phase, the liquid membrane phase and the continuous outer phase have to be separated. This is often actualized by the density differences in a settler unit. The recovered emulsion phase must be broken in a coalescing unit and the dispersed inner phase recuperated or discarded. The liquid membrane phase, being the most valuable component, is recycled to the emulsifier, where fresh inner phase is introduced.

2. The supported liquid membrane (SLM). These membranes (also called "immobilized liquid membranes") are obtained by impregnating a microporous solid support with the liquid containing the carrier molecules. The liquid is immobilized in the support by the capillary sorption forces of the pores. In contrast to the previous type of LM, the transport of components between the two bulk phases separated by the membrane (feed and stripping phase) is a continuous process with a stationary membrane phase. In figure 1.3 a schematic representation of this type of liquid membrane is given.

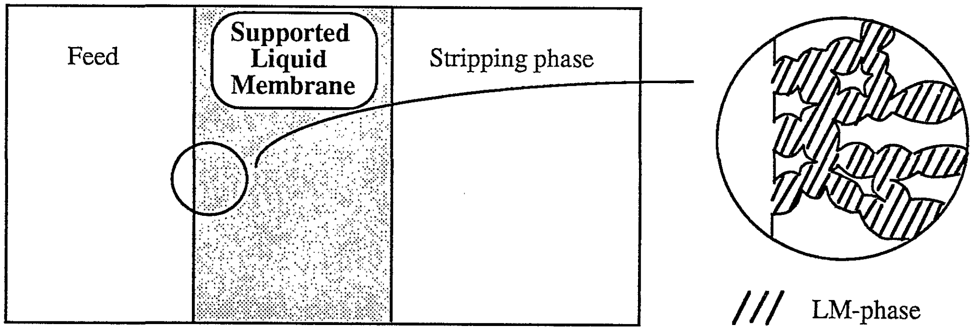


Figure 1.3. Supported Liquid Membrane (SLM)

Apart from the removal of components from a liquid solution this type of LM can also be used for the separation of gas mixtures (18, 19, 20). Different configurations of the SLM-process are:

- flat membranes; this rather simple technique, is especially used in laboratory experiments;
- hollow fibers; for this configuration the membrane liquid is immobilized in the microporous wall of the fiber and the feed and stripping phases stream at the "shell-side" and through the bore of the fibers. The big advantage of this mode is that large surfaces can be obtained per unit of volume($\pm$ 1.000 m^2/ m^3 (21)).
- spiral-type supported liquid membranes; in this type of LM-process, which is especially developed by Teramoto et al. (22), the support films are spirally wound around the tubes through which either feed or strip solutions are supplied.

All experiments described in this thesis are performed on SLM-systems in which flat membranes where used.

An alternative form of the supported type liquid membrane is the so called solvent polymeric membrane, which consists of a polymer film containing a plasticizer solution (23, 24, 25). Because of the high viscosity of the liquid phase here, the diffusion of permeant ions is depressed as compared to the other types of LMs. This type of membrane process will be discussed in more detail in chapter 5.

A modified design for the types of liquid membrane process mentioned is the so called liquid film pertractor (LFP), developed by Boyadzhiev et al (26, 27). Besides the feed and the stripping phases in this process the liquid membrane phase is also in motion, which decreases the diffusional resistances of the LM. The aqueous feed and stripping phases stream downwards along porous hydrofilic supports, while the organic membrane, filling the gaps between them, flows in counter-current direction.

Apart from this there are a number of separation systems closely related to liquid membrane processes. One example is the process in which the extraction liquid streams through the lumina of hollow fibers which are placed in two modules connected with each other (28). The feed streams around the fibers in the first unit and the components which have to be removed are sorbed. In the second unit, in which the stripping phase streams around the fibers, these components are desorbed. The advantage of such a process is that the instability problems of SLMs are avoided. The disadvantages of this method are given in paragraph 1.3.2. The process is plotted schematically in figure 1.4.

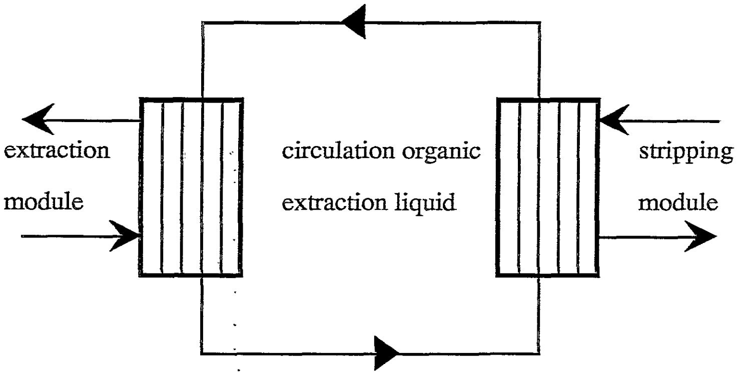


Figure 1.4. Extraction and stripping process using hollow fibers in two modules

A modification of this method is the one in which the sorption and the desorption unit are placed in one module (29). The feed and the stripping phases are streaming through the lumen of different fibers which are surrounded by extraction liquid. An advantage, as compared to the method with separated extraction and stripping modules, is that in this case less extraction liquid is needed for the separation.

An alternative to the method where two modules are used is developed by Enka (30). In their process the extraction liquid streams again through the lumen of the fiber in the absorber unit with the feed flowing at the shell side of the fibers. In the stripping unit, however, the organic phase is mixed with the stripping phase by stirring. The mass transfer is increased by this action and so less membrane surface would be needed as compared to the method with two modules.

These last mentioned systems (in which the membrane has the function to avoid mixing of the phases) are no real LM-processes. In the literature they are usually entitled with a special name like"membrane extraction" or "pertraction" (31).

1.3. Supported liquid membranes

1.3.1. Properties

The properties of SLMs can be best illustrated by comparing this separation method with other related separation methods like solid polymeric membrane-separations, solvent extraction and emulsion type liquid membranes.

Comparison with polymeric membranes
It is obvious to compare SLMs with polymeric membranes because of their similarities in configuration and because of the fact that their potential fields of application overlap each other to a large extent. Advantages of SLMs as compared to polymeric membranes are (32):

- high selectivities can be obtained by adding a selective complexing agent to LM-phase;
- fluxes are higher because diffusion through a liquid is much faster than through a solid material;
- ions can be pumped "up hill" by a coupled transport mechanism.

In contrast to these advantages, especially the **instability** of the SLMs is a disadvantage (see 1.3.2).

Comparison with solvent extraction

Advantages of LM-processes, in fact one-step extraction processes, as compared to conventional solvent extraction (SX) processes mentioned in literature are:

- The volumetric extraction rate of LM processes is considerably higher than for SX (33); this leads to:
  - more compact installations with lower investment costs
  - a large reduction in the amount of solvent uses; compared with traditional solvent extraction techniques up to 90% of the costs of the solvent phase can be saved (34). This results in lower running costs for an LM-process (36), especially when expensive carriers are used.

- Especially very diluted solutions can be concentrated in LM processes, in contrast to SX (28).

- Solvents with high distribution coefficients are needed for SX because this is an equilibrium process. Since in a dynamic LM-process the concentration of the permeating component can be kept low at the stripping side, solvents with considerably lower distribution coefficients can be used in a LM-process. This often diminishes the problem of the solubility of water in the organic phase (a problem that occurs especially in extraction of phenol from water, using higher alkanes; (35)). So concentrations of carrier can be much lower for LM than for SX and less carrier is lost (4).

LM-processes are promising especially in case of low feed concentrations; in particular when using expensive extractants or separating valuable components (37). Experiments showed that the separation of phenol or copper from water is more efficiently done with LM than with SX, over a broad range of operating conditions (38).

Comparison with emulsion type liquid membranes

The following aspects are mentioned in literature when comparing the two types of LM-processes:

- In the case of ELMs emulsions must be formed and later coalesced, while SLMs do not need this. This results in the following advantages for the SLM-system:
  - the use of expensive emulsifiers is not necessary which is also favourable from the ecological point of view (35)
  - SLM is a continuous one step operation while the preparation and destruction of emulsions for ELM-processes are discontinuous and energy consuming (35).
  - an SLM-separation installation, without apparatus for the preparation and destruction of emulsions, is smaller and contains no mechanically moving parts (33).
  - the direct contacting method of ELM asks for special properties of the solvents like surface tension, density, viscosity and they must be able to give good emulsions and phase separation; furthermore the feed must be free of components which can cause phase separation. SLM doesn't show these limitations for the solvent (28), but does have other restrictions due to the instability problem.

- SLM-installations can easily up-scaled by:
  - stacking more fibers per unit;
  - connecting units parallel to each other (33).

- For SLMs only an extremely small quantity of liquid membrane solution is required to fill the pores of the supporting membrane; therefore the use of expensive carriers is possible (39).

- A larger surface area per volume can be obtained by using hollow fibers than by using dispersions; furthermore the optimal magnitude of the dispersion droplets is often limited by coalescence of the droplets (33).

- The mass transfer through ELM is larger than through SLM due to convective flow caused by the motion of the droplets in the emulsion (38).

Important notes for the SLM-process are:

- especially the **instability** of SLMs is an important shortcoming or uncertain factor of this process; in the next paragraph more attention will be paid to this problem.

- the energy consumption can be considerable when a large pressure drop is present over the lumen of the fiber especially when using long fibers and high flow velocities (33).

A further comparison of SLMs with other separation processes will be given in Chapter 2 specified for the problem of the removal of nitrate from water.

Economics

Little is known about the costs of SLM-processes because of the lack of practical experience with SLM-installations. The largest problem is that parameters such as membrane selectivity, stability and life time have not yet been well defined. However the economics were estimated by Bend Research for coupled transport of chromium and for the recovery of uranium from a feed stream. The results of this speculative analysis show that the value of the metal recovered exceeds by far the projected operating costs, indicating "extremely favourable and encouraging process economics" (40, 41).

The real costs of the ELM-process also are not known completely. However calculations show that this process is also quite attractive compared to most industrial waste water cleaning processes (42). This conclusion is supported by the experimental results which were obtained by Marr et al (43,44) from pilot plant and large scale plant experiments.

1.3.2. Instability problems

Despite the very promising perspectives the supported liquid membrane is used only on a very limited practical scale. This originates from the instability of these membranes (5, 32, 45 - 47), which is brought about by the removal of the membrane liquid from the pores of the support. The consequences of this removal are that the permeability of the membrane reduces (by removal of the carrier from the membrane) or that the liquid membrane function disappears. A direct connecting channel in the membrane between the feed and the stripping phase is formed in this last case, by which non-selective transport can take place. It influences the separation process negatively and the waterphases which flow along the membrane are polluted with components from the membrane liquid. In the next part of this thesis we will treat this problem extensively.

Several methods have been developed to get around the instability problems of SLMs. Using ingeneous methods the liquid, which is removed from the pores, is filled up again.

An example of this is described by Danesi et al (48). They supplied new membrane liquid via a liquid reservoir at the top of the vertically placed hollow fibers. An alternative to this method is patented by Klein et al (49), in which in a similar way membrane liquid is added to the fibers and in which reservoirs are present at the bottom of the fiber bundles to withdraw or to collect the liquid. By recirculating this liquid with pumps a continuous process of liquid replenishment is developed. Another method is described by Nakano et al (50). They use the buoyant force of the membrane solvent in the continuous pores of the support. Via a liquid reservoir, placed at the bottom of the vertical fibers, the membrane liquid is regenerated continuously.

All these methods, and also using the "membrane extraction" processes, have the advantage that the instability effects of the liquid membrane processes are avoided but remaining disadvantages are:

- the phases which flow along the liquid membrane interface are still polluted with components from the membrane liquid;
- the liquid which is removed from the membrane has to be filled up again;
- for this type of operation more complex constructions, apparatuses and procedures are required.

The research described in this thesis is focussed at the study of the causes of SLM instability with the aim of preventing this instability factor rather than to cure it and to develop a stable and simple liquid membrane process.

1.4. Structure of this thesis

An important conclusion from the survey described above is that the applicability of supported liquid membranes as a new separation technique is retarded by the insufficient stability of the system. Therefore a project was formulated which fitted in the Innovation Oriented Program on Membranes (IOP-m). This program is funding membrane research at universities and research institutes in the Netherlands. The main objective of the project under study was the understanding and improvement of SLM stability.

In **Chapter 2** a description is given of the SLM-process which is developed for the exchange of nitrate ions with chloride ions in a counter transport process. The influence of process variables and compositions of the various phases on the overall permeability are investigated. The results are explained using models known from literature.

Chapter 3 deals with the instability of SLMs. A number of parameters influencing transport and membrane stability are measured. It is found that the stability of the membrane largely depends on the compositions of the different phases. It seems to be impossible to give a consistent description of the membrane instability with existing theories from literature.

Based on the results of the previous chapter a hypothesis is formulated to describe membrane instability. **Chapter 4** gives the verification of the hypothesis. From the results it could be shown that the instability of liquid membranes originates from emulsion formation induced by shear forces. These are predominantly effective at the feed side of the membrane.

Guide-lines for the development of stable SLMs could be given based on previous results. One of the conclusions was that gelation of the LM-phase in the pores of the support could reduce the instability effects. The influence of this gel network on the permeability and stability of SLMs is described in **Chapter 5**. Generally these new types of (pseudo) liquid membranes were prepared by adding a small amount of polymer to the LM-phase. Two different types of gelled liquid membranes were developed. In the first type a homogeneous gel network was present through the entire LM-phase. In the second type a thin gel layer was applied at one of the two surfaces of the membrane. The results show that the stability of the SLMs is significantly enhanced by both types of gelation methods.

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Jan van Goyen; Rivierlandschap met veerpont (1627)

Zoals een veerpont heen en weer pendelt tussen de twee oevers van een rivier om een bepaalde vracht te transporteren, zo pendelen "carrier moleculen" tussen de twee grensvlakken van een vloeibaar membraan om ionen te transporteren.

Chapter 2

Nitrate removal using supported liquid membranes transport mechanism

2.1. Summary

A new method is developed for the removal of nitrate ions from water. Nitrate ions can be removed from water almost completely, with a mobile carrier, by counter-transport of chloride ions through a supported liquid membrane. The transport characteristics of this process, in which the water phases are flowing parallel to flat membranes, are described. The results show that depending on the experimental conditions the flux is determined by the diffusion of the carrier through the membrane or by the diffusion of the nitrate ions through a laminar water layer at the feed side. The selectivity of the membrane, which depends on the type of the organic solvent, determines the influence of the chloride concentration in the stripping phase on the membrane flux. Furthermore the effect of carrier structure and concentration is investigated.

2.2. Introduction

Supported liquid membranes (SLMs) have been introduced as a promising new separation technique for the selective removal of ions from an aqueous solution. Especially for low concentrations of ions in water (below some hundreds of ppm (1)) it is useful to employ SLMs because high enrichment factors can be obtained. The quantity of nitrate ions in ground water is in that range, which is becoming a problem for preparing drinking water.

Almost every research work on SLMs is done on systems in which metal ions are being recovered, obviously for economical reasons. Besides hundreds of cation separation systems published in literature only a few examples are known for the separation of anions. Drioli et al (2) used a counter-transport of chloride ions to remove CrO_4^{2-}-anions from a water phase. Another example of a counter-transport process, between chloride- and hydroxide ions, is given by Cussler et al (3). In this latter article the transport mechanism was not entirely clear and some complexities in the chemistry of facilitated diffusion were observed. Anions can also be removed by a co-transport mechanism. In this way systems were developed for the concentration of picrate ions (4, 5), nitrate ions (6) and chloride ions (7). In these cases transport depends on the concentration of the co-ions (usually protons) in the feed solution.

In this paper the development of a SLM-process for the removal of nitrate ions with a counter-transport of chloride ions will be described. To approach the circumstances of a practical separation process, a membrane module has been used in which the water phases are not stirred but flow parallel to the flat membrane. The influence of process parameters, like water flow velocities, composition of the SLM phase and of the water phases, on the transport is studied. These data are not only of interest for insight in this new method, necessary to optimize it, but are also important in relation to the stability of the SLMs. Other experiments showed that these parameters, the hydrodynamics and the composition of the system, have a large influence on the life times of the membranes (chapter 3 and 4).

2.3. Nitrate removal from water

The contamination of groundwater with nitrates is becoming a serious problem for the preparation of drinking water both in Europe and in the United States. It has been said that "nitrate is the first world-wide environmental pollutant resulting from man's ingenious technology" (8). In the Netherlands the EC-norm of 50 ppm nitrate in ground water sources is more and more being exceeded. Especially on sandground concentrations of nitrate of 100 ppm in wells are no exceptions and even a tenfold of the norm has been registrated (9). One predicts that in the near future 25 % of the wells for drinking water in the Netherlands will have exceeded the EC-norm (10). The waterworks strive for delivering water with a nitrate content of less then 25 ppm (11).

The problem of high nitrate concentrations in drinking water is that the nitrate in the human body can be converted into nitrite, which binds itself to the hemoglobin. The oxygen transport through blood can be hindered in this way. In particular very young children (till ± 6 months) can show suffocation phenomena ("blue babies") caused by an intake of too much nitrate. Nitrates are also suspected of forming carcinogenic substances (nitroso compounds) in the body.

Solutions for the nitrate problem have to be found in the first place in the prevention or the reduction of nitrate release in the environment, by for instance agriculture and industrial activities. But also at short notice the waterworks have to take measures for the delivery of acceptable drinking water. In some cases a possible solution is found in diluting nitrate-rich water with water with a lower nitrate content. However, in a lot of other cases this is not an acceptable solution and special techniques have to be used to lower the nitrate concentration in the water. These measures have as a consequence that, the Dutch "Raad van Advies voor de Ruimtelijke Ordening" expects that the price of the drinking water will be doubled in the near future (12).

2.3.1. Nitrate separation methods

Especially in the last few years new processes for the removal of nitrate from water have been developed or adjusted. A selection of these methods mentioned in literature is:

- Fixed-bed anion-exchange;
- Electrodialysis (ED);
- Reverse osmosis (RO);
- Bacteriological treatments;
- Solvent extraction (SX).

Fixed-bed anion-exchange; in this process the ion-exchange membrane is first brought in contact with the feed solution and subsequently, in a different stripping step, the adsorbed nitrate is usually exchanged against chloride. In California a pilot plant is in operation in which 4 million litre of contaminated water per day is being treated (13). However together with a decrease of the nitrate concentration from 72 ppm to 12 ppm also bicarbonate and sulfate ions are being removed from the feed. With this extra removal the consumption of chloride increases and therefore the chloride concentration in the treated feed rises to an unacceptable high value.

Electrodialysis; with this method the transport velocity of anions through a membrane is accelerated by applying an electric potential difference over the membrane. A disadvantage of this technique is that it is not selective for specific ions. Therefore research is started to develop selective electrodialysis membranes (14). The results of the investigation are not very promising until now.

Reverse osmosis; This technique removes ions from a feed solution by pressing the water phase with a high pressure difference through (the pores of) a hyperfiltration membrane while the ions are being rejected from passing through the membrane. Disadvantages of this method are the high energy costs, the non selectivity of the separation process and the relatively small concentration factor which can be obtained. Because of environmental constraints Rautenbach c.s. (15) developed a hybrid process in which the brine is afterwards concentrated to a higher level with electrodialysis and then the last residual water is evaporated.

Bacteriological treatments: Van der Hoek and Klapwijk at the Agricultural University in the Netherlands developed a method in which nitrate ions are converted via nitrite into nitrogen gas by denitrificating bacteria (16, 17). For this purpose the solution of nitrate ion first should be concentrated. This is done by a process of anion-exchange against bicarbonate ions with the use of a fixed bed ion-exchanger. Bicarbonate is used because this compound is being formed during the nitrate conversion. An advantage of this method is that the nitrate is converted and therefore no residual brine is formed. A problem is that sulfate ions accumulate in the stripping phase of the ion-exchange process and for this reason the regenerating solution has to be exchanged after a number of cycles.

Other methods of biological treatments have the disadvantage that an after treatment is necessary due to the direct contact between the groundwater and the bacteria.

Solvent extraction; In this method nitrate ions are extracted from water making use of a secundary amine in kerosene (18). In the stripping phase the nitrate-amine complex decomplexes due to a high KCl- concentration. By decreasing the temperature of this phase from 25 ^{O}C to 19 ^{O}C potassium nitrate crystals separate out.

2.3.2. SLM-separation

The use of SLMs can be advantageous as compared to the five methods mentioned above. Two possible methods, by which ions can be removed via a coupled transport mechanism, are:

- co-transport; Kreevoy c.s. developed a method in which nitrate ions are removed from a water phase together with protons by a complexation with a very strong alkaline lipophilic carrier in a supported liquid membrane (6). In this process the transport is regulated by the pH and the nitrate concentrations in the water phases. Due to the removal of protons from the feed the pH in the feed increases and the driving force for nitrate complexation is diminished.

- counter-transport: by applying a counter-transport mechanism the problem of the dependence of the transport on the pH can be overcome. Therefore a process was developed in this work, making use of a continuous anion-exchange between nitrate and chloride ions through an SLM. In figure 2.1 a schematic representation of this process is given.

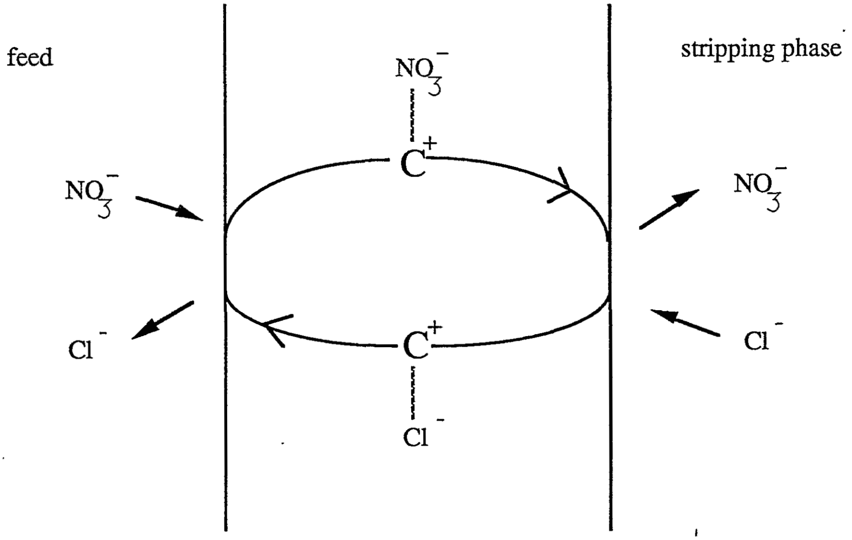

Figure 2.1. *Counter-transport mechanism; continuous anion-exchange between nitrate and chloride ions*

The nitrate ions are selectively removed from the feed by complexation with the carrier in the membrane. Because of the high concentration of carrier in nitrate form at the feed side this complex diffuses through the membrane to the stripping phase. Here the the nitrate ions are exchanged by chloride ions when a high chloride concentration is present in the stripping phase. The carrier in chloride form diffuses back to the feed side, where the process is repeated.

Advantages of such a process as compared to the use of a co-transport of protons is that the driving force for the "up-hill" concentration is provided by the high chloride concentration in the stripping phase and it therefore is independent of other than nitrate ions in the feed.

In general the advantages of SLMs were already given in chapter 1. Especially for the removal of nitrate ions from water the advantages of SLMs are here compared to competitive methods:

1 Continuity; compared to methods like fixed bed ionexchange and SX no separate complexation and stripping steps are needed. This lowers investment costs and running expenses.

2 No carry-over effects; undesirable carry-over effects of compounds from the treating solution to the feed can take place during SX, fixed bed ion-exchange and the combination of this last technique with bacteriological denitrification. Because in the case of SLMs the feed and the stripping solution are separated by a hydrofobic membrane, no components of the stripping phase can get into the feed unless transported through the membrane. Comparing to SX (where stable emulsion formation can occur) there also will be a diminished loss of organic phase. This saves expensive extractants and avoids the need of after treatment.

3 Higher selectivity; compared to ED and RO it is above all advantageous to remove only the undesired component from the feed. Compared to fixed bed ion-exchange the problem of sulfate exchange into the stripping phase can be avoided by making a proper (selective) choice of the LM-phase. This saves the consumption of counterions which also gives a smaller increase in the concentration of counterions in the feed and (in combination with bacteriological denitrification) the stripping solution has to be regenerated less often.

4 The energy consumption is small, especially compared to RO and ED.

5 More concentrated brines can be obtained as compared to fixed bed ion-exchange, RO, ED and SX.

In general it can be stated that the use of SLMs is a very efficient technique for the concentration of ions. However the problem of the treatment of the concentrated brine also plays a significant role for this method. By making use of a combination with another technique, in which the stripping phase is treated with e.g. bacteriological denitrification (like in ref. 16, 17), electrodialysis (similar to the process described in ref. 15) or crystallisation (like in ref. 18), this problem can be solved.

2.3.3. Selectivity of the carrier

The choice of a suitable carrier for the concentration of nitrate ions from ground water using the SLM technique depends on a number of criteria to be set for the properties of the carrier:

- the carrier is highly selective for nitrate ions;
- it forms reversible complexes with the nitrate ions and the counter-transport ions;
- it has a good solubility in the membrane phase;
- it is insoluble in water;
- it has a high diffusion mobility in the membrane phase.

These conditions are comparable to the demands that are made to the active component in nitrate ion selective electrodes. A lot of examples of this type of components are known in literature. The compounds most frequently used are lipophilic quaternary ammonium salts; also phosphonium- and nickelcompounds are sometimes used for this purpose. In general for all these compounds the selectivity sequence is given by the Hofmeister series. This series is determined by the free hydration energy, which depends on the dimensions and the valency of the anions. This selectivity sequence, in decreasing order, is:

$MnO_4^- > ClO_4^- > I^- > \boldsymbol{NO_3^-} > Br^- > NO_2^- > \boldsymbol{Cl^-} > HCO_3^- > F^- > CO_3^{2-} > SO_4^{2-} >$
$HPO_4^- > PO_4^{3-}$.

The nature of the lipophilic carrier and of the organic solvent does not change the sequence of the Hofmeister series, but can largely influence the absolute selectivity towards the various anions. This will be shown in section 2.6.2.

For the selection of a suitable counter-ion in the SLM process the chloride ion is a proper choice. According to the Hofmeister series the difference in selectivity with the nitrate ion is sufficiently large but not too large to enable the process of complexation - decomplexation. Furthermore the relatively small increase in chloride concentration in the feed, as a consequence of the equimolar ion-exchange with nitrate ions, is not a problem in drinking water and sodium chloride is a very cheap chemical compound.

2.4. Transport model

A number of separate steps can be distinguished when a (specific) ionic species is transported from the feed to the stripping phase. These steps consist of:

1 Diffusion of the ion from the bulk of the feed to the membrane surface;
2 Complexation at the surface with a carrier molecule;
3 Diffusion of the carrier bounded ion through the LM-phase;
4 Decomplexation at the surface with the stripping phase;
5 Diffusion of the permeate ion to the bulk of the stripping phase.

In figure 2.2 an ideal concentration profile, with linear concentration gradients, for the permeating ion (in our case NO_3^-), is given. In this figure $[NO_3^-]_F$ and $[NO_3^-]_S$ are the bulk concentrations of nitrate ions in the feed and stripping phase respectively; the index "i" denotes the concentrations in the water phases at the membrane interface. The concentration of ions bound to the carrier in the membrane is indicated by a bar. Because of the low dielectrical constant of the organic phase the concentrations of free ions are negligibly small. In case of a counter-transport mechanism a similar profile can be given for the second ion.

The thicknesses of the laminar boundary layers are given by ∂_F and ∂_S. These values are a function of the flow conditions of the water phases parallel to the membrane. In general in literature one assumes that the chemical reactions taking place at the interfaces are very fast as compared to the diffusion steps and that these reactions do not influence the overall flux.

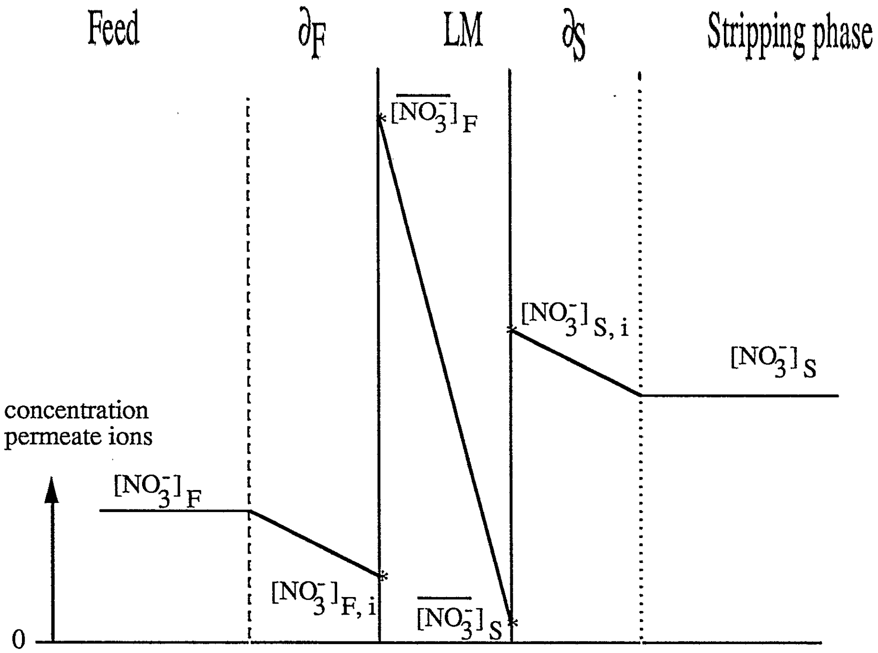

Figure 2.2. Schematic concentration profile for transport of permeating ions through a SLM

The concentration of ions at each boundary, in the membrane and in the water phases, is determined by the following equilibrium reaction:

$$\overline{Cl^-} + NO_3^- \rightleftarrows Cl^- + \overline{NO_3^-} \qquad (2.1.)$$

For this anion-exchange system an extraction constant K_{ex} (valid at each of the two boundaries) can be defined as:

$$K_{ex} = \frac{[Cl^-] \cdot \overline{[NO_3^-]}}{\overline{[Cl^-]} \cdot [NO_3^-]} = \frac{k_{NO_3^-}}{k_{Cl^-}} \qquad (2.2)$$

in which $k_{NO_3^-}$ and k_{Cl^-} are the distribution coefficients for nitrate and chloride ions

between the membrane and water phases.
At stationary transport through the membrane the different diffusive fluxes are equal to each other and equal to the overall flux J. The complex transport model is getting considerably more simple when transport is limited by diffusion through only one phase (either the membrane phase or one of the boundary layers). During the permeation experiments to be described the influence of different parameters on the overall flux will be determined.

2.5. Experimental

2.5.1. Materials

- the carrier; Symmetrical quaternary ammonium salts (with a length of the alkyl chain varying from 8 to 18 C - atoms) were used as carriers. All carriers were delivered in bromide form, by Fluka, and used without further purification.

- the solvent; Ortho-nitrophenyloctylether (o-NPOE; Fluka) and decanol ("gold marke"; Aldrich) have been used as membrane solvents. Both solvents were used without further purification.

- the support; flat sheets Accurel®, microporous polypropylene membranes, (obtained from Enka) have been used as supports. The thicknesses of the supports has been measured with a Mitutoyo digital thickness meter and the porosities by determining the weight of the absorbed LM-phase with a known density. The average thickness of these membranes was 92.5 µm and the porosity 69 %. The average pore size of the supports was 0.1 µm (Enka specification). This is the size of the open connections between much larger cellular voids in the membrane.

The solubility of the carriers in the membrane solvent has been determined by preparing a solution of the ammonium salts in the solvent at elevated temperatures and studying the homogenity of the solution after cooling to 25 °C. When the solution was clear the amount of ammonium salt was increased till saturation was obtained.

Membranes were prepared as follows: LM-solutions were prepared by dissolving the carrier in the solvent. By soaking the support in these solutions for at least 15 minutes the LM-phase is absorbed in the pores. Before using the membrane the attached liquid is removed from the surfaces with a tissue.

The feed and stripping phases were prepared by solving respectively sodium nitrate and sodium chloride in ultrafiltered demi water.

2.5.2. Extraction experiments

The distribution of nitrate and chloride ions over the LM-phase and the water phases were determined by extraction experiments. In contrast with the usual extraction methods described in literature the LM-phase was immobilized in the pores of a support before it was brought in contact with the water phase.

The carriers in the membrane liquid were brought in nitrate form by immersing the SLMs overnight in 40 ml of 1 M $NaNO_3$-solution (the volume of the LM-phase in the support was 0.3 ml). After rinsing the membranes with distilled water they were then immersed overnight in 30 ml aqueous solutions with different NaCl concentrations, varying from 0.00 M till 1.00 M. The nitrate and chloride concentrations in the water phase was analysed by High Performance Liquid Chromatography (HPLC; anion colum). The distribution coefficients of the ions over membrane / aqueous phase then was calculated from the ion concentrations in the aqueous phase.

2.5.3. Permeability measurements

The experimental set up is illustrated in figure 2.3. The membrane module and the buffer vessels are made of glass and connected with silicone rubber tubes. The microporous membrane with imbibed LM-phase is placed in the module and then the system is filled with the aqueous phases. The total volume of each of the aqueous phases, including that of tubes, pumps, flow meters, buffer vessels and cel-halves, is 130 ml. The aqueous phases are flowing parallel to the membranes, in a tangential flow, with the help of centrifugal pumps (Ikawi MD-67) at room temperature. The water flow velocities are adjusted by flowmeters (Porter). With a volume of the cell half of ± 40 ml and a flow velocity of the aqueous phases of 5 ml/s the average residence time in the cell half is 8 seconds. The buffer vessels are neccesary to remove air bubbles from the water phases. In experiments with different flow velocities of feed and stripping phases, small pressure differences over the membrane are avoided by adjusting the height of the buffer vessels.

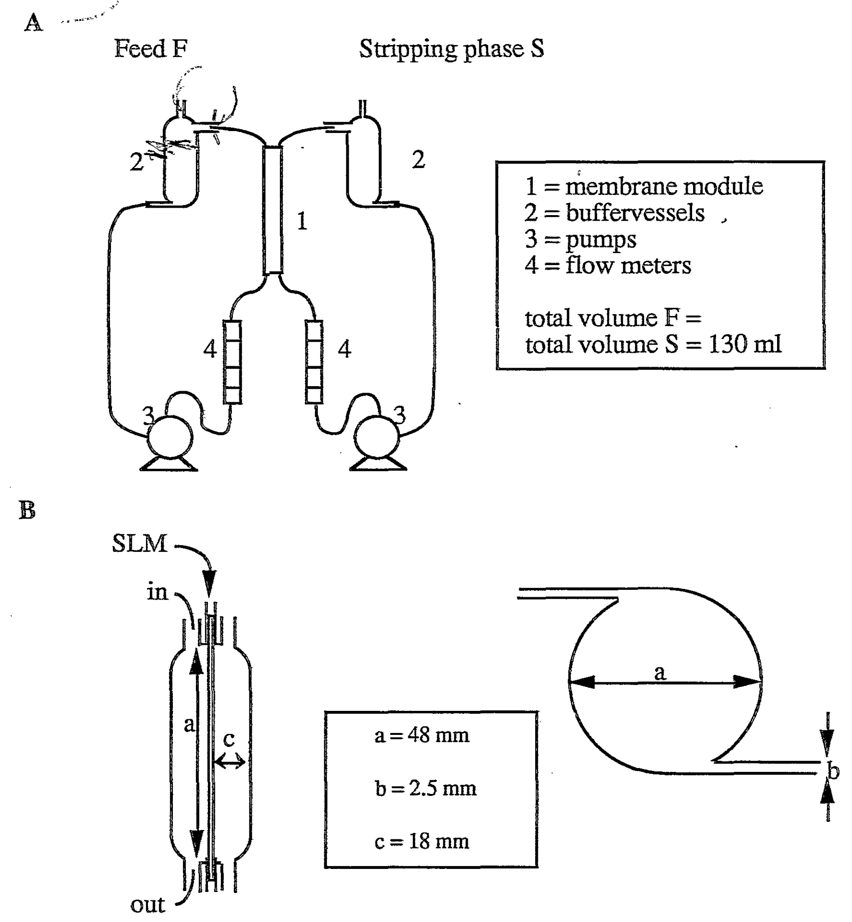

Figure 2.3. A Experimental set up for the permeability measurements; B Dimensions of the membrane module

The flowing pattern of the aqueous phases parallel to the membrane surface is badly defined because of the shape of the membrane module. This means that the mass transfer of components from the bulk of the water phases to the membrane interface can not be calculated. The flowing pattern of water phases which are pumped parallel to the surface of flat membranes, which are not supported by a screen, will always be influenced by little movements of the membranes.

Periodically samples were taken from the feed and analysed by HPLC. It should be noticed that in all experiments reported in this chapter a one to one exchange of nitrate by chloride ions in the feed was obtained.

The stability of the SLMs (with o-NPOE as solvent) has also been checked by comparing the weight of the membrane before and after the permeation experiment. It was found that in all cases less than 2 % of the LM-phases has been removed from the support during 7 hours under actual flow conditions of feed and stripping phases.

2.5.4. Viscosity

The kinematic viscosities of the LM-phases are determined with an Ubbelohde viscometer. The densities of the LM-phases needed for the calculation of the dynamic viscosity have been determined with a digital density meter (Paar DMA 50). All measurements were performed at 25 ^{o}C.

2.6. Results and discussion

Because of the literature data mentioned before, quaternary ammonium salts with long lipophilic chains have been chosen as carriers. Since the solubility in water of these compounds decreases when increasing the chain length of the alkyl group (19) the carriers used had at least 3 alkyl chains with 8 or more C-atoms. From stability experiments we found that quaternary ammonium salts with one short alkyl chain are very surface active and lead to rapid SLM-degradation (chapter 3 and 4). Therefore tetra-octylammonium (TeOA) compounds have been used as standard carriers. The permeation behaviour using symmetrical carriers with longer alkyl chains (C_{10}, C_{12} and C_{18}) has also been studied.

The most important demands that can be made to a LM-solvent are that a sufficient amount of the carrier dissolves in it and that the solubility in the aqueous phases is extremely low. O-NPOE has been used during the permeation measurements because, out of the solvents investigated, this solvent gave the most stable membranes (chapter 3). In the extraction experiments decanol has also been used to compare the influence of the type of solvent on the extraction behaviour.

5569 7736.
1547
6189

2.6.1. Extraction

The advantages of the extraction method used here (in which the LM-phase is immobilized in the support) compared to extraction methods usually described in literature are:

- the contact area between the LM-phase and the water phase is high, because the liquid layer in the membrane is very thin;
- the separation of the water phase and the organic phase is very simple; no special techniques are needed (e.g. the use of centrifugation).

Figure 2.4 gives the relative amount of carrier (TeOA) complexed with nitrate ions as a function of the chloride ion concentration in the water phase, at equilibrium, for SLMs with o-NPOE and decanol as solvent. HPLC-analysis of the aqueous samples with a chloride concentration higher dan 0.1 M was not possible. The absolute error in these results has been estimated at ± 5%.

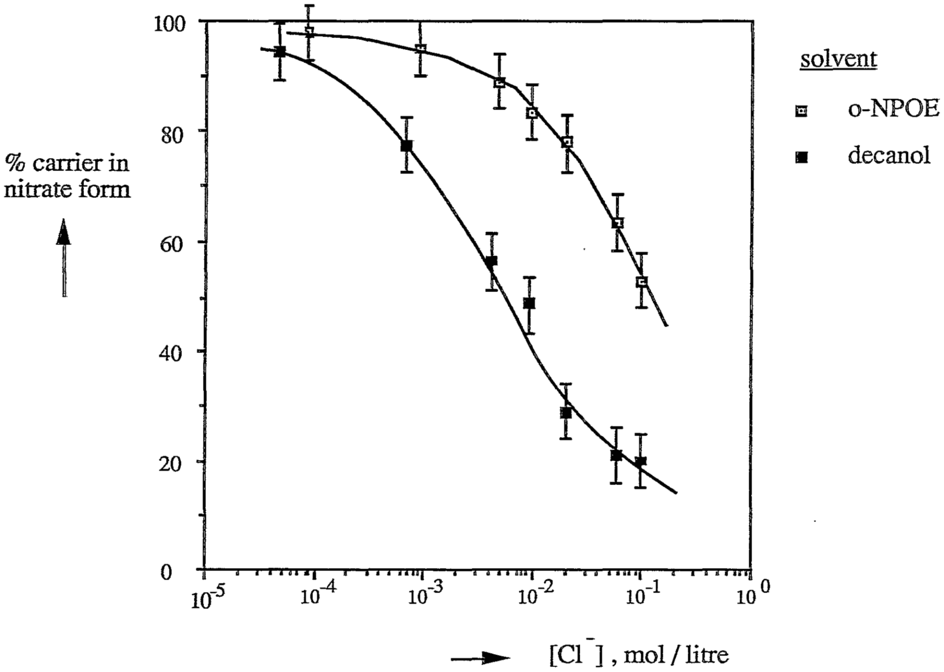

Figure 2.4. Influence of chloride ion concentration and type of solvent on nitrate extraction; volume LM-phase 0.3 ml; volume water phase 30 ml; carrier TeOA

In this figure the principle of the SLM-separation process is illustrated clearly. Under the given circumstances nitrate ions are being complexed with the carrier in the LM-phase at a low Cl^- concentration ($< 10^{-2}$ M) in the aqueous phase (feed side of a SLM-process); these nitrate ions are being exchanged by chloride ions at high $[Cl^-]$ ($> 10^{-1}$ M) (stripping phase).

The calculated distribution coefficients $k_{NO_3^-}$ and k_{Cl^-} are given in figure 2.5.

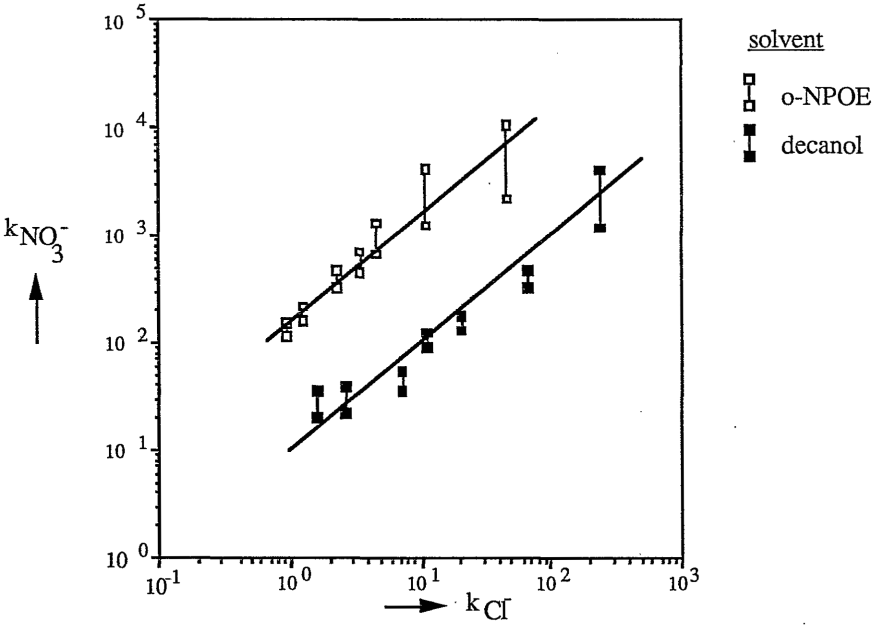

Figure 2.5. Distribution coefficient of nitrate as a function of the distribution coefficient of chloride; carrier: TeOA

The errors in the distribution coefficients, in figure 2.5 only given for $k_{NO_3^-}$, are relatively large when the distribution coefficient is either very high (nitrate concentration in the water phase very low) or when the distribution coefficient is very low (nitrate concentration in the membrane phase very low).

Rewriting equation 2.2 we find:

$$\log(k_{NO_3^-}) = \log(k_{Cl^-}) + \log(K_{ex}) \qquad (2.3)$$

From this equation straight lines with a slope of 1 can be expected when $\log(k_{NO_3^-})$ is plotted as a function of $\log(k_{Cl^-})$ (Nernst behaviour). Figure 2.5 shows that within experimental accuracy this behaviour is found. From the experimental lines we calculated the extraction constants:

$$K_{ex,}\ (\text{o-NPOE}) = 154 \qquad (2.4)$$
$$K_{ex,}\ (\text{decanol}) = 10 \qquad (2.5)$$

These values are comparable with literature values for ion selective electrodes with similar compositions (19, 20, 21). The same dependence of the selectivity on the nature of the membrane solvent (high selectivities for aromatic solvents) have been published for these systems. The causes for these phenomena, mainly given by the strength of the association between the anion and the exchanger, are discussed in ref.20. The possibility to vary the selectivity of an SLM with the character of the solvent can be very attractive for practical applications. To enable an effective desorption of the nitrate ions in the stripping phase to take place, it should be mentioned that the highest K_{ex} is not always desirable.

2.6.2. Permeation

The influence of various variables on the nitrate transport through the membrane will be discussed in comparison with the permeation under standard conditions.

2.6.2.1. Standard conditions

The standard conditions were chosen such that the transport of nitrate is determined only by the diffusion of the carrier through the membrane. These standard conditions are:

support : Accurel ®, thickness 92.5 µm
carrier : TeOA
carrier concentration : 0.2 M
solvent : o-NPOE
feed: $F_{t=0}$: 0.004 M $NaNO_3$
stripping phase: $S_{t=0}$: 4.0 M NaCl
water flow velocities F & S : 5.0 ml/s.

Figure 2.6 gives the nitrate concentration in the feed as a function of time when the feed is treated under standard conditions.

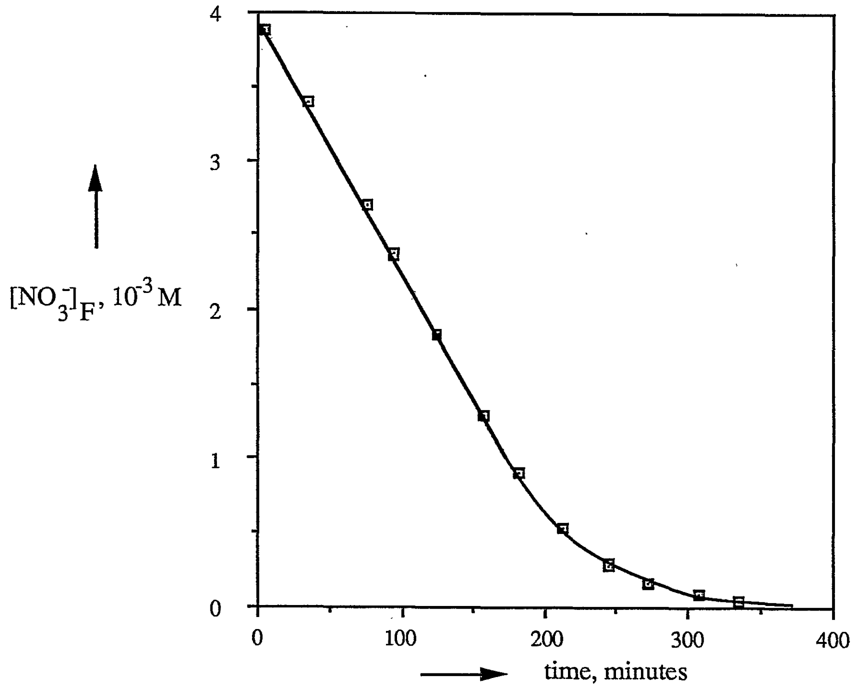

Figure 2.6. Nitrate concentration in the feed as a function of time; standard conditions as defined in the text

The concentration of nitrate in the feed after 6 hours of permeation has decreased to less than 10^{-5} M and it is below the detection limit of the HPLC. So nitrate can be removed completely from the feed and transported to the stripping phase, in which the nitrate concentration is at least 400 times higher then the last measured value in the feed.

The first part of the curve (up to a time of three hours) can be described by a straight line. From the slope of this line the nitrate flux J through the membrane can be calculated by:

$$J = -d[NO_3^-]_F / dt * V / A \qquad (2.6),$$

in which A is the membrane area in contact with the water phase (18.1 cm^2) and V is the volume of the feed (130 ml). Because some variation is present in the thickness of the different membranes used the calculated fluxes have been normalized to the average thickness of 92.5 µm. Under these conditions J is: 19.7 $* 10^{-10}$ mol/cm^2 s. The error in the flux determination is ±10%.

The linear relationship between $[NO_3^-]_F$ and time can be understood by applying Fick's law to the rate determining step of diffusion through the liquid membrane phase:

$$J = \Delta C \cdot D / d \qquad (2.7),$$

in which ΔC is the concentration gradient of the carrier in nitrate or chloride form in the membrane, D is the diffusion coefficient of the carrier through the membrane and d is the effective pathlength of the carrier through the membrane. During the experiment D and d are constant, so J should be proportional with ΔC. When we assume that the diffusion coefficients of the carrier in the nitrate and chloride form are equal to each other then ΔC is determined by the lowest concentration gradient of either of the two carrier forms. This gradient is determined by the concentrations at the boundaries and therefore by the exchange equilibrium. In section 2.6.2.3 and 2.6.2.4 it will be shown that at the beginning of the experiment at the feedside about 100 % of the carrier molecules in the membrane are in the nitrate form and at the stripping side roughly 96 % in the chloride form; these percentages change less than 10 % during the first three hours of the experiment. So ΔC is nearly constant and a straight curve can be expected for the nitrate concentration in the feed as a function of time.

It should be noticed that in the beginning of the experiment the carrier is in the bromide form (which type of ion is situated between nitrate and chloride in the Hofmeister series). This will result in some uptake of nitrate from the feed into the membrane without direct transport to the stripping phase. But it can be calculated that this "nitrate-loading" effect of the membrane is less than 2 % of the nitrate in the feed. This is confirmed by an experiment in which the carrier was brought in the nitrate form before starting up the permeation experiment. This had no significant influence on the nitrate flux.

2.6.2.2. Effect of flow velocities of the aqueous solutions

In figure 2.7 the influence of the water flow velocities on the nitrate flux through the SLM is given while maintaining the other variables at their standard values. The flow velocities of F and S have been varied separately, while in addition experiments have been carried out in which the velocities of F and S were equal and have been varied simultaneously.

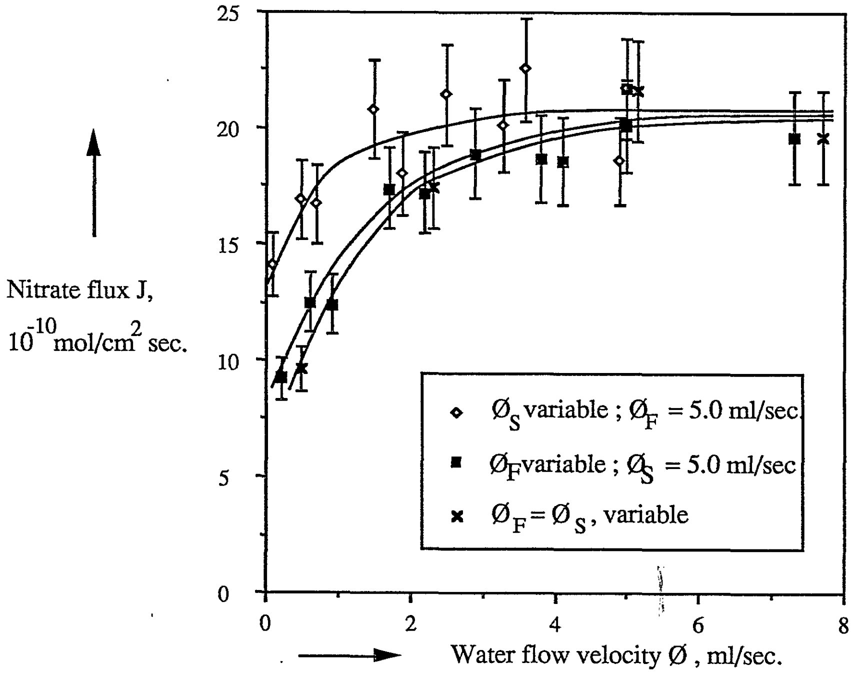

Figure 2.7. *Influence of the water flow velocity on nitrate permeation*

Figure 2.7 shows that for all three curves the fluxes reach a plateau value with increasing water flow velocities. This means that at low water flow velocities the resistance against mass transfer through the laminary water layers (∂_F and ∂_S in figure2.2) also has an influence on the overall flux. While increasing the water flow velocities, the thickness of the laminary layers will decrease and the concentration at the membrane boundaries will change: $[NO_3^-]_{F,i}$, will increase while $[NO_3^-]_{S,i}$ will decrease (see figure 2.2). Via the ion exchange equilibrium these boundary concentrations determine the composition of the complexes at the interfaces of the membrane phase and also the concentration gradient which acts as the driving force for transport. When reaching the plateau value a further change in these boundary concentrations obviously has no effect and the transport is limited by the diffusion of the carrier through the membrane. The experiments, described in the following paragraphs, will show that supply and removal of chloride ions does not play a significant roll in this process under these conditions.

Figure 2.7 also shows that the reduction of the flux below the plateau value is reached at a higher flow rate when lowering the feed velocity than when lowering the velocity of the stripping phase. Furthermore, the curve obtained when varying only the flow velocity of the feed nearly coincides with the curve which is obtained when the flow velocities of both the feed and the stripping phase are varied simultaneously. From these facts it can be concluded that concentration polarisation effects are more important in the feed than in the stripping phase and that at equal velocities of the feed and the stripping phase the resistance against mass transfer in the feed boundary layer determines the overall concentration polarisation behaviour. This means that the limited supply of nitrate ions in the feed has a much larger influence on the amount of carrier in nitrate form in the membrane phase than a limited nitrate removal in the stripping phase does.

This can be understood when one takes into account the selectivity of the membrane and the difference in concentration of the permeants in the feed and the stripping phase as will be illustrated later. The same influence of varying the flow velocities on the flux was noticed by other workers in the field. For instance Babcock et al (22) found for a SLM-system in which copper ions were removed that the flux decreases sharply when decreasing the flow velocity of the feed, while the flux was independent of the velocity at the stripping side.

For practical applications, e.g. making use of hollow fibers modules, this means that for an optimal operation of the process different flow velocities of the feed and the stripping phase can be used. For process design in which the extraction and stripping processes are performed in two different modules it is also possible to have different membrane surface areas at the feed and stripping side.

Taking notice of the results given in figure 2.7 equal flow velocities of F and S of 5.0

ml/s were used during further experiments. The effects of concentration polarisation can then be neglected and the diffusion of the ions through the SLM phase is the rate determining step in the transport process.

2.6.2.3. Effect of nitrate concentration in the feed

Figure 2.8 shows how the flux is influenced by the nitrate concentration in the feed. This has been measured during the first period of the experiment. The chloride concentration in the feed was zero at the start of each measurement to be sure that the flux was not influenced by the presence of chloride ions (open points in figure 2.8). From figure 2.6 (an experiment in which one starts with 0.004 M NO_3^-) also a nitrate flux can be calculated as a function of the nitrate concentrations at different times, with using eq. 2.6. These results are also given in figure 2.8.

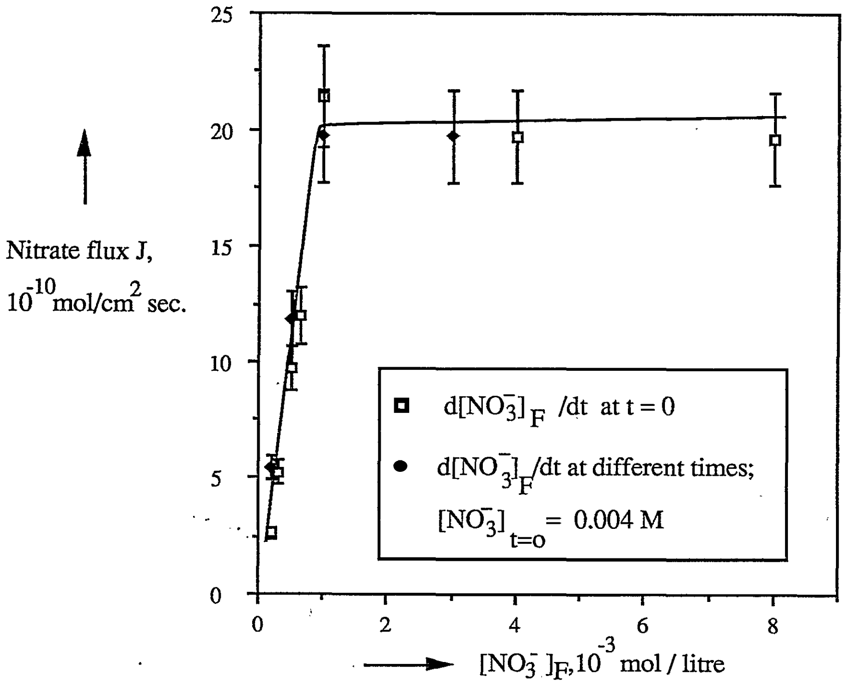

Figure 2.8. Influence of nitrate concentration in the feed on nitrate permeation

It appears from figure 2.8 that the same curve is obtained for both methods by which the flux was determined. This means that the presence of chloride ions in the feed, in this concentration region, has no influence on the overall flux.

The linear part of figure 2.6 results in the plateau value in figure2.8, while the change in the decline of the [NO_3^-] - time curve at nitrate concentrations lower than 0.001 M gives a lower flux. The explanation for this decrease in flux is that at lower bulk concentrations of nitrate in the feed than 10^{-3} M the amount of carrier molecules in nitrate form at the feed interface diminishes and so the driving force for transport will reduce.

There are two possible causes for this reduction in driving force:

1 A reduced complexation of nitrate ions due to the ion exchange equilibrium;
2 A delayed nitrate supply due to concentration polarisation effects.

On account of the anion exchange equilibrium (equation 2.2 and 2.4), it can be calculated that above 0.001 M nitrate in the feed at least 98 % of the carrier molecules in contact with the feed would be in the nitrate form; above the value of 0.0001 M nitrate still more than 85 % would be in the nitrate form. Because of equation 2.7 a proportional decrease of the flux in this concentration region could be expected. However the flux decline shown in figure 2.8 is much stronger. So concentration polarisation effects must be responsible for the reduction in driving force for transport. It is obvious that this behaviour (and so the critical nitrate concentration below which the resistance for mass transfer change from diffusion through the membrane to diffusion through the boundary layer) depends on the flow velocities of the aqueous phases.

Because of these results a nitrate concentration in the feed of 0.004 M, at the start of the experiment, has been chosen as a standard condition. So almost all the carrier molecules at the membrane interface in contact with the feed are in the nitrate form and the transport rate is determined by the diffusion of the carrier through the liquid membrane phase.

2.6.2.4. Effect of chloride concentration in the stripping phase

Figure 2.9 gives the flux as a function of the sodium chloride concentration in the stripping phase.

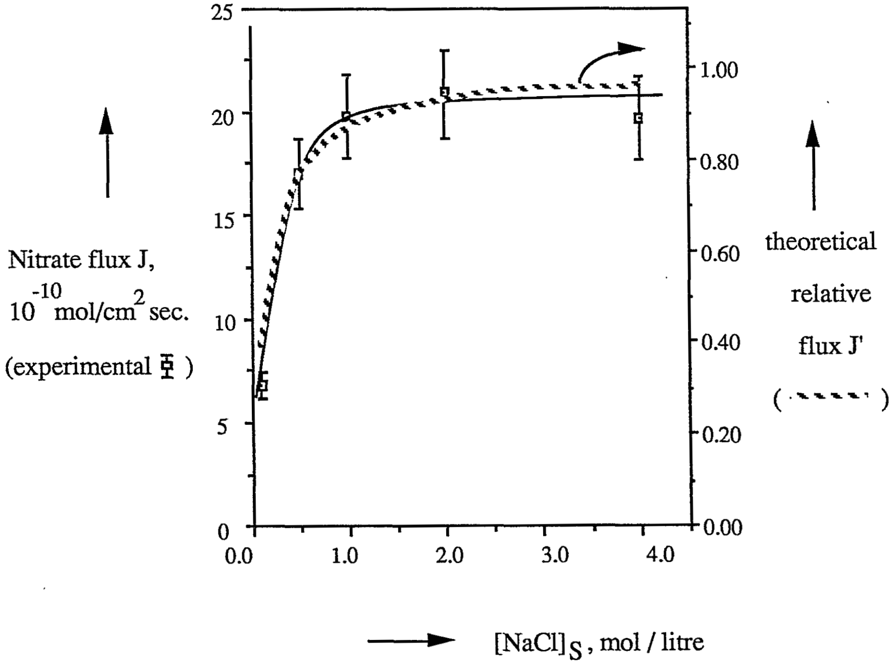

__Figure 2.9.__ Influence of chloride concentration in the stripping phase on nitrate permeation

The nitrate flux increases with increasing NaCl concentration and reaches a plateau value for $[NaCl]_S > 2.0$ M. Qualitatively we can understand this behaviour if we realize that an increasing percentage of carrier in nitrate form is being transformed in chloride form when increasing the chloride concentration in the stripping phase. For a more quantitative discussion we assume that the overall flux is determined by diffusion of the carrier through the membrane phase and that equation 2.7 is valid:

$$J = \Delta C * D/d \qquad (2.7)$$

If the diffusion velocities of the carriers in both nitrate and chloride form are equal to each other equation 2.7 can be converted to:

$$J = \{ \overline{[NO_3^-]}_F - \overline{[NO_3^-]}_S \} * \text{Constant} \qquad (2.10)$$

A relative flux J' can be defined as:

$$J' = J / J_{max} \qquad (2.11)$$

in which J_{max} is the maximal attainable flux for a certain membrane; this means that flux J_{max} is obtained when all the carrier molecules at the feed side are in the nitrate form and at the stripping side all are in the chloride form.

As stated in the previous paragraph the assumption can be made that at the feed side (under the prevailing conditions) all the carrier molecules are in the nitrate form; so $\overline{[NO_3^-]}_F = 0.2$ M.

$\overline{[NO_3^-]}_S$ can be calculated by applying equation (2.2) to the conditions at the interface between the membrane and the stripping phase, using the experimentally determined value for K_{ex}:

$$\frac{\overline{[NO_3^-]}_S}{\overline{[Cl^-]}_S} = \frac{[NO_3^-]_{S,i}}{[Cl^-]_{S,i}} * 154 \qquad (2.12)$$

As a result of the high chloride concentration in the bulk of the stripping phase it can be supposed that the influence of concentration polarisation effects, for the chloride concentration at the membrane-interface, is negligible, so: $[Cl^-]_{S,i} = [Cl^-]_S$. Assuming a value for $[NO_3^-]_{S,i}$ the relative flux can be calculated. Based on the previous paragraphs at the start of the experiment $[NO_3^-]_{S,i}$ is assumed to be 0.001 M (equal to the concentration polarisation of nitrate ions in the feed). The influence of $[Cl^-]_S$ on the theoretical relative flux has been given as a dashed curve in figure 2.9. To compare the trend between the two curves in this figure the maximal theoretical flux is fitted to the experimental plateau value of $22 * 10^{-10}$ mol/cm^{2}s. The fact that the curves in both cases have the same trend towards $[Cl^-]_S$ confirms the validity of the theory and the assumptions.

So an intermediate conclusion is that, contrary to the problems of concentration polarisation at the feed side, at the stripping side the ion exchange equilibrium is responsible for the reduction in the flux value when lowering the chloride concentration in the stripping phase.

The relative flux is a direct measure for the amount of carrier molecules which are in the chloride form at the stripping side, because all the carrier molecules in contact with the feed solution are in the nitrate form, under the given conditions. From figure 2.9 it can be concluded that for 4 M NaCl, 96 % of the carrier molecules in contact with the stripping phase is in the chloride form. Using equation 2.12 it can be calculated that at a removal of 75 % of the 0.004 M nitrate concentration from the feed and consequently at 0.003 M nitrate concentration in the stripping phase still 86 % of the carrier molecules in contact with the stripping phase are in the chloride form. When the concentration of nitrate ions in the stripping phase increases to a higher value, the driving force for transport will be reduced substantially. This effect will be illustrated in the next chapter, where nitrate ions are transported to a stripping phase with a much smaller volume than the feed volume.

Because of these results a NaCl concentration in the stripping phase of 4.0 M has been chosen as the standard condition, so almost all the carrier molcules in the membrane in contact with the stripping phase are in the chloride form.

in bewerking : kerosine af (conc 0, 20, 40, 60, 80 procent)
. carrier -

2.6.2.5. Effect of the carrier concentration

Figure 2.10 shows the dependence of the nitrate flux on the carrier concentration in the membrane phase.

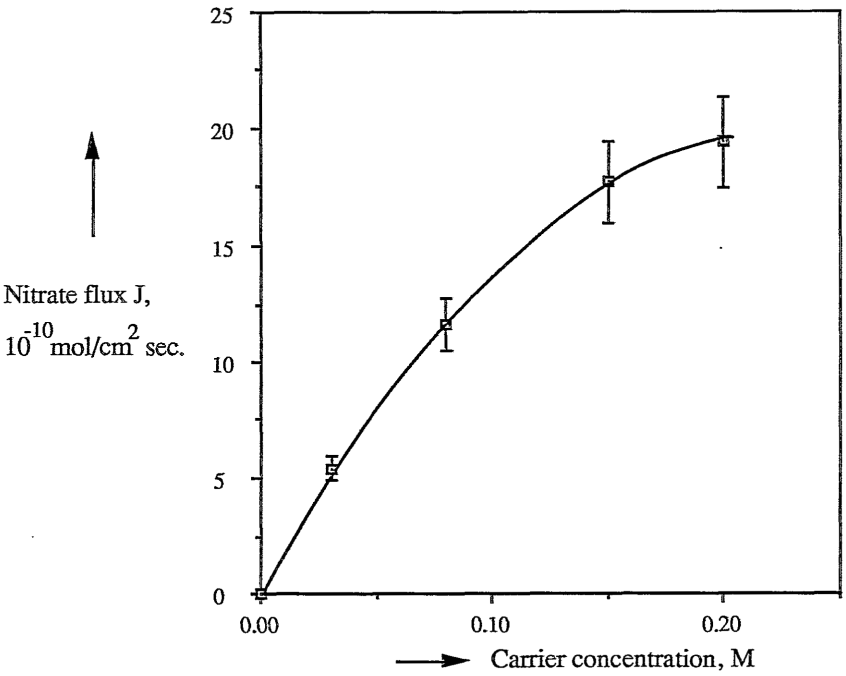

Figure 2.10. Influence of the carrier concentration on nitrate permeation

An increase in the carrier concentration in the membrane phase leads to a steeper concentration gradient of carrier molecules in nitrate or chloride form. This increase in the driving force for transport gives a higher flux value. According to Fick's law (eq. 2.7) and the assumption that, in our case, ΔC should be proportional to the carrier concentration, a linear increase of J as a function of the carrier concentration could be expected. However the viscosity of the LM-phase also increases leading to a decrease in the diffusion coefficient D. For this reason the relation between carrier concentration and dynamic viscosity has been measured. The results are given in figure 2.11.

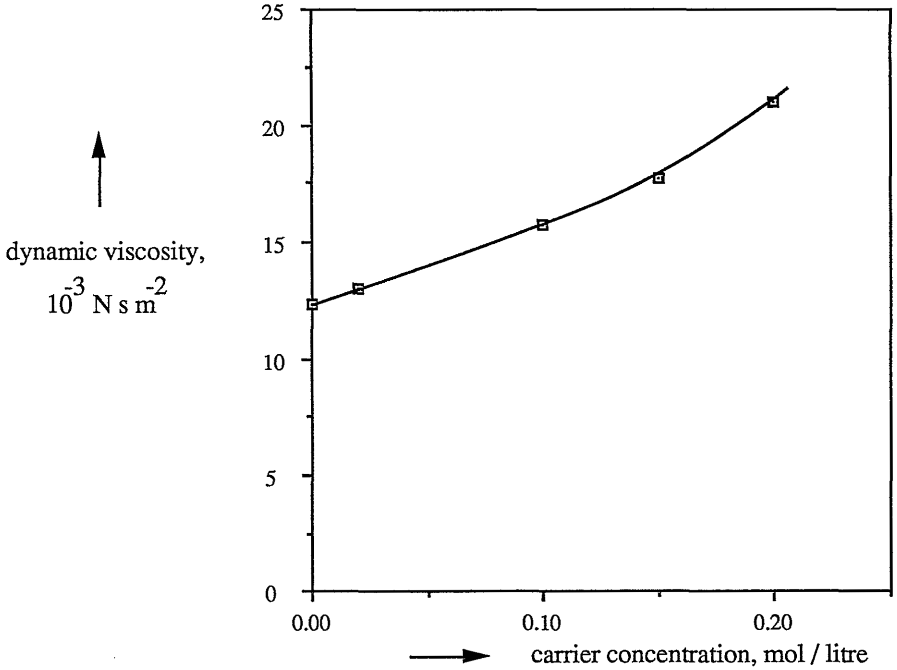

Figure 2.11. *Dynamic viscosity of the LM-phase as a function of carrier concentration*

The actual diffusion coefficient can be calculated from eq. 2.7 :

$$D = J_* \, d / \Delta C \qquad (2.7)$$

In this formula the effective pathlength of the carrier through the membrane d can be obtained by multiplying the membrane thickness with the tortuosity factor τ of the support. This value is unknown and also influenced by the shape of the pores. Yet to be able to estimate this value the equation of Mackie and Meares is used (23) :

$$\tau = (1 + V_p) / (1 - V_p) \qquad (2.13)$$

where V_p is the volume fraction of polymer in the support. The porosity of the membrane used in this work was 69 %; a tortuosity factor of 1.90 is then calculated from eq. 2.13.

To calculate the carrier concentration gradient in the LM-phase it is assumed that 100 % of the carrier in contact with the feed is complexed with nitrate ions and at the stripping side 96 % of the carrier is complexed with chloride ions. This value has to be multiplied by the porosity of the support to yield the concentration gradient ΔC over the total SLM. This gives:

$$\Delta C = C * 0.96 * 0.69 \qquad (2.14)$$

in which C is the concentration of carrier in the LM-phase.

For the diffusion of spherical particles through a liquid the Stokes-Einstein equation is valid (24):

$$D = k * T / 6\pi * r * \mu_0 \qquad (2.15)$$

in which k stands for the Boltzmann constant , T is the absolute temperature, r is the radius of the diffusing species and μ_0 is the dynamic viscosity of the liquid. In figure 2.12 the actual diffusion coefficients calculated from eq. 2.7, 2.13 and 2.14 and based on measured flux values are given as a function of the reciprocal viscosities.

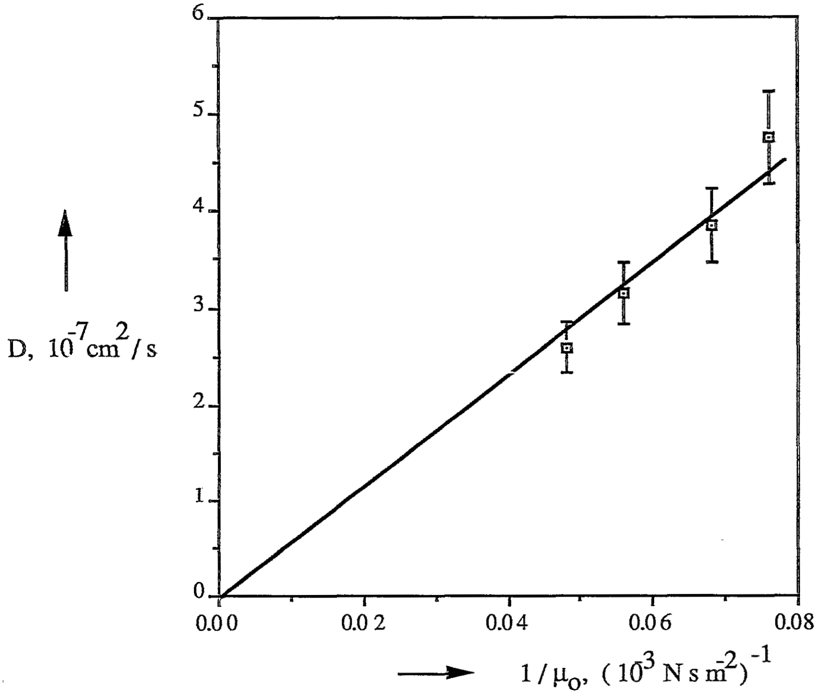

Figure 2.12. The diffusion coefficient as a function of the reciprocal viscosity

From this figure it can be concluded that in our system the Stokes-Einstein equation is valid for the diffusion of carrier molecules through the LM-phase, within experimental error. This means that when correcting for the change in viscosity in figure 2.10 the flux indeed would increase linearly as a function of carrier concentration.

From the slope of the curve in figure2.12 and using eq. 2.15 the radius of the carrier molecules in the LM-phase can be calculated to be $3.9 \cdot 10^{-10}$ m. It should be noticed that the uncertainty in this value is determined predominantly by the uncertainty in the tortuosity of the support.

2.6.2.6. Effect of type of carrier

In table 2.1 the solubilities of 4 types of symmetric quaternary ammonium salts with different lenghts of the alkyl chains in o-NPOE at 25 ^oC are given.

Table 2.1. *Solubilities of R_4NBr in o-NPOE at 25 ^oC*

R	Solubilty
C_8H_{17}	between 0.200 M and 0.220 M
$C_{10}H_{21}$	between 0.075 M and 0.085 M
$C_{12}H_{25}$	between 0.025 M and 0.027 M
$C_{18}H_{37}$	< 0.009 M

The results show that the solubility of the quaternairy ammonium salts in o-NPOE decreases with increasing length of the alkyl chains. This behaviour agrees with observations in similar solutions (25) in which the decreased solubilty has been attributed to an increase in crystallinity and melting point of the quaternairy ammonium salts.

The first three compounds mentioned have been used as carriers in permeation experiments with a concentration of 0.025 M in o-NPOE. For these carriers the same kind of behaviour has been obtained as for TeOA, when the removal of nitrate from the feed as a function of the time was studied. The viscosity of the LM-phase increases less than 3 % with increasing length of the alkyl chains of the carriers. In figure2.13 the influence of the length of the alkyl chain on the diffusion coefficient is given.

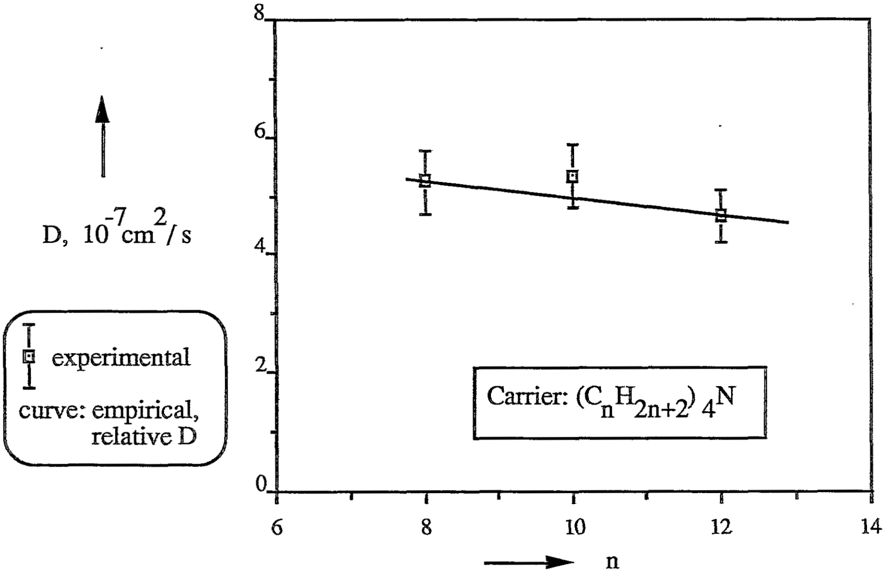

Figure 2.13. Influence of length of alkyl chain on diffusion coefficient of carrier through LM-phase.

A theoretical model for calculating the diffusion coefficients can not be used because the influence of the length of the alkyl chain on the molecular radius is not known; especially the distance between the anion and the kation in an organic solvent is not unambiguously clear. A linear relationship between the molecular volume and the molecular weight of a compound is normally used in literature. The influence of the relative molecular radii on D, calculated from this relationship (and the Stokes-Einstein equation (2.15)) is also given in figure 2.13. In this figure the empirically calculated D has been fitted on the experimentally determined diffusion coefficient for TeOA.

From this curve it appears that in this region there is only a slight decrease in the diffusion coefficient with increasing length of the alkyl chains of the quaternairy ammonium salts. Within experimental error, the experimental results are in good agreement with the theoretical curve.

2.7. Conclusions

A continuous anion exchange method has been developed for the removal and concentration of nitrate ions from water by counter-transport of chloride ions using a proper carrier molecule. This process is also applicable to transport of other anion combinations provided that the compositions of the aqueous phases are such that a reversible complexation of the ions can take place.

The transport mechanism could be described with a set of relations that are generally used for coupled transport of cations through liquid membranes.

The extraction results show that the selectivity of the liquid membrane depends on the type of solvent used.

The permeation measurements show that:

- the overall flux is limited by diffusion of the carrier molecules through the liquid membrane phase at standard conditions (carrier: 0.2 M TeOA; solvent: o-NPOE; feed concentration at t = 0: 0.004 M $NaNO_3$; stripping phase at t = 0: 4.0 M NaCl; flow velocities of feed and stripping phases: 5.0 ml / s.);
- concentration polarisation effects on the feed side have a larger influence on the flux values than those in the stripping phase when the flow velocities of the aqueous phases are lowered. The supply of nitrate ions through the laminary boundary layer is also becoming rate determining for the overall flux when the nitrate concentration in the feed is decreased below a critical value of 10^{-3}M;
- transport decreases when the chloride concentration in the stripping phase is lowered below 2 M. In contrast to the concentration polarisation effects at the feed side this is caused by a diminished nitrate desorption and so determined by the ion exchange equilibrium;

- the influence of the carrier concentration on the flux value can be explained using the diffusion law of Fick and the equation of Stokes-Einstein. These relations are also valid for describing the diffusion transport of other carriers with longer alkylchains, for which the molecular radii have been estimated with an empirical relation.

For practical applications the stability of the liquid membrane is of utmost importance. Since the variables investigated in the present chapter influence the stability of the membrane, further research concerning the optimization of the process has to be done. This will be described in the following chapters.

2.8. Symbols and abbreviations

A	membrane area	m^2
C	carrier concentration in LM-phase	$mol\ m^{-3}$
ΔC	concentration gradient of the carrier in the SLM phase	$mol\ m^{-3}$
∂_F; ∂_S	thicknesses of laminar boundary layers at feed or stripping phase interfaces respectively	m
d	effective membrane thickness	m
D	diffusion coefficient of carrier molecule in LM-phase	$m^2\ s^{-1}$
J	overall flux of nitrate ions through SLM	$mol\ m^{-2}\ s^{-1}$
J'	theoretical relative flux	-
J_{max}	maximal attainable flux	$mol\ m^{-2}\ s^{-1}$
k	Boltzmann constant	$J\ K^{-1}$
$k_{NO_3^-}$, k_{Cl^-}	distribution coefficients of ions between the membrane and the water phase	-
K_{ex}	extraction constant	-
μ_o	dynamic viscosity of LM-phase	$N\ s\ m^{-2}$
Ø	volumetric flow velocity of aqueous phases along the membrane	$m^3\ s^{-1}$
r	radius of diffusing carrier molecules in LM-phase	m
τ	tortuosity factor	-
t	time	s
T	absolute temperature	K
V_F; V_S	volume of the feed or the stripping phase	m^3
V_p	volume fraction of polymer in the support	-

$\overline{[NO_3^-]}_F$; $\overline{[NO_3^-]}_S$	concentration of ions bound to the carrier in the membrane at the interfaces	mol m^{-3}
$[NO_3^-]_F$; $[NO_3^-]_S$	bulk concentration of ions in the aqueous phases	mol m^{-3}
$[NO_3^-]_{F,i}$; $[NO_3^-]_{S,i}$	concentration of ions in the aqueous phases at the membrane boundary	mol m^{-3}

LM	liquid membrane	F	feed
SLM	supported liquid membrane	S	stripping phase
ED	electrodialysis	TeOA	tetra-octylammonium
RO	reverse osmosis	o-NPOE	ortho-nitrophenyloctylether
SX	solvent extraction		

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Chapter 3

SLM-instability effects

3.1. Summary

The instability behaviour of several supported liquid membranes (SLMs) has been studied for a system in which nitrate ions are removed from an aqueous feed phase and concentrated in a stripping phase. The composition of the aqueous phases and of the membrane liquid has been determined after the aqueous phases flowed parallel to the membranes for a period of six days. From the experimental data it can be concluded that SLM-failure results from the removal of LM-phase from the support. Contrary to literature data this is not caused by an osmotic pressure difference. It is shown that the membrane stability depends largely on the type of solvent and the molecular structure of the carrier. Furthermore the membrane stability increases with an increasing salt content in the stripping phase (at constant composition of the feed solution).

3.2. Introduction

The use of SLMs for the selective removal of ions from aqueous solutions is very promising because of the high selectivity and the relative high flux values which can be obtained. However, in practice only a few SLM-systems are being applied, since the stability of the membranes is insufficient and therefore the lifetime of the membranes unpredictable.

3.2.1. Literature data

In spite of the fact that in the last few years the instability problem has time and again been mentioned (1, 2), little systematic research has been done to find the causes of this instability. In this paragraph we will summarize and discuss these literature data.

At the same time there is a reasonable number of observations on the consequences resulting from the instability problem. Two types of SLM instability effects can be distinguished. In the first place there is the problem of a decline in permeability as a function of time (3-10), which is generally ascribed to the loss of carrier from the membrane phase (3, 4, 11). In the second place a "break down" of the system can be observed, which means that a direct transport between the two water phases is taking place (6, 11-15). The period of time after which such instability effects are observed can vary from some minutes to several months (in a very few cases). This depends particularly on the type of solvent (5, 11) and on the support used (17, 12, 13, 16). It is remarkable that in the last three references mentioned the use of Accurel® (microporous polypropylene from Enka) provides the most stable SLMs.

causes of SLM-instability

It is evident that the solubilty of components from the LM-phase into the aqueous phases causes SLM-instability effects. Apart from this it is also possible that the LM-phase is pressed out of the pores of the support because of a pressure difference over the membrane. The maximum acceptable pressure difference which a membrane can resist is given by the Laplace equation. However, in practice it appears that even by preventing LM-components to dissolve into the aqueous phase and by an absence of a pressure difference over the membrane, instability effects do occur.

The same model to describe the degradation mechanism of SLMs is put forward by two different research groups (18, 19). They proposed a mechanism in which the degradation of the supported liquid membranes results from an osmotic pressure gradient.

Fabiani et al (19) described the determination of water transport through a liquid membrane as a result of an osmotic pressure gradient ($\Delta\pi$) over the membrane. They found that the water transport increases with an increase in $\Delta\pi$. It is concluded that the water flow through the membrane induces a repulsion of the LM-phase out of the pores of the support which causes the SLM to degenerate.

Danesi et al (18) investigated the correlations between different physical variables and the stability of SLM-systems. The (salt) permeation and the water transport measurements show that no water transport occurs when stable SLMs are used. Furthermore it has been concluded that when the LM-phase can dissolve a large quantity of water and when additionally an osmotic pressure difference is present transport of water will take place. Apart from these observations stable SLM-systems are characterised by high interfacial tensions between the aqueous- and LM-phase, small contact angles of drops of aqueous phase in contact with SLMs and a low solubility of water in the LM-phase.

The most important objection against the "osmotic pressure model" is that the results do not prove in any way that the LM-phase is expelled by an osmotic water flow. Another explanation wich agrees with the phenomena observed is that the (osmotic) water flow is the result of the removal of the LM-phase from the support by a different primary cause.

Another article dealing with the causes of SLM-instability has recently been published by Takeuchi c.s. (20). In this article a study of the instability behaviour of SLMs with different solvents is given. They determined a so-called "water leakage" based on the leakage transport of ions through the membrane. From the results it was concluded that the stability varies notably with the solvent type and decreases roughly with decreasing interfacial tensions. Furthermore the instability increases with an increase of the flow velocity of the aqueous phases along the membrane and by an increasing hydrostatic pressure gradient over the membrane. The pressure differences applied are substantially smaller than the breakthrough pressures which are needed to expell the absorbed LM-phase from the pores and which can be calculated from the Laplace equation. An explanation for these phenomena has been found in the replacement of the LM-phase by the water phase, in which the small pressure differences used facilitate the penetration of the water into the pores. However the instability mechanism has not been formulated clearly and the relationship between SLM-stability and interfacial tensions is not unambiguous.

From these literature data it appears that until now a consistent model describing the degradation mechanism is missing. However a breakthrough of the SLM technique such that it can be applied on a practical scale needs a better understanding of the mechanism of SLM degradation. From the studies performed untill now it is clear that this will be a difficult and complex investigation because of the large number of variables that are involved. Danesi (18) illustrates this by calling it a "painful and often frustrating work".

In this chapter a start is made with a systematic investigation of the instability factors. The strategy will be followed to make an inventory of instability effects first and then, on the basis of these results, to develop a theory which will be tested afterwards.

Based on the literature data mentioned above we studied the influence of the compositions of the aqueous phases and the membrane phase on SLM-instability. We also measured some physical properties of our system with the purpose to investigate the relevance of these properties to SLM stability. So the effect of solvent viscosity, the solubility of water in the LM-phase and the interfacial tensions between the LM-phase and the aqueous phases were determined in addition to actual nitrate enrichment measurements.

In order to approach the practical conditions and to get as much information as possible we modified our experiments compared to the permeation measurements normally described in literature. These modifications are:

- the feed volume is much larger than the volume of the stripping phase as is the case in practical situations;
- the aqueous phases are flowing parallel to the membranes day and night;
- apart from the determination of the concentration of the permeating ions in the feed we also determine the concentration of counter ions in the feed;
- at the end of the experiment the membranes are analysed and the amount of carrier and solvent which has been removed from the membrane is determined.

3.3. Experimental

The stability of a number of liquid membranes, which are suitable for the removal of nitrate ions from water, has been studied. A description of the transport mechanism has been given earlier (chapter 2; (21)).

Materials

carrier

Two different lipophilic quaternary ammonium compounds are used as carriers: tetraoctyl ammonium bromide (TeOA; Fluka) and trioctylmethyl ammonium chloride (TOMA; Fluka). The first compound was used for studying the transport mechanism (chapter 2) while the second compound is being applied frequently for the extraction of anions from an aqueous solution (22, 23).

solvent

The following 4 compounds have been used as solvents: decanol ("Gold Marke"; Aldrich), dibutylphtalate (DBP; Merck), dioctyladipate (DOA; Merck) and ortho-nitrophenyloctylether (o-NPOE; Fluka). These solvents have been chosen out of a series of solvents with an extremely low solubility in water of less than 0.01 w/w %; only in the case of decanol a more precise solubility value of 0.037 g/l is given in literature (24). These solvents have a low volatility, a viscosity lower than 20 cP and they are able to dissolve the carrier sufficiently (at least to an extent of 0.2 M).

All chemicals have been used without further purification.

support

Flat sheet Accurel®, microporous poly propylene membranes, (Enka) have been used as supports. The thickness of the supports was approximately 100 μm, the porosity 69 % and the average pore size was 0.1 μm.

membrane preparation

The SLMs have been prepared by soaking the support for at least 15 minutes in a 0.2 M carrier solution in one of the solvents mentioned. Before using the membranes the attached liquid was removed from the surfaces of the support by wiping it with a tissue.

Methods

viscosity measurements

The kinematic viscosities of the solvents and the LM-phases were determined with an Ubbelohde viscosimeter. For the calculation of the dynamic viscosities we also measured the densities of the LM-phases with a digital density meter (Paar DMA 50). All measurements were performed at 25 °C.

solubility of water in LM-phase

Equal quantities of LM-phases (or solvent only) and feed or the stripping phase were brought in contact intensively by shaking in a test tube during two hours. The mixture was at rest during three days, in order to establish an equilibrium and to let the phases separate, before samples were taken from the organic phase with an injection syringe. The water content of these samples was analysed according to the Karl Fischer method.

interfacial tension measurements

Interfacial tensions were measured by the Wilhelmy plate technique as described elsewhere (25). The effect of the composition of the aqueous phase on the interfacial tension was investigated by measuring the interfacial tension values against demi water and also against a solution of 4.0 M NaCl. Before the measurements were executed the two liquids were equilibrated by bringing them in contact in a beaker during one night. The interfacial tension was determined from the "maximum pull" by moving the Wilhelmy plate upwards through the interface. For the measurements ultraclean plates were used which were wetted completely by the heaviest, lower liquid phase. So the contact angle at the plate for the lower liquid was zero during the measurement. This means that for those systems in which the water phase was the lower phase a glassplate was used, while for the other systems a glassplate covered with a gold layer was used.

analytical methods

The chloride and nitrate concentrations in the feed were determined by HPLC,in the way described in chapter 2. The nitrate content in samples of the stripping phase were analysed spectrophotometrically at a wave length of 420 nm. First the nitrate ion was reduced to nitrite with sulphuric acid and then complexed with sodium salicylate.

The concentration of the carrier in the membrane was quantitatively determined by the method described by Itoh et al (22). For this purpose the LM-phase from the membrane was dissolved in chloro-benzene. After an anion exchange step with the PAR^- ion (4-(2-pyridylazo) resorcinol) in aqueous solution at pH 10, the concentration of the carrier-PAR complex was determined spectrofotometrically at a wave length of 395 nm.

nitrate enrichment experiments

Nitrate enrichment experiments were performed by flowing a feed aqueous phase with a volume of 4.1 litre and a sodium nitrate concentration of 0.004 M parallel to the membrane. An aqueous 0.5 M or 4.0 M sodium chloride solution with a volume of 0.13 litre was used as the stripping phase.

Preliminary measurements learned that for the SLMs with decanol and DBP as solvent the removal of LM-phase from the support was considerable. In these cases the aqueous phases were saturated with the LM solvent before starting up the experiment to prevent the removal of the liquid membrane by solution effects. This was done by adding 0.5 ml organic solvent per litre to the water phase under stirring. An organic phase in contact with the water phase was constantly visible during the experiment because of this large excess. The experimental set up is given in figure 3.1.

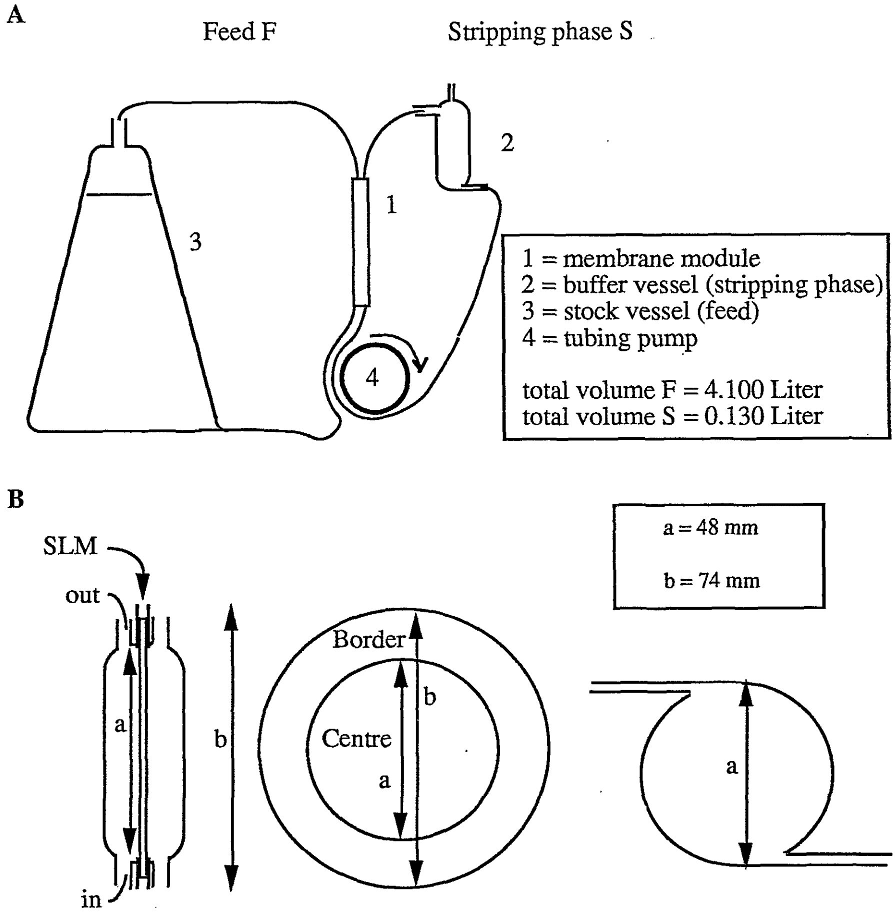

Figure 3.1. *A ; experimental set up; **B**; dimensions of the membrane and membrane module*

To prevent hydrostatic pressure differences over the membrane during the experiment, the inlet-openings of the aqueous phases to the buffer vessel containing stripping phase and to the stock vessel containing feed were kept at the same level. The flow velocities of the aqueous phases along both sides of the membrane were also kept equal to a value of 5.5 ml/s with the use of "tubing pumps" (Masterflex®). The measurements ran 24 hours per day in a thermostated room at 25 °C.

Feed-samples of 1 ml were taken regularly and analysed to obtain the chloride and nitrate content. Likewise the nitrate content of the stripping phase was determined spectrophotometrically to controll the mass balance.

From the decrease in nitrate content in the feed with respect to the initial concentration ($-\Delta[NO_3^-]$) and the increase in chloride concentration in the feed ($\Delta[Cl^-]$) during the experiment a counter transport factor CTF was calculated:

$$CTF = (-\Delta[Cl^-] / \Delta[NO_3^-])_{Feed} \qquad (3.1)$$

This factor can be used as a measure for the direct (leakage) transport of chloride ions through the membrane.

Before starting the experiment the masses of the different membranes were determined. After 6 days the experiments were stopped and the centres and the borders were separated (by cutting the centres out of the membranes) and the carrier concentrations and the masses of these membrane parts were determined. The removal of solvent and carrier during the experiments both for the border part and for the centre part of the different membranes can be calculated from the changes in carrier concentrations and the masses determined.

3.4. Results and discussion

The carrier TOMA was soluble in all four solvents to at least 0.2 M, while TeOA only dissolved in decanol and o-NPOE up to this concentration. So altogether 12 different nitrate enrichment experiments were done.

3.4.1. Nitrate concentration in the feed as a function of time

Figure 3.2.A and 3.2.B show the nitrate concentrations in the feed as a function of time, with a chloride concentration in the stripping phase of 0.5 M and 4.0 M respectively.

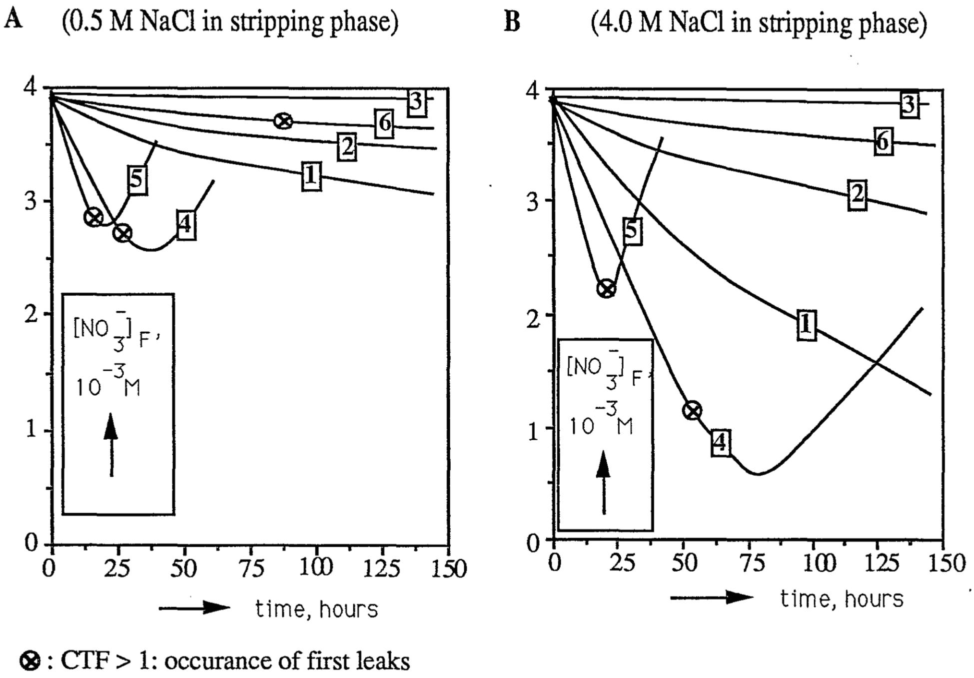

Figure 3.2. Nitrate concentration in the feed as a function of time for the systems: (1) TeOA - o-NPOE, (2) TOMA - o-NPOE, (3) TOMA - DOA, (4) TeOA - decanol, (5) TOMA - decanol and (6) TOMA - DBP. Feed: 0.004 M $NaNO_3$; stripping phase: (A) 0.5 M NaCl and (B) 4.0 M NaCl.

The special marks indicate the moment at which a counter transport factor larger than 1 is measured. This means that at this time a direct diffusion transport of chloride ions from the stripping phase to the feed phase occurs through leaks in the LM-phase. Because of these leaks the chloride concentration in the feed can increase to such an extent that an accurate nitrate determination with HPLC is not possible any more.

3.4.2. Nitrate concentration in the stripping phase

To illustrate that we are dealing with a process in which nitrate ions are being concentrated some stripping phases were analysed. Because more nitrate is removed from the feed in the experiments with 4.0 M NaCl in the stripping phase than with 0.5 M NaCl, the nitrate content in 2 stripping phases with the composition of 4.0 M NaCl was determined. Based on the spreading in results of duplo measurements the error in these spectrofotometric nitrate determinations are rather big and the errors have been estimated to ± 10 mM. These errors are caused by the presence of large amounts of chloride ions, which disturb the quantitative nitrate determination. Figure 3.3 shows the nitrate concentration in the stripping phase for the experiments with TeOA as carrier and decanol and o-NPOE as solvents (experiments 4 and 1 in figure 3.2. B).

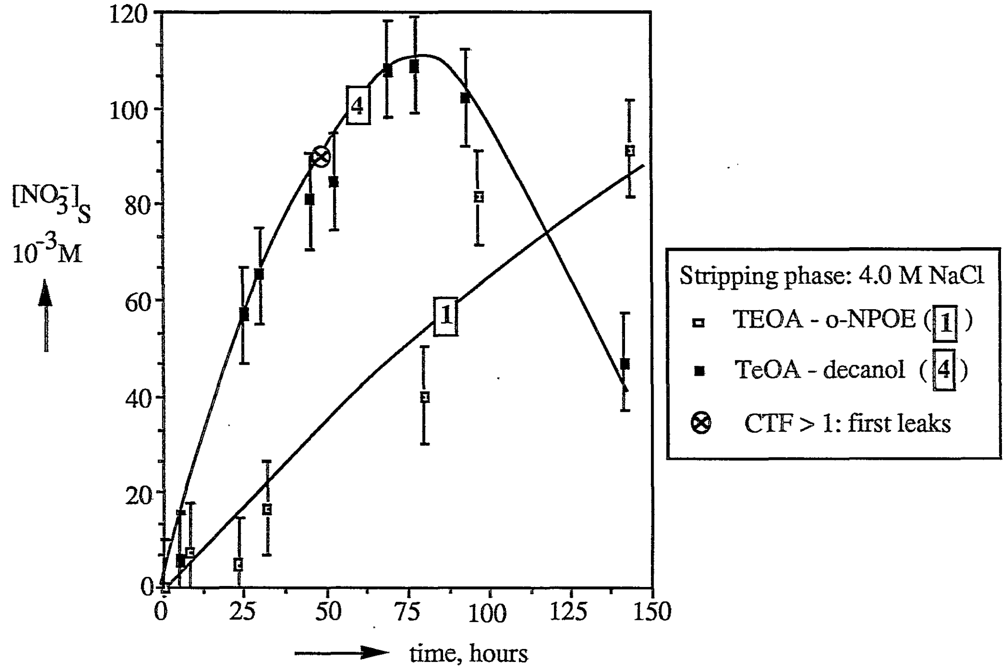

Figure 3.3. Nitrate concentration in the stripping phase as a function of time

When comparing the change in nitrate concentration in the stripping phase (figure 3.3) with the decrease in nitrate concentration in the feed for the same systems (figure 3.2) it appears that the increase in nitrate content in the stripping phase agrees quite well with the decrease in nitrate concentration in the feed multiplied by the volume ratio factor (31.5). The leakage behaviour of the membrane using decanol as solvent is illustrated also in this curve. It can be concluded that the nitrate that is removed from the feed is indeed concentrated in the stripping phase.

3.4.3. Counter transport factor (CTF)

Figure 3.4 shows the countertransport factors for the different SLM-systems as a function of time.

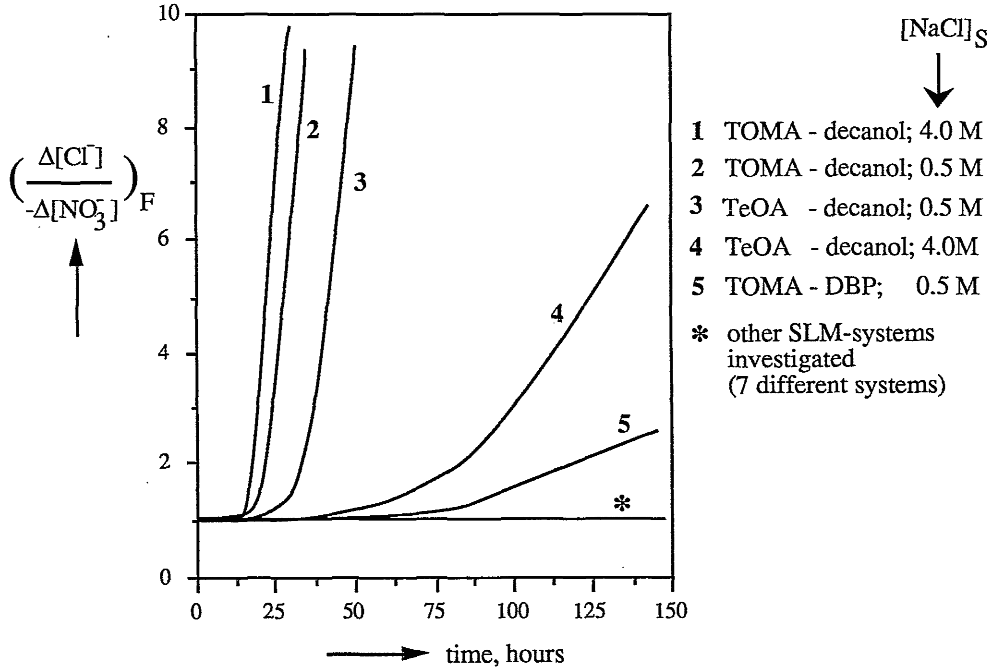

Figure 3.4. Countertransport factor as a function of time

In chapter 2 we found that the transport mechanism prescribes an equimolar ion exchange between the carrier - nitrate complex and the chloride ion, which means that a counter transport factor of 1 should be expected. It appears that this value is being exceeded for 5 systems after some time. This means that a direct diffusive chloride transport from stripping phase to feed occurs through leaks in the LM-phase. For the other systems no leakage takes place.

3.4.4. Removal of LM-phase

Immediately after finishing the experiments the masses of the membranes (centres and border area) were measured. In table 3.1 the removal of LM-phase is given for the different membranes at the two different compositions of the stripping phase. For both the border and the centre area of the membrane the percentages of solvent and carrier that were removed are recorded. These data will be discussed in section 3.4.7.

Table 3.1. *Removal of LM-phase for different SLMs and [NaCl]$_S$ (after 6 days of nitrate enrichment experiments)*

LM		[NaCl]$_S$		LM-removal			
				Centre part		Border part	
solvent	carrier	0.5 M	4.0 M	carrier (± 5 %)	solvent (± 2 %)	carrier (± 5 %)	solvent (± 2 %)
o-NPOE	TeOA	X		-7 %	-5.5 %	-13 %	+0.6 %
"	"		X	-5 %	-4.5 %	-7 %	+0.2 %
o-NPOE	TOMA	X		-74 %	0.0 %	-28 %	-3.4 %
"	"		X	-76 %	+1.3 %	-16 %	-2.2 %
DOA	TOMA	X		-80 %	-3.2 %	-24 %	-2.1 %
"	"		X	-76 %	-4.4 %	-21 %	-7.1 %
decanol	TeOA	X		+4 %	-84 %	-63 %	-74 %
"	"		X	+18 %	-76 %	-45 %	-60 %
decanol	TOMA	X		-77 %	-92 %	-54 %	-76 %
"	"		X	-74 %	-92 %	-34 %	-62 %
DBP	TOMA	X		-84 %	-62 %	-66 %	-62 %
"	"		X	-84 %	-30 %	-44 %	-36 %

3.4.5. Visual observations

For a number of experiments, transport of water from the feed to the stripping phase was observable after some time. This could be noticed by an increase of the volume of the stripping phase in the buffer vessels which resulted in an overflow. It was often accompanied by a slight bulging of the membranes to the feedside. The membrane deformation is caused by the hydrostatic pressure difference due to the transport of

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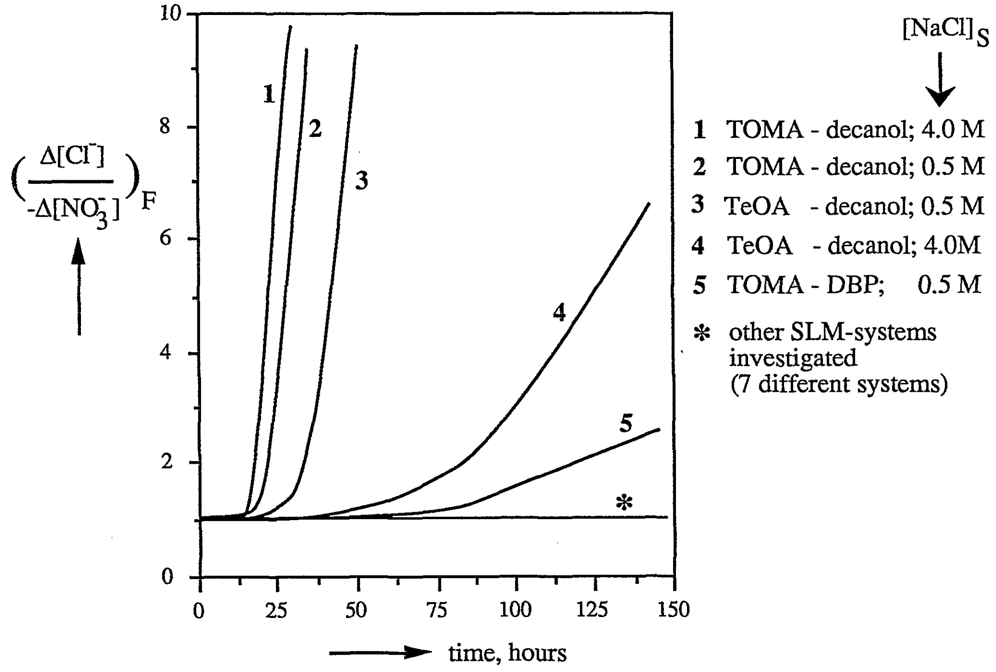

***Figure 3.4.** Countertransport factor as a function of time*

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LM		[NaCl]$_S$		LM-removal			
				Centre part		Border part	
solvent	carrier	0.5 M	4.0 M	carrier (± 5 %)	solvent (± 2 %)	carrier (± 5 %)	solvent (± 2 %)
o-NPOE	TeOA	X		-7 %	-5.5 %	-13 %	+0.6 %
"	"		X	-5 %	-4.5 %	-7 %	+0.2 %
o-NPOE	TOMA	X		-74 %	0.0 %	-28 %	-3.4 %
"	"		X	-76 %	+1.3 %	-16 %	-2.2 %
DOA	TOMA	X		-80 %	-3.2 %	-24 %	-2.1 %
"	"		X	-76 %	-4.4 %	-21 %	-7.1 %
decanol	TeOA	X		+4 %	-84 %	-63 %	-74 %
"	"		X	+18 %	-76 %	-45 %	-60 %
decanol	TOMA	X		-77 %	-92 %	-54 %	-76 %
"	"		X	-74 %	-92 %	-34 %	-62 %
DBP	TOMA	X		-84 %	-62 %	-66 %	-62 %
"	"		X	-84 %	-30 %	-44 %	-36 %

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For a number of experiments, transport of water from the feed to the stripping phase was observable after some time. This could be noticed by an increase of the volume of the stripping phase in the buffer vessels which resulted in an overflow. It was often accompanied by a slight bulging of the membranes to the feedside. The membrane deformation is caused by the hydrostatic pressure difference due to the transport of water. This phenomenon was only noticed for those SLMs which showed chloride-leakages (on account of an increasing countertransport factor). The time at which the osmotic water transport was observable coincided with the moment at which the deviation from 1 of the counter transport factor was measured.

From the transparency of the membrane it could also be seen that during the experiment LM-phase is removed from the support. This gives the opportunity to get a qualitative impression of the stability of the membrane. The membranes with an aromatic solvent (O-NPOE and DBP) provide a transparant membrane at the moment the LM-phase is added to the support. The SLMs with decanol and DOA as solvents are somewhat less transparent at the start. During the experiments the SLMs are generally becoming less transparant due to a partial removal of LM-phase out of the support. It was noticable that allways the border of the membrane was less turbid than the centre, indicating that more LM-phase is removed from the centre of the membrane than from the border.

3.4.6. Physical properties

The viscosities, water solubilities in the LM-phase and the interfacial tensions of the different organic (LM) phases against aqueous phases are given in table 3.2.

Table 3.2. *Physical properties of LM-systems*

LM			solubility of water in LM-phase		interfacial tension	
solvent	carrier	viscosity	0.004 M $NaNO_3$	4.0 M NaCl	demi	4.0 M NaCl
	0.2 M	cP	%	%	10^{-3} N·m^{-1}	10^{-3} N·m^{-1}
o-NPOE	none	12.3	0.1	0.1	27.9	35.0
"	TeOA	21.0	0.6	0.7	16.4	17.3
"	TOMA	17.1	1.3	1.1	5.0	7.3
DOA	none	11.1	0.2	0.2	19.1	24.0
"	TOMA	15.2	2.2	1.7	2.0	6.2
decanol	none	11.8	3.9	2.5	7.7	10.1
"	TeOA	20.4	3.6	2.5	8.8	11.4
"	TOMA	16.8	4.8	3.1	6.6	10.6
DBP	none	15.8	0.4	0.3	19.1	23.5
"	TOMA	22.7	2.0	1.5	4.3	5.9

Viscosity

The results of the viscosity measurements (given in table 3.2) show that the viscosities of the different organic phases are of the same order of magnitude. As could be expected the viscosity increases when carrier is added to the organic phase and TeOA has a larger effect on the viscosity increase than TOMA.

Solubility of water in the LM-phase

Table 3.2 shows that in general the solubility of water in the organic phase increases when carrier is present. This is probably caused by the hydration of the carrier molecules. The higher increase in water solubility with TOMA than with TeOA can be explained by the larger interaction that can occur between water and TOMA-molecules than between water and TeOA-molecules. Because of the presence of one methylgroup in the TOMA-molecule, the hydrophilic N^+- part can be approached better by water than in case of the TeOA-molecule with 4 relatively long alkyl chains.

Interfacial tension

The experimental results given in table 3.2 also show that the presence of carrier molecules in the organic phase generally leads to a reduction in the interfacial tension against water because of the surface activity of the quaternary ammonium salts. The fact that TOMA lowers the interfacial tension more than TeOA, can be explained again by the larger interaction between water and TOMA than between water and TeOA as a result of the geometric structure of the carriers.

3.4.7. General Discussion

From the different results it can be concluded that there are large differences in the stability of the SLMs depending on the composition of the membranes and somewhat on the composition of the aqueous phases. In agreement with observations in literature mentioned before, the instability effects can not be explained by the molecular solubility of LM-components into the water phase.

In view of the relatively small differences in viscosities of the different organic phases and the large differences in SLM-stabilities it is also concluded that there is no direct relation between the stability and the viscosity of the membrane phase. This means that the flow of the organic phase through the pores of the support, which depends on the viscosity of the liquid, is not the major factor which determines the stability of the SLMs.

There is some connection between the interfacial tensions and the instability effects. In general the LM-phases which have the highest interfacial tensions provide the most stable SLMs. But this relation is not unambiguous. These observations are in agreement with the conclusions of Takeuchi c.s. (20) who could not formulate an explicit instability mechanism based on interfacial tensions.

SLM-failure

The results given in table 3.1 clearly show that a large amount of solvent is removed after 6 days especially from the SLMs having decanol and DBP as solvent and which show leakage of chloride ions within a couple of days (figure 3.4). The other membranes, which did not fail, show appreciably less solvent removal. Apparently SLM-failure is induced by LM-removal and the extent of LM-removal appeares to be determined predominantly by the choice of the solvent.

The fact that SLM-failure is the outcome of LM-removal is not so hard to understand when we realize that the LM-phase, which is removed from the pores, is replaced by the aqueous phase. A complete removal of LM-phase from one of the pores will short-circuit the feed and the stripping phase. Once there is a continuous water path in the membrane this will lead to chloride leakage into the feed due to ion diffusion and to water transport through the membrane into the stripping phase as a consequence of the osmotic pressure difference between the two aqueous phases. But, from the point of view of the first observation of leakage, it appears that the transport of water is a consequence of SLM-instability and not the cause of LM-removal.

The values of the solubility of water in the LM-phase show that there is no correlation between this property and the stability of SLMs. In view of these results the mechanism (as suggested in ref. 18 and 19) of LM-repulsion due to a transport of water as a consequence of the solubility of water in the LM-phase combined with an osmotic pressure difference can be seriously doubted. In any case it is necessary to have a continuous pathway for the aqueous phase in the LM-phase in order to create an effective osmotic pressure difference that could remove the LM-phase out of the pores based on convective, frictional effects. The quantities of water which dissolve into the LM-phase are so low that this is not very probable.

It is interesting to note from the results given in figures 3.2 and 3.3 that even when the counter transport factor deviates from one (and hence the membrane is leaking) the process of nitrate removal generally continues for some time before the nitrate concentration in the feed increases again by back diffusion from the stripping phase. This means that we are dealing with just a restricted breakthrough of the membrane, while the largest part of the membrane is still intact and keeps on functioning.

Permeability

It is conceivable that the permation behaviour, as represented in figure 3.2, will be influenced to a large extent by the ease of removal of the carrier from the membrane. The quantity of carrier removed from the membrane is determined especially by the structure of the carrier. It follows from table. 3.1 that the carrier TeOA (with a symmetrical structure) is removed from the membranes to a much smaller extent than TOMA.

From figure 3.2 it also appears that the nitrate fluxes are generally larger for a stripping phase of 4 M NaCl than for 0.5 M. On the one hand this is caused by an increased level of desorption of nitrate ions into the stripping phase (resulting in an increase in driving force for transport), while on the other hand the influence of the composition of the stripping phase on the SLM-stability also determines these differences. As can be seen in table 3.1 always more *carrier* is removed from the membrane when 0.5 M NaCl is used in comparison with a strip concentration of 4.0 M NaCl. This effect also causes lower fluxes for the 0.5 M NaCl stripping phases.

It is remarkable (in table 3.1) that the composition of the stripping phase has no special effect on the removal of *solvent* from the membrane. Only in case of decanol and DBP as solvents somewhat more solvent has been removed from the SLMs when a stripping phase of 0.5 M NaCl is used compared to a stripping phase with 4.0 M NaCl. Once again this is in contradiction with the mechanism in which osmotic pressure differences are believed to be the reason for the instability effects. Such a model predicts greater instability effects for a larger osmotic pressure difference over the membrane. The results however show that the opposite is true. Generally the SLMs are more stable when using a stripping phase with 4 M NaCl than with 0.5 M NaCl. Because of these results the influence of the composition of the aqueous phases on the stability of the SLMs will be studied further in the next chapter.

It is also seen in table 3.1 that generally both solvent and carrier are removed from the border area to a lower extent than from the central area. An explanation for this difference might be that the LM-phase is removed from the central area and is partly replenished by LM-phase from the border by lateral diffusion through the pores of the support.

Finally, as will be shown in the next chapter (26), there are strong indications that the instability is caused by the formation of emulsions. While performing the determination of the solubility of water in the organic phases the formation of stable emulsions has been observed for several systems. The ease with which these emulsions were formed coincides to a large extent with the instability effects observed for the different SLM-systems. In the following chapter this hypothesis is tested for the description of the degradation mechanism.

3.5. Conclusions

An onset to a systematic investigation of the instability mechanism of SLMs was performed by collecting information about instability effects of different SLMs. From the results of the experiments one can conclude that SLM-failure is induced to a great extent by solvent-removal from the support and by the removal of the carrier from the membrane-phase. The first mentioned effect is determined predominantly by the type of solvent used whereas the second effect largely depends on the molecular structure of the carrier.

The instability effects are generally larger when a stripping phase of 0.5 M NaCl flows parallel to the membrane than for 4.0 M NaCl. Furthermore the removal of LM-phase from the central part of the membrane is generally larger than from the border area, which is not in contact with the aqueous phases.

There is no direct relation between the instability effects of the liquid membranes and the viscosity of the LM-phases. There is some connection with the solubility of water in the organic phase and with the interfacial tension between water and the LM-phases but these relations are not unambiguous. The instability effects observed are in disagreement with the model of LM-repulsion due to an osmotic pressure difference over the membrane.

3.6. References

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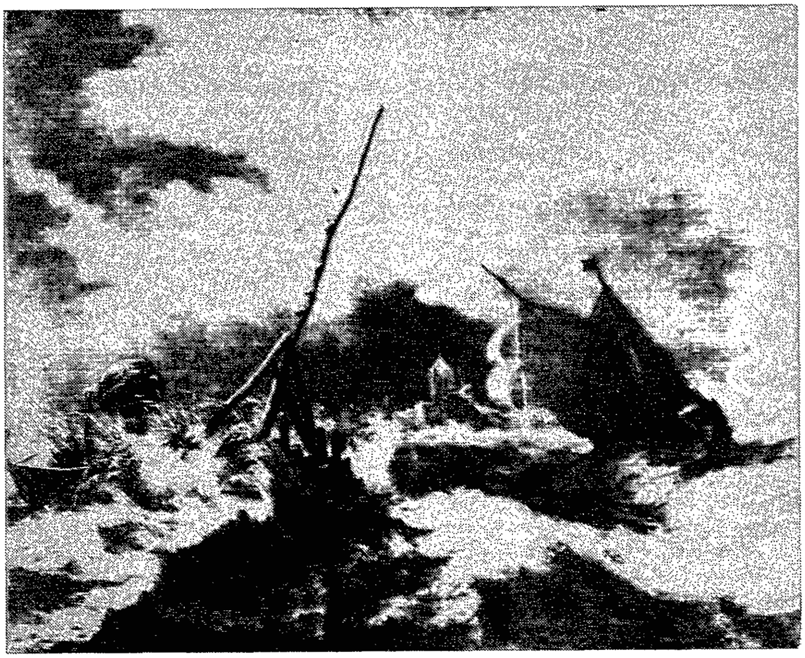

Allart van Everdingen; Sneeuwstorm op zee (1621 - 1675)

Zoals een storm resulteert in de vorming van golven op een wateroppervlak, zo leidt de stroming van waterfasen langs een vloeistofmembraan tot vervorming van het vloeistof grensvlak. Hierdoor worden emulsie druppels afgesplitst en is het membraan instabiel.

Chapter 4

Mechanism of SLM degradation:

emulsion formation

4.1. Summary

A new hypothesis for the degradation mechanism of SLMs is advanced: *emulsion formation induced by shear forces*. Experiments show that the removal of LM-phase from the membrane depends on the molecular structure of the carrier and the type of solvent. The instability of SLMs is regulated by the presence of counter-ions in the same way as in the case of emulsion stability: a decrease in salt concentration in the aqueous phases and an increase in flow velocity of these phases parallel to the membrane surface both lead to an increase in instability effects, while emulsion formation is stimulated by these circumstances.

4.2. Introduction

One of the main problems in using the SLM technique in practical situations is the lack of stability of the liquid membrane. Therefore the stability of these membranes should be enhanced drastically. Because there are still many unknowns about the reasons for SLM-instability, further investigations are necessary. In chapter 3 (1) a first impulse to this study was given. In this chapter the results of a more systematic search into the factors influencing the stability will be described to get a better knowledge of the mechanism of SLM-degradation.

The results given in the foregoing chapter showed that the stability of SLMs depends very much on the type of solvent used, on the molecular structure of the carrier and also on the composition of the aqueous phases. In this chapter two aspects of SLM-instability will be studied further: to begin with the leakage behaviour of SLMs with decanol as solvent gets extra attention. Secondly the long term permeability behaviour of two SLMs with different carriers will be investigated.

A clear correlation is found between the instabilities which are observed for SLMs and the degree of emulsion formation between the same aqueous phases and the LM-phases. This leads to the hypothesis that the instability of SLMs is caused by the formation of emulsions. To test this hypothesis the stability behaviour of SLMs is studied by flowing aqueous phases with similar compositions along the feed and strip-side of the membranes to exclude any effect of osmotic pressure differences. It will appear that following this line of investigations the instability problem can be approached more directly.

Furthermore a number of quantities affecting emulsion formation and emulsion stability are measured and compared with SLM-instability effects. A model describing the mechanism of SLM-degradation will be proposed.

4.3. Experimental set-up

In this chapter two experimental routes will be followed: on the one hand measurements are done in which aqueous phases are flowed parallel to a membrane and on the other hand experiments are performed in which the formation of emulsions between the LM-phase and these aqueous phases is studied.

4.3.1. SLM-instability measurements

For the experiments in which aqueous phases are flowed parallel to the SLMs, the permeability apparatus as described before (in chapter 2; (2)) was used. The chemicals that are used as components of the LM-phase are the same as those mentioned in chapter 3 and the membranes are prepared in the same way as described there. Celgard® 2500 (microporous polypropylene from Celanese; thickness: 25 μm; porosity 45%; pore dimensions 0.04 μm) has been used as support for all the experiments described in this chapter.

Membrane failure for decanol as membrane phase

In these experiments the membrane phase consists of decanol without carrier. The starting compositions of the aqueous phases are: 0.004 M $NaNO_3$ ("feed F") and 4.0 M NaCl ("stripping phase S"). Before starting the experiment the aqueous phases are saturated with decanol by adding an excess of 0.5 ml decanol per liter of aqueous phase under stirring. An organic phase in contact with the aqueous phase remained visible during the experiment because of the excess of decanol added.

The two aqueous phases passed along the membrane with a flow velocity of 5.5 ml/s. or 0.0 ml/s. In case of different flow velocities, we compensated for the resulting pressure difference by a correction in height of the buffer vessels. Samples of the feed were taken periodically (each half hour) and the chloride and nitrate content was determined with HPLC. From this analysis the occurrence of an extra transport resulting from membrane leakage could be determined.

The masses of the membranes were determined before starting and after finishing the experiment (after 7 hours). From the difference the percentage decanol removed from the microporous support was obtained.

Long term permeation

The long term permeation behaviour was studied for SLMs with o-nitrophenyloctylether (o-NPOE) as solvent and using as carriers (0.2 M): tetraoctylammonium bromide (TeOA) and trioctylmethyl ammonium chloride (TOMA) respectively. At the beginning of the flux measurements the aqueous phases, which flowed along the membrane day and night with a flow velocity of 5.5 ml/s, had a composition of 0.004 M $NaNO_3$ (F) and 4.0 M NaCl (S). The nitrate and chloride content was measured as a function of time by analyzing samples, which were taken periodically from the feed, using HPLC. The nitrate flux was calculated from the slope of the curve giving the nitrate concentration as a function of time.

After 3 or 4 days both water phases were replaced by fresh starting solutions, after which the flux was determined again. After about 8 days the presence of tiny gasbubbles became visible at the surface of the membrane with TeOA as carrier. These bubbles were removed by tapping.

From the increase in chloride content in the feed, and the calculation of the counter transport factor (CTF) as a function of time as given in chapter 3, the occurrence of direct leakage from stripping phase to feed could be determined.

Removal of LM-components

During these measurements feed and stripping phase consisted of exactly the same compositions when flowing along the membrane surfaces for some time. The salt concentrations in the aqueous phases are varied from 0 M till 4 M NaCl. In one series of experiments we used aqueous phases with $NaClO_4$, with a concentration varying from 10^{-4} till 10^{-2} M. Furthermore the water flow velocities and the duration of the experiments are varied.

Solvent-removal

In these measurements the support is filled with a pure solvent. The amount of LM-phase removed from the support was calculated by determining the weight of the membranes before the experiment was started and by weighing the centres of the membranes after the measurements were finished, analogous to the experiments described in chapter 3 (section 3.4.2).

Carrier-removal

The amount of carrier removed from the central area of the membranes was determined spectrophtometrically as described in chapter 3. In those cases where $NaClO_4$-ions were present in the aqueous phases the membranes were soaked in a 4 M $NaNO_3$ solution after the experiment. This was done to achieve an ion-exchange between the ClO_4^- (bound to the carrier) and NO_3^-. This extra step in the analysis is necessary since, according to the Hofmeister series, the ClO_4^--ion is more lipophilic (i.e. more strongly complexed) than the 4-(2-pyridylazo) resorcinol ("PAR^-") -ion with which the carrier should be complexed to carry out the analysis. Also the carrier concentrations in the aqueous phases were determined spectrophotometrically after extraction of these phases with chloro-benzene.

4.3.2. Emulsion formation and stability

Preparation of emulsions; emulsions of an LM-phase in an aqueous phase are prepared in three different ways:

- by stirring; three droplets of an organic phase are added to 50 ml salt solution of varying concentrations in a beaker. This mixture is stirred during 3 minutes with a stirrer (Janke & Kunkel ®) at a speed of 250 revolutions per minute. Samples of these mixtures are put into a spectrophotometer tube and the transmission is determined as a function of time.

- by shaking; 1 ml LM-phase and 3 ml water phase are added to a spectrophotometer tube. This tube is plugged and shaken by hand rather strongly. After 5 minutes the transmission of the aqueous phase is determined.

- by ultrasonic vibration; approximately 0.05 gram of the LM-phase is added to 500 ml demi-water in a beaker. This beaker is vibrated ultrasoniccally for 45 minutes in the water bath of a Bransonic ® (50 - 55 kHz). Hereafter 1 ml samples of the emulsion are added to spectrophotometer tubes containing 5 ml of salt solutions of varying concentrations and mixed. The transmission of these emulsions then is determined as a function of time.

In all cases the transmission of the emulsions in the spectrophotometer tubes is determined with a Spectronic 20 ® at a wavelenght of 500 nm.

For the emulsions prepared by the ultrasonic vibration method we also measured the particle size distribution in the emulsion with a Malvern Master Sizer ® and the zeta-potential of the particles with a Malvern Zetasizer ®.

4.4. Results and discussion

4.4.1. Membrane failure for decanol as membrane phase

It was shown before (chapter 3) that membranes with decanol as solvent showed the largest instability effects. This gives the opportunity to investigate the factors influencing this instability within a reasonable period of time. The time needed to reach the point where the membrane showed leakage (CTF larger than 1) and the amount of removal of the LM-phase proved to be independent of:

- the volume of the feed phase (varying from 4.1 L to 0.13 L);
- the saturation of the aqueous phases with decanol;
- the saturation of decanol with water before filling the support;
- the presence of the carrier TeOA (till 0.2 M) in the membrane phase.

Thereupon it was examined whether the flow of one of the aqueous phases in special (the feed with 0.004 M $NaNO_3$ or the stripping phase with 4.0 M NaCl) was responsible for the removal of LM-phase from the support, resulting in chloride leakage. To make the system as simple as possible SLMs with pure decanol were used. At first these experiments were carried out with Accurel as support. Later on Accurel was replaced by Celgard since this latter support showed the same trends in instability effects, but in a shorter time. In agreement with the results of other researchers (3) it was found that the use of Accurel as support leads to substantially more stable SLMs. It appears from our measurements that the first signs of leakage of chloride were observable in a 10 times shorter time for Celgard than for Accurel. Since the relative instability effects were comparable to each other, for practical reasons Celgard was chosen as support. In figure 4.1 the chloride concentration in the feed is given as a function of time for three SLMs, with decanol as LM-phase and Celgard as support, for different flow velocities of feed and stripping phase.

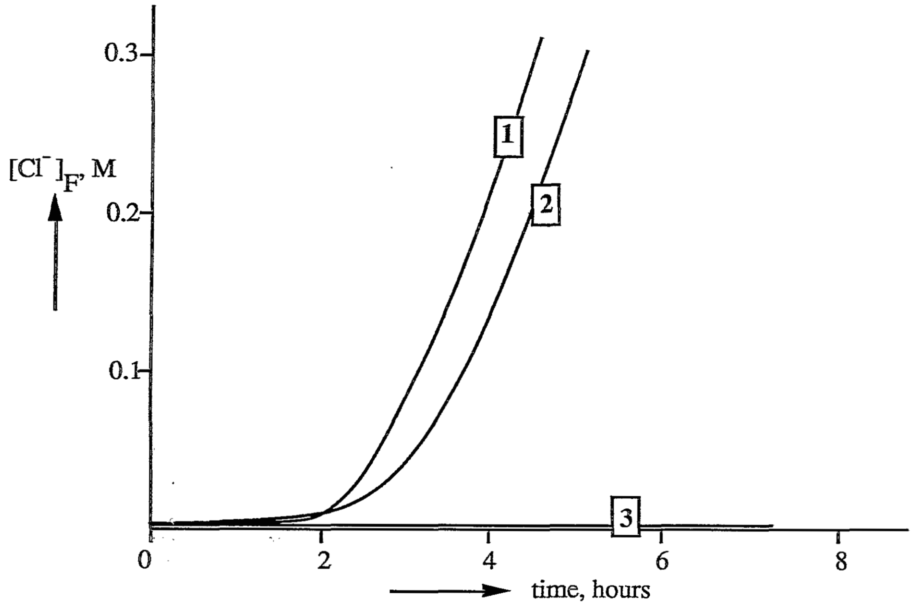

Figure 4.1. Influence of flow rate of aqueous phases on chloride leakage through decanol-SLMs; 1 : flow rate F = flow rate S = 5.5 ml/s; 2 : flow rate F = 5.5 ml/s and flow rate S = 0 ml/s; 3 : flow rate F = 0 ml/s and flow rate S = 5.5 ml/s.

The amounts of LM-phase which are removed from the membranes in these systems by letting the aqueous phases flow during 7 hours are given in table 4.1.

Table 4.1. *Influence of aqueous flow rate on LM-removal, after 7 hours, from decanol-SLMs*

No	flow rate F, ml/s	flow rate S, ml/s	LM-removal
1	5.5	5.5	44 %
2	5.5	0.0	43 %
3	0.0	5.5	19 %

From table 4.1 it can be concluded that the flow rate at the stripping side (with a high salt concentration) is of minor importance for the amount of LM-phase removed. Furthermore it appears that the larger part of LM-removal results from shearing forces excerted at the feed side having a low salt concentration. These results agree with the leakage behaviour of the SLMs as given in figure 4.1. Especially for those systems where the feed is flowing at 5.5 ml/s and where a large amount of LM-phase has been removed, the membranes start to leak within a short time. When the feed does not flow at all a relatively stable SLM is obtained which shows no sign of chloride ion leakage within 7 hours. Obviously a short-circuiting between the F and the S phases arises at that moment when a certain amount of LM-phase (above 20 %) has been removed from the pores of the membrane.

4.4.2. Long term permeation

Apart from a possible leakage of SLMs, the decrease in nitrate flux as a function of time is also an important aspect in SLM-stability. It is possible that this behaviour is determined largely by the degree in which the carrier has been removed from the support. To investigate the influence of the structure of the carrier, we measured the long term permeability for membranes using TeOA and TOMA as carriers. It was shown before (chapter 3) that the degree to which these carriers were washed out from a membrane phase differed largely. To minimize the influence of the solvent, o-NPOE was chosen because this solvent gives the most stable membranes as was shown previously.

Based on previous measurements it could be expected that, for a system with TeOA as carrier and Accurel as support, such an investigation would last at least several months before leakage through the membrane would occur. Therefore Celgard was chosen as support to determine the influence of the structure of the carrier on flux decline.

In figure 4.2 the long term permeability of SLMs with TeOA and TOMA is given as a function of time.

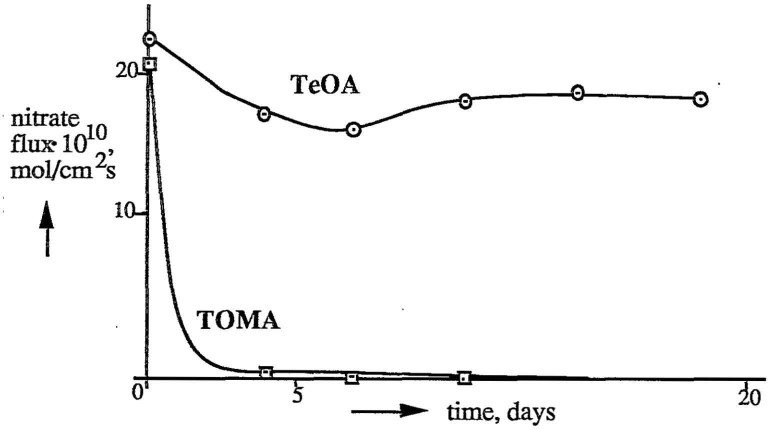

Figure 4.2. Long term permeation; flux as a function of time and type of carrier; LM-phase: 0.2 M carrier in o-NPOE; support Celgard; feed 0.004 M NaNO$_3$; stripping phase 4.0 M NaCl.

During these measurements the countertransport factor (CTF) was also measured. From the results we concluded that the membrane with TeOA as carrier was leaking chloride ions (CTF > 1) from the 4th day on. The membrane with TOMA as carrier showed a leakage of chloride ions for the first time on day 7. Furthermore the degree of chloride leakage was larger for the TeOA-membrane than for the TOMA-membrane. Similar results were obtained from duplo measurements. It is remarkable that, as already mentioned in chapter 3, the process of nitrate removal generally continues after leaks in the membrane have appeared. Apparently we are dealing with a restricted occurrence of channels in the membrane, while the larger part of the membrane is still intact and keeps on functioning.

The results given in figure 4.2 show that the membrane with TeOA as carrier gives a nearly constant flux indicating that we are dealing with a rather stable membrane. The slight decrease in flux during the first 7 days is probably caused by the adsorption of air bubbles which are present or being formed in the system, onto the membrane surface: the effective contact area between the aqueous phases and the liquid membrane decreases and so does the flux. Removal of these air bubbles after 8 days leads to a slight increase in flux. Air bubble adhesion to the hydrofobic material can be a general problem for the application of SLM-separation processes and the magnitude of this effect will depend on the hydrodynamic conditions.

LM phase removal from the TeOA membrane is directly confirmed by the result that the membrane shows a chloride-ion leakage after a reasonable short time (4 days). Obviously LM-phase is being removed at some loci to such an extent that direct channels of aqueous phase can be formed and the flow between F- and S- side is short-circuited. The fact that despite loss in carrier concentration (see chapter 3) and channeling the nitrate flux is rather constant during a much longer time than 4 days leads to the following tentative conclusions:

- direct channeling is only a scarce phenomenon for these TeOA membranes (otherwise back diffusion of NO_3^- through the channels would outway the normal nitrate transport);
- a reduction in carrier concentration in the LM-phase is compensated by a reduction in diffusion pathlength through the membrane (the membrane gets thinner by solvent loss).

Contrary to this the membrane with TOMA as a carrier shows an entirely different stability behaviour. Only at the start the flux is comparable to the case where the TeOA-membrane is used, but then it decreases drastically till after about 3 days the process of nitrate removal has practically stopped. It is obvious that this is due to removal of especially TOMA from the membrane. This agrees with the results of previous research described in chapter 3 (table 3.1), where it was found (using Accurel as support) that the carrier TOMA is removed to a much larger extent from the membrane than TeOA.

It is remarkable that the situation for which CTF > 1 is reached sooner for the TeOA-membrane having a more constant flux behaviour. As was stated before this point is reached when some water channels have been formed by the degradation mechanism. Therefore we have to conclude that the solvent is removed to a higher extent (or more localized) for the system with TeOA compared to that with TOMA. This agrees with the results described in chapter 3 (table 3.1) where it was found that after 6 days more o-NPOE is removed from a membrane with TeOA as carrier than from a membrane with TOMA. This again can be explained by the very fast removal of the carrier TOMA from the membrane. The concentration of TOMA in the LM-solvent decreases so drastically that the driving force for solvent-removal disappears and therefore the breakthrough (leakage) point is reached at a later time.

4.4.3. Removal of LM-phase components

4.4.3.1. Removal of solvent

Based on the experimental results described in the previous section, using decanol as solvent, the preliminary conclusion was drawn that the LM-phase is removed from the membrane by shearing forces excerted at the membrane interface by an aqueous phase with a low salt concentration. To verify this assumption identical aqueous phases were brought on both sides of the membrane and the amount of solvent removed was determined under different experimental conditions. This behaviour was also investigated for membranes with dibutylphtalate (DBP), dioctyladipate (DOA) and o-NPOE as solvent to enable a further comparison with the instability results obtained in chapter 3. When using an SLM with decanol or DBP the aqueous phases were saturated with the solvent in question in the way described before to exclude solubility effects causing SLM-instability.

To simplify the system, these experiments were carried out in the absence of carriers in the solvents. For the same practical reasons as mentioned before Celgard was used as support. The experimental conditions (duration of the experiment, waterflow velocity and NaCl concentration) were chosen such that the instability effects could be measured accurately. In figure 4.3 the removal of the various solvents from the membranes is given as a function of the NaCl concentration in the aqueous phases. These measurements were made after a period of 7 hours and the flow velocity of the aqueous phases was 5.5 ml/sec.

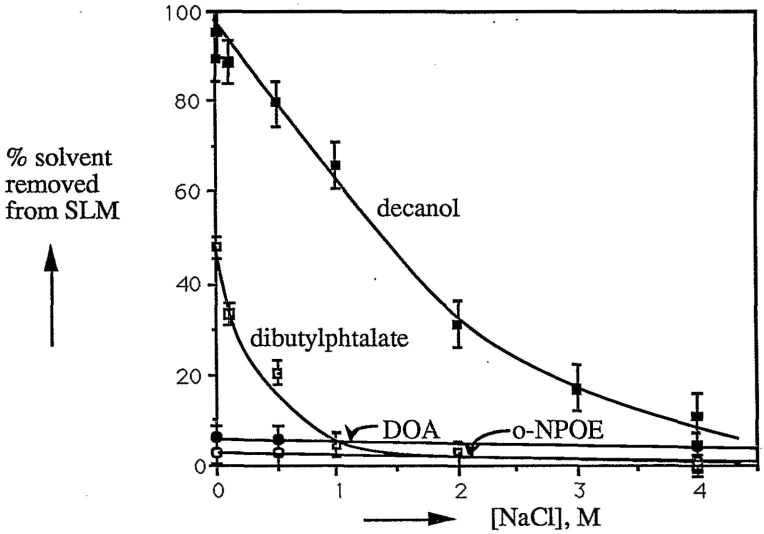

Figure 4.3. Solvent removal from SLM after 7 hours as a function of [NaCl] of the aqueous phases; water flow rate: 5.5 ml/s; F- and S- side equal salt concentration.

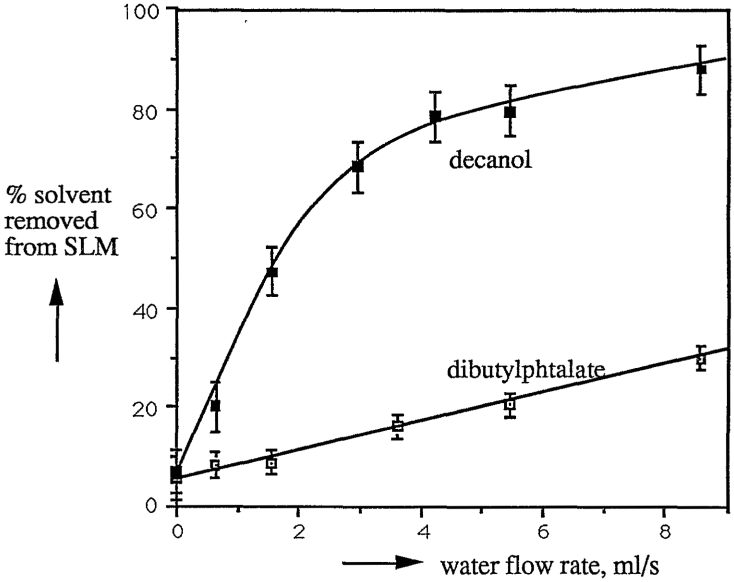

Figure 4.4. Solvent removal from SLM after 7 hours as a function of flow rate of the aqueous phases; $[NaCl]_F = [NaCl]_S = 0.5$ *M.*

Figure 4.4 shows the removal of decanol and DBP from the membrane as a function of the water flow velocity. This behaviour has not been studied for DOA and o-NPOE because of the small amount of these two solvents removed from the membrane at a flow velocity of 5.5 ml/s.

Finally the removal of decanol as function of time is examined and given in figure 4.5.

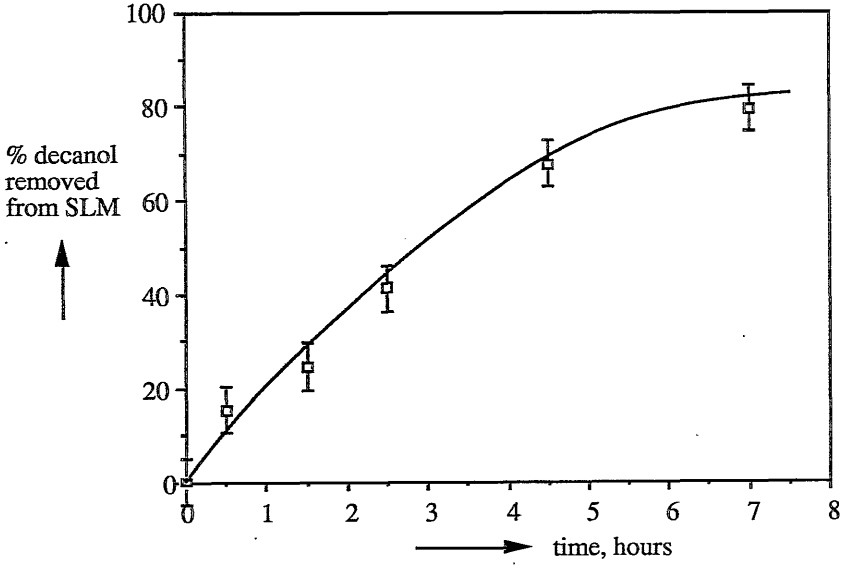

Figure 4.5. Decanol removal from SLM as a function of time; $[NaCl]_F = [NaCl]_S$ = 0.5 M; water flow rate: 5.5 ml/s.

From the results given in figures 4.3 to 4.5 it can be concluded that decanol and DBP are being removed gradually from an SLM and that the amounts removed increase with a decrease in the salt concentration of the aqueous phases and with an increase in their flow velocities. This result is in agreement with the results of paragraph 4.3.1 and chapter 3. It shows why, in chapter 3, with a stripping phase of 0.5 M NaCl, more decanol and DBP is removed from the membrane than using 4.0 M NaCl. Furthermore it explaines why the DBP-membrane failed at a composition of 0.5 M NaCl in the stripping phase and stayed intact with 4.0 M NaCl.

On the other hand we find that DOA and o-NPOE are hardly removed from the membrane, even with low salt concentrations in the water phase.This is in agreement with the results given in chapter 3, in which the use of these two solvents leads to relatively stable SLMs.

These results clearly show that the instability of SLMs is not caused by the presence of an osmotic pressure difference over the membrane: there simply is no osmotic pressure difference operative during these experiments.

4.4.3.2. Removal of carrier

During the long term permeation experiments described in section 4.4.2 we found that the carrier TOMA was removed much faster from the membrane than TeOA. When shaking aqueous phases with LM-phases in a test tube sometimes relatively stable emulsions are formed, depending on the composition of the phases. In all cases more LM-phase is being emulsified and more stable emulsions are formed in the presence of TOMA than in the presence of TeOA. Based on these data the hypothesis arises that SLM-instability does result from the formation of stable emulsions. We also found that less stable emulsions were formed when the salt concentration in the aqueous phases was increased. To test the hypothesis that emulsion formation causes SLM-instability, the influence of the composition of the aqueous phases on SLM-stability has been determined. Like before completely identical compositions were chosen for the feed and stripping phase at both sides of the membrane.

At first the aqueous phases were analysed for the presence of carrier. Due to adsorption of the carrier to the glass-parts of the apparatus these measurements were time dependent and therefore irreproducible. Because an accurate determination of the carrier was impossible in this way it was decided to study the removal of carrier by analysing the residual carrier content in the SLMs itself. A disadvantage is that this method is destructive which means that for the determination of the leaching out behaviour as a function of time different membranes had to be tested. In these experiments the conditions again were chosen such that the instability effects were well measurable.

Results

In figure 4.6 a the removal of the carriers TOMA and TeOA (from LM-phases with o-NPOE as solvent) is given as a function of the NaCl-concentration in the aqueous phases. For the sake of clearness the curves representing the system with TeOA as a carrier are plotted bold-faced.

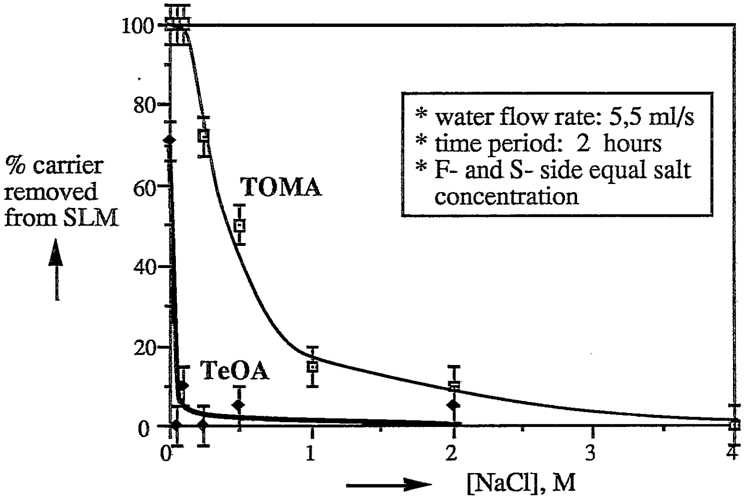

Figure 4.6 a *Carrier removal as a function of NaCl-concentration in the aqueous phases and of carrier structure; (solvent: o-NPOE)*

Because of the steep change in TeOA removal when aqueous phases with very low salt concentrations are used, we examined carrier removal from the membrane in more detail in the region of these low salt concentrations. The results are given (on a logaritmic scale) in figure 4.6 b. In these experiments NaCl-solutions as well as $NaClO_4$-solutions were used as the aqueous phase.

To obtain the mass of the LM-phase removed (i.e. carrier and solvent) the weight of the membranes was determined before and after the experiments. The mass of the carrier removed was calculated from spectrophotometric analysis of the remaining LM-phase. The quantity of o-NPOE which had been removed from the membrane was obtained from these values. Based on these data the relative amounts of carrier and solvent removed are calculated as a function of the salt concentration. In table 4.2 these data are given for the experiments in which NaCl-solutions were used.

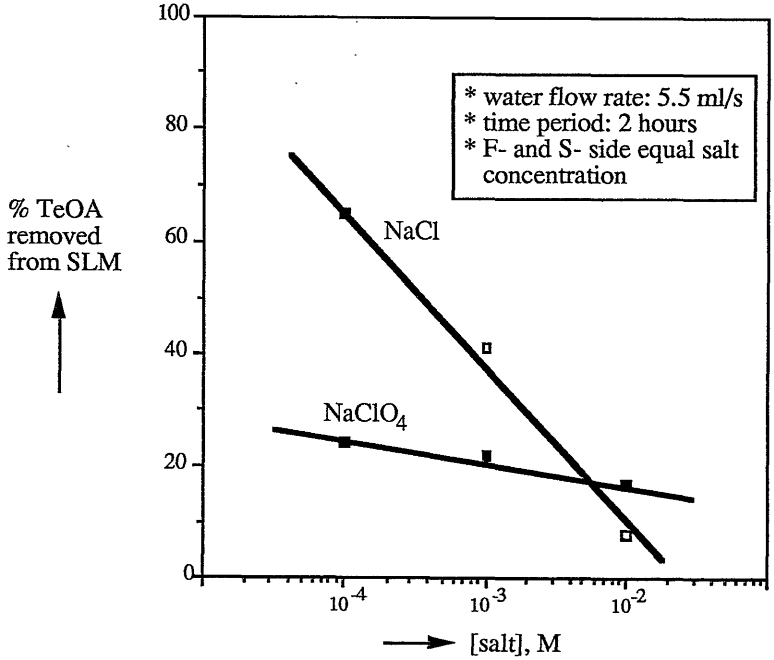

Figure 4.6 b. Removal of TeOA (from LM-phases with o-NPOE as solvent) as a function of type of salt and salt concentration

Table 4.2. Relative removal of carrier and solvent from SLMs for small NaCl concentrations (equal salt content at F- and S-side)

[NaCl]	total LM-phase removed	removal of carrier	removal of o-NPOE	carrier content of removed LM-phase
	± 0.2 mgram			
10^{-4} M	1.7 mgram	1.5 mgram	0.2 mgram	73 - 100 %
10^{-3} M	1.2 mgram	0.9 mgram	0.3 mgram	59 - 100 %
10^{-2} M	0.9 mgram	0.2 mgram	0.7 mgram	6 - 43 %

Figure 4.7 shows the carrier removal from the membrane as a function of the flow velocity of the feed and the stripping phases for a number of cases with varying salt concentrations in the aqueous phases and at different measuring times.

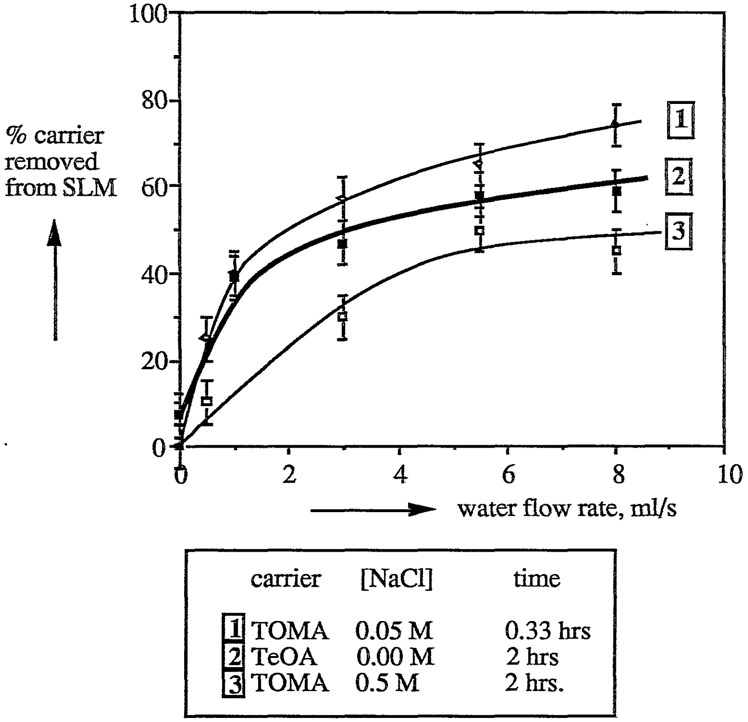

Figure 4.7. *Carrier removal from LM-phases with o-NPOE as solvent as a function of flow rate of aqueous phases*

Figure 4.8 shows the removal of carrier from the membrane in relation to the measuring time for different salt contents in the aqueous phases.

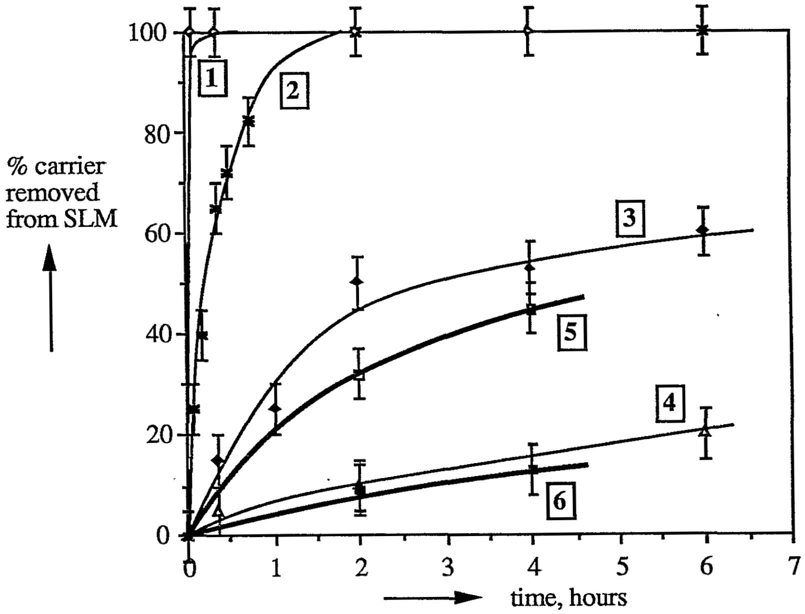

Figure 4.8. Carrier removal as a function of time; carrier TOMA (curves 1 - 4), TeOA (curves 5, 6); solvent o-NPOE; waterflow 5.5 ml /s; [NaCl]: 0.000 M (1), 0.05 M (2), 0.5 M (3), 2.0 M (4), 0.001 M (5), 0.01 M (6). Salt concentration on F- and S-side equal.

Figures 4.6 a and 4.6 b show that the removal of carrier from the SLM depends on the nature of the carrier, the salt concentration in the aqueous phases and the nature of the salt used. An increase in NaCl-concentration in the water phases leads to a decrease in the percentage of carrier that is removed from the membrane. Furthermore from figure 4.8 and 4.7 it follows that this removal increases gradually with time (till complete removal is reached) and increases when enhancing the flow velocity of the aqueous phases.

From the various figures it is evident that under comparable conditions the carrier TOMA is removed much faster from the membrane than TeOA. The large increase in

TeOA removal at high salt dilutions (10^{-2} to 10^{-4} M NaCl) is quite remarkable. Even more remarkable is the influence which ClO_4^-- ions in the aqueous phases have on the stability of the membrane (see figure 4.6 b). Even extremely low concentrations of this type of salt (10^{-4} M) suppress the removal of the carrier from the membrane quite effectively.

With these rather simple laboratory experiments a rapidly applicable method has been developed which can provide relevant information on the influence of various stability factors of our SLMs. Perhaps this method is also applicable for other SLM-systems so that it can provide a prediction (on short term) for the long term permeability and stability behaviour of the membranes.

Considering the correlation between the formation of emulsions, in test tube shaking experiments, and the removal of carrier from the membrane, these facts reinforce the hypothesis that formation of emulsions causes the SLM-degradation.

The results given in table 4.2 can also be used to get a rough estimation of the size of the emulsions droplets which are removed from the membrane for the system with TeOA / o-NPOE as LM-phase. Assuming that the concentration of carrier in the bulk of the emulsion droplet is equal to the concentration in the bulk of the liquid membranes (0.2 M) and that the skin of the spherical emulsion droplet consists of a close packed monolayer of TeOA-molecules with a cross-sectional diameter of 0.8 nm (chapter 2) the following average emulsion droplet diameters can be calculated.

Table 4.3. *Calculated average size of emulsions droplets removed from TeOA / o-NPOE membranes by a lateral flow of NaCl-solutions*

[NaCl]	diameter of emulsion droplets removed from SLM
10^{-4} M	2 - 8 nm
10^{-3} M	2 - 11 nm
10^{-2} M	20 - 140 nm

The relative errors in table 4.3 are large because the relative error in the determination of the carrier content of the removed LM-phase was rather large and the calculation of the size of the emulsion droplets is very sensitive for this quantity.

4.4.4. Emulsion formation and stability

As already mentioned before, shaking an LM-phase with an aqueous phase leads to a more or less turbid emulsion phase, depending on the composition of the phases. This occurs for LM-phases containing carriers as well as for pure solvents. Studied microscopically the emulsions appear to contain moving small spheres. Depending on the preparation method these emulsions droplets have sizes varying from 0.1 μm to tens of microns (as determined with the Mastersizer ®).

The emulsions were characterized by measuring the zeta-potential of the droplets and the stability behaviour of the emulsions was quantitatively studied by turbidity measurements as a function of time. For these measurements, in the systems without carrier, decanol was chosen as the organic phase because this solvent provides the largest instability effects, also depending on the salt content of the aqueous phase. A comparison with other pure solvents is hard to make because of the influence of the specific gravities on the light transmission at the time of measurements. For a correlation with previous experiments (4.4.3.2) the LM-system with o-NPOE as solvent and TOMA or TeOA (0.2 M) as carrier has also been studied.

Zeta-potential

The results of the electrophoretic measurements for a number of systems emulsified in demi water are given in table 4.4.

Table 4.4. *Zeta-potentials for emulsions of LM-phases in demi-water*

emulsified LM-phase	zeta-potential (mV)
decanol	- 33
TeOA / o-NPOE	+ 41
TOMA / o-NPOE	+ 58

Light transmission measurements

Decanol; the light transmission as a function of time for 50 ml aqueous phase with different salt content after 3 minutes of stirring with three droplets of decanol is plotted in figure 4.9.

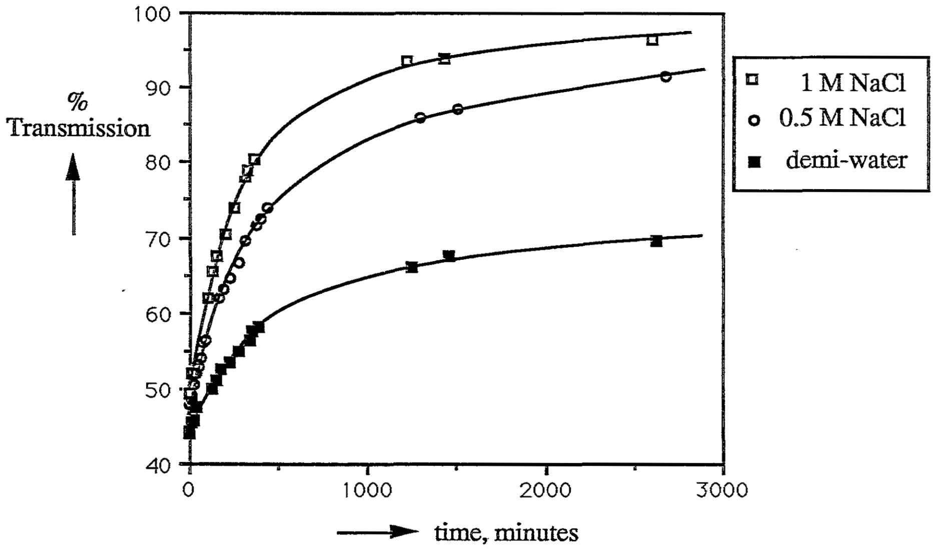

Figure 4.9. *Light transmission of decanol emulsions (obtained by stirring) as a function of time and NaCl-concentration*

In all cases the same trends were observed. An increase in salt content leads to more rapid clarification of the emulsions. However the reproducibility of these measurements is low.

LM-phases with carrier; the behaviour of emulsion formation of o-NPOE containing carrier is studied by shaking 1 ml organic phase with 3 ml NaCl solution in a spectrophotometer tube. The transmission of the resulting emulsion after 5 minutes as a function of NaCl-content is given in figure 4.10. At low salt concentrations the emulsions with TOMA as carrier were very stable. Even after several months no coalescence of the droplets was observed.

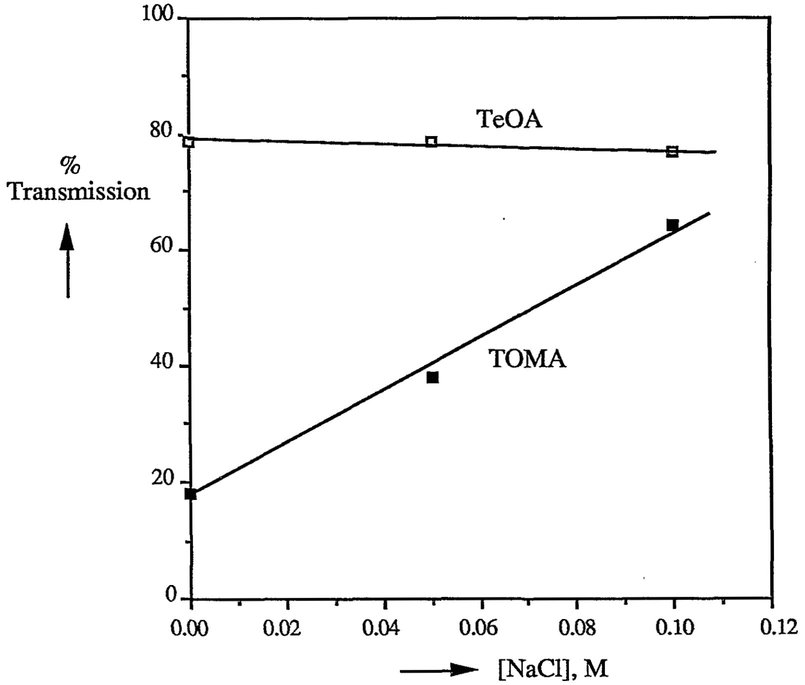

Figure 4.10. Light transmission of emulsions (obtained by shaking) as a function of NaCl concentration and type of carrier; solvent: o-NPOE

LM-phase with TeOA as carrier; it is clear from previous measurements that almost no emulsion formation took place of the LM-phase with TeOA as carrier under given conditions. Since it was assumed earlier that the removal of this carrier from the membrane by shearing with aqueous phases having a very low salt content could also be ascribed to the formation of emulsions, a more powerful method (ultrasonic vibration) has been used to prepare emulsions of this LM-phase. By diluting the so formed emulsions using aqueous solutions with different salt content the stability behaviour of the emulsions could be studied as a function of the salt content under comparable starting conditions. In this way the problem of the poor reproducibility of emulsion formation by shaking or stirring is avoided and the results can be compared also for different types of salts in the aqueous phases. An example of the change in transmission as a function of time when the NaCl content is varied is given in figure 4.11.

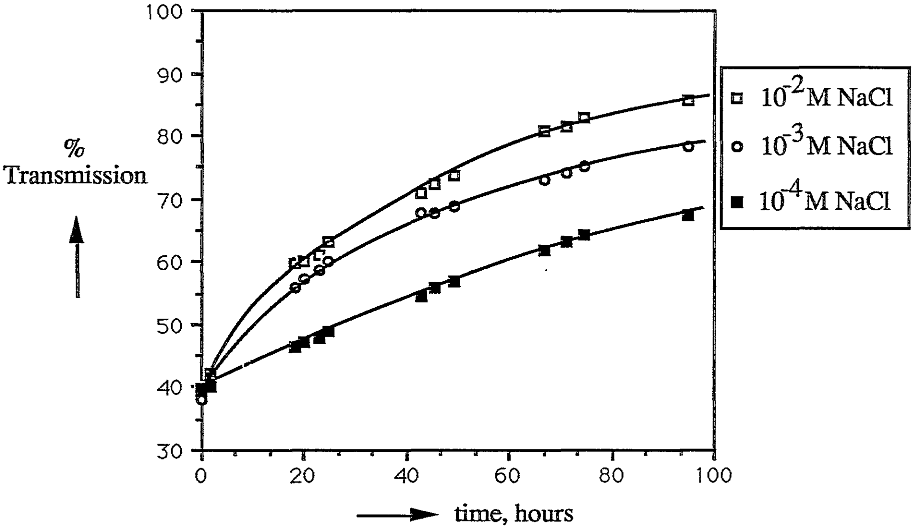

Figure 4.11. Light transmission of TeOA / o-NPOE emulsions (obtained by ultrasonic vibration) as a function of time and NaCl-concentrations

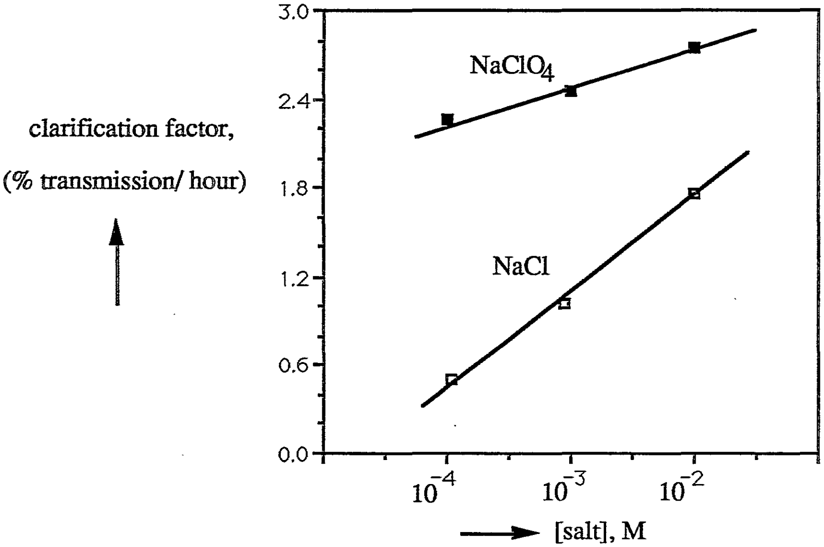

Figure 4.12. Clarification factor at t --> 0 for TeOA / o-NPOE emulsions as a function of type of salt and its concentration in aqueous phases

As an indirect measure for the instability of the emulsions we used the clarification factor. This value can be determined from the slope of the light transmission curve extrapolated to short times (Δ % transmission / time). This factor is plotted in figure 4.12 as a function of the salt content in the aqueous phases.

Discussion of emulsion stability measurements;

Table 4.4 shows that in the three systems studied emulsions are present which are stabilized by charge. The negative zeta-potential for the decanol emulsions is problaby caused by the adsorption of negative ions at the oil / water interface. Usually the anions will be somewhat more oil soluble and adsorbable than the cations, so the oil droplets should have a net negative charge (4).

For the systems with carrier the positive zeta-potential is explained by the adsorption of positively charged quaternary ammonium ions at the droplet interface. The larger zeta-potential of emulsions with TOMA as carrier agrees with the more surface active behaviour of this carrier in comparison with TeOA.

From figures 4.9, 4.10 and 4.11 it follows that for all three systems mentioned the turbid emulsions become transparant more rapidly for increasing NaCl concentration. This is caused by the creaming or sedimentation of coalesced emulsions droplets. The decreasing stability of the emulsions when increasing the salt content is explained by the "DLVO-theory" (5) which describes the stability of colloidal systems. Charge stabilized emulsion droplets encounter Londen- van der Waals attraction forces and electrostatic repulsion forces by the overlap of the electrical double layer of the droplets. The zeta-potential, the potential at the hydrodynamic shear plane, is a measure for the repulsion energy and so for the stability of the emulsions. By increasing the salt content this electrical double layer is getting thinner and the repulsion forces of the emulsions droplets will decrease by which their stability decreases.

The stationary velocity v by which a stabilized emulsion droplet creams or sediments due to the difference in density with the continuous phase, is given by (6):

$$v = \Delta d \cdot g \cdot r^{2} \cdot 2 / 9 \eta$$

In this formula η is the viscosity of the medium, g the acceleration due to gravity, r the radius of the emulsion droplet and Δd is the difference in density between the droplet phase and the water phase. From this equation it follows that by increasing the radius of the emulsion droplets, due to coalescense, the emulsions will cream or sediment more rapidly and so they will clarify more rapidly.

Because decanol has a density of 0.83 coalesced decanol emulsions will cream. When studying the influence of the salt content on the creaming of these emulsions a correction had to be made for the increase in the density difference when increasing the salt content. The effect of this correction is rather small (e.g. 17 % for [NaCl] = 0.5 M compared with demi-water) as compared with the differences in the turbidity of the decanol emulsions (see figure 4.9, almost a factor of 2), that it can be concluded that the stability of decanol emulsions does decrease when increasing the NaCl concentration.

The LM-phases with o-NPOE as solvent and TOMA or TeOA as carrier have a density of 1.03 g/ml. Because aqueous solutions with a NaCl concentration lower than 10^{-2} M have densities below 1.0005 g/ml, the coalesced emulsion droplets will sediment. The increase in density of the aqueous phases with these very small salt concentrations is so minute that it has no measurable influence on the behaviour of sedimentation. So here also we can conclude that for increasing NaCl concentrations the emulsions are getting less stable.

The irreproducibility in the formation of decanol emulsions when stirring the organic / aqueous phases is quite normal for these type of systems. It correlates with the fact that emulsification is a complicated process and that this process until now is not very well understood as was expressed by Walstra (7) in the following way: "Unfortunately, much knowledge about emulsification is still of a cookbook nature."

From figure 4.10 it followes that the LM-phase with TOMA as carrier is emulsified much better than using TeOA. This is caused by the differences in geometric structure of the carriers. It is known from literature that the structure of the surfactant plays an important role when forming emulsions. Generally a surfactant dissolved in an organic solvent is less surface active when the hydrophilic group is placed more in the centre of the molecule. For our system this means that the TOMA-molecule having one methylgroup is much more surface active than the TeOA-molecule with its symmetrical structure of four octyl chains.

Apart from the structure of the carrier molecule the type of counter-ion is also of importance for the stability of emulsions, as is shown in figure 4.12. The emulsions with perchlorate-ion as a counter-ion had a much higher clarification rate than with chloride-ion at equal salt concentrations. Two possible explanations for this are:

- because the perchlorate-ion is larger than the chloride-ion, it will show more specific adsorption, by which it will have a larger effect on the charge compensation;
- the perchlorate-ion is less hydrated as compared to the chloride-ion (according to the Hofmeister series, see chapter 2). Therefore the perchlorate-ion has a stronger interaction with the ammonium cation at the interface compared to the chloride-ion.

For both reasons the electrical double layer of the emulsion droplet with perchlorate-ions will be thinner and the repulsion energy will be lower which results in less stable emulsions.

4.4.5. SLM-degradation by emulsion formation

We want to point out here that we have three clear examples of a direct correlation between membrane instability (solvent and carrier removal run parallel with membrane instability) and emulsion stability of the LM-phase dispersed in aqueous solutions. These examples are:

a Comparing figures 4.3 and 4.9 for decanol as LM-phase (without carrier) it is seen that an increasing salt content in the aqueous phases decreases the solvent removal from SLMs, hence enhances membrane stability (figure 4.3), while the stability of decanol emulsions is decreased (transmission enhanced at higher salt concentration, see figure 4.9).

b A similar correlation is found for the salt effect on carrier removal and emulsion stability for the system with o-NPOE as solvent and TeOA or TOMA as carriers, figures 4.6 a and 4.10. Especially for TOMA the high level of carrier removal at low salt concentration, giving a very instable membrane (figure 4.6 a), correlates strongly with a low level of light transmission indicating a stable emulsion at low salt content (figure 4.10). On the other hand the system with TeOA as carrier shows for all NaCl concentrations, except for extremely low values, both a small percentage of carrier removal (figure 4.6 a), hence more stable membranes, and a high light transmission for the emulsions (figure 4.10), i.e. instable emulsions.

c Finally a comparison between figures 4.6 b and 4.12 for the system with o-NPOE / TeOA as LM-phase and very low salt concentrations in water provides the same correlation as above between a decrease in carrier removal (figure 4.6 b) and an increase in emulsion clarification (less stable emulsions) for the higher salt content. Furthermore the most stable SLMs are formed for the system with perchlorate as counter-ion, which has the highest emulsion clarification factor (least stable emulsions).

In view of this significant similarity between the stability of emulsions and the instability of SLMs the conclusion is justified that instability of SLMs is caused by the loss of emulsion droplets from the LM-phase into the aqueous phase.

For the sake of completeness it is put forward once more that a correlation of any importance is not found between the instability of SLMs and other physical parameters; e.g. the relation between the SLM-instability and the lowering of the interfacial tension is not unambigious (as was already mentioned in chapter 3). The large influence of the salt content on the removal of LM-phase from the membrane is not at all reflected in the change in interfacial tensions between the LM-phase and the aqueous phases (see chapter 3).

Molecular solubility of components from the LM-phase into the aqueous phase can also be excluded as a cause for these instability effects since neither the carrier TeOA nor solvent o-NPOE do show any substantial solubility in the aqueous phase. In contrast it was shown from the experiments described in our study that they do form emulsions when mixed thoroughly with the aqueous phases.

The interfacial tensions between the different LM-phases and the aqueous phases (chapter 3, table 3.2) are so large that the instability effects of the SLMs can not be attributed to spontaneous formation of emulsions. It is evident that, when in a certain system emulsions could form spontaneously between the LM-phase and an aqueous phase it would undoubtedly lead to notorious SLM-instability effects.

A mechanism which does agree with the instability phenomena observed, is that local deformations of the liquid meniscus in the pore of the support may lead to the splitting off of emulsion droplets. The roughly calculated sizes of emulsion droplets removed from the system with TeOA / o-NPOE as LM-phase (table 4.3), show that these emulsion droplets are small enough that only a part of the meniscus has to be deformed. This means that for a pore diameter of about 200 nm and a droplet size from 4 to 80 nm only about 2 à 40 % of the width of the meniscus has to be deformed. Such local deformations are given schematically in figure 4.13.

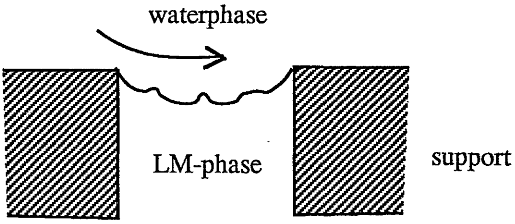

Figure 4.13. Local deformations of the meniscus of the LM-phase in the pore of the support

These deformations can originate from one of the following sources:

- "Kelvin - Helmholz instabilities"; these instabilities arise when two phases move with different velocities parallel to the interphase (8). It causes, for instance, waves to develop on a water surface over which the wind blows.
- vibration of the membrane; because the membrane is not supported by a rigid screen it is repeatedly deformed a bit due to the pulsating aqueous phases. These vibrations can cause formation of ripples on the surface of the LM-phase, because any disturbance of the interface will cause waves to develop (7).

The next step then is to explain how these ripples at the interface can lead to the formation of droplets which were found to be the cause for membrane degradation. A possible explanation is the formation of interfacial tension gradients which result in Marangoni-effects. If the interface is locally curved so that the concave side is the phase that provides the surfactant, the curved part will have a higher interfacial tension, since it receives the smallest quantity of surfactant molecules per unit surface area. Hence interfacial transport of surfactant and a flow of liquid dragged along towards the point of the strongest curvature will occur leading to an instable situation. This may well cause droplet shredding. However, the action of dynamic interfacial effects forms a formidable problem that is far from being understood (7).

That we are dealing with Marangoni effects is also indicated by the very small sizes of the emulsion droplets removed from the membrane (table 4.3). The formation of emulsion droplets, as a consequence of Marangoni effects, with diameters varying from 10 to 50 nm has for instance been published earlier (9).

Table 4.3 shows that when decreasing the salt content in the water phases also the size of the emulsion droplets which are removed from the membrane decreases. So very few relatively large emulsion droplets are removed from the membrane for a salt content of 10^{-2} M NaCl in the aqueous phases, while many rather small emulsion droplets are removed for 10^{-3} M NaCl and 10^{-4} M NaCl. These results will be confirmed by experimental results described in chapter 5 (10). In other words a large number of energetically unfavourable, small emulsions droplets are formed as they are stabilized better.

From figure 4.10 it followed that under identical conditions an LM-phase with TOMA as carrier is emulsified to a larger extent than an LM-phase with TeOA as carrier. Because of the better stability of emulsions with TOMA as surfactant, emulsion droplets which are removed by lateral forces on an SLM with TOMA as carrier will in the average be smaller than with TeOA as carrier. This explains why more solvent is removed from the membrane with TeOA as carrier, which results in membrane leakage at an earlier time, as compared to the membrane with TOMA as a carrier (paragraph 4.4.2).

An emulsion droplet which is splitted off can coalesce again immediately with the "parent"-phase. Coalescence is problaby of importance only for droplets that have just been formed and have not yet acquired an equilibrium adsorption layer (7). It is clear that stable emulsion droplets, with a fully developed electrical double layer, will coalesce much less readily than emulsion droplets with a lower stability. This explains also the similarity between the stability of emulsions and the instability of SLMs.

The considerations just given are based on reference points found in the literature with respect to emulsion formation. However, it shows that there is still much obscure with regards to the mechanism of emulsion formation and the rate of coalescense. For that reason it is impossible at this moment to formulate and proof the hypothesis of emulsion formation at an SLM interface more rigorously.

Final remarks on the degradation mechanism

Removal of LM-phase will force the meniscus of the LM-phase to withdraw in the pore of the support. Water will be filling up the volume in the pore (see also chapter 3). Eventually the meniscus of the LM-phase will reorientate and be found again at one of the boundaries of the membrane. This could occur spontaneously due to the fact that there are gradients in pore-diameters in the support. The smallest pores of the support are present at the membrane surface. A REM-picture of a crosssection of an Accurel support as given in figure 4.14 illustrates this. In the Celgard support the smallest pores are also present at the boundary (11).

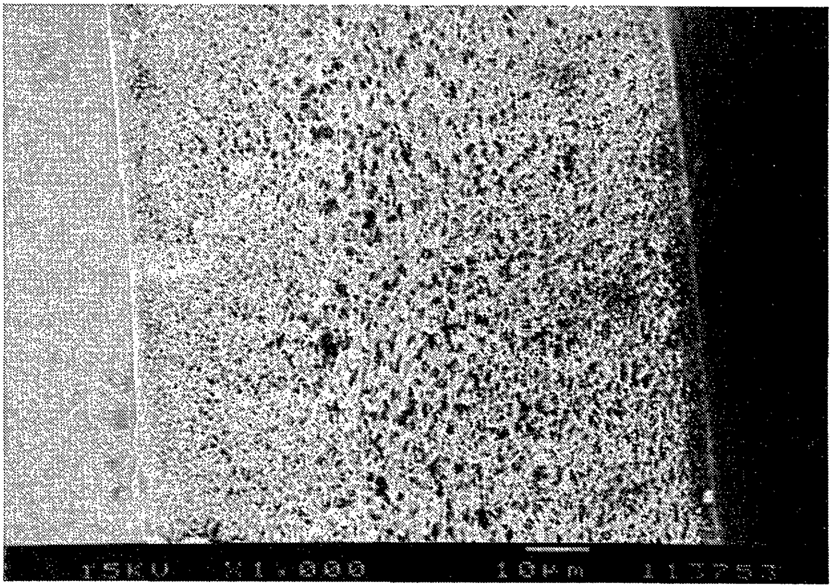

Figure 4.14. *REM-picture of a crosssection of an Accurel support; enlargement factor: 1.000.*

When spontaneous transport of LM-phase to the interface is hindered by bottle-necks in the pore structure the transport might be promoted by the vibrations of the membrane. Another driving force for transport of LM-phase to the interface of the membrane could be small pressure differences over the SLM. The pressure differences are "infinitesimal" in the experiments described here. But it is known (12) that pressure differences over the membrane as low as $0.02 \cdot 10^5$ Pa can increase instability effects of an SLM. When the meniscus of the LM-phase contacts again the water phase which flows along the membrane, the formation of emulsion droplets will continue according to the mechanism described above.

4.5. Conclusions

The results discussed in this chapter show that the instability of SLMs does not result from osmotic pressure differences or spontaneous emulsification. It is clear that the structure of the carrier, the salt content and the type of the counter ions in the aqueous phase influence emulsion stability and SLM instability in parallel fashion. Therefore we propose a mechanism for the degradation of SLMs in which shear induced break away of emulsion droplets at the feed interface plays the main role.

For the development of stable SLMs the composition of the LM-phase has to be chosen in such a way that it has little capacity for the formation of emulsions. Especially the structure of the carrier is important. Furthermore the instability effects can be diminished by varying the composition of the aqueous phases, although in practice the boundary conditions are determined by the total process occuring in the SLM-system.

Finally the type of experiments studied extensively in this chapter (in which the removal of solvent and carrier is followed by flowing identical aqueous phases parallel to the membrane surface) are very suitable for an investigation into the influence of the composition of the phases on SLM-stability. In this way the influence of various parameters on the long term permeablity of the membranes can be predicted using short term experiments.

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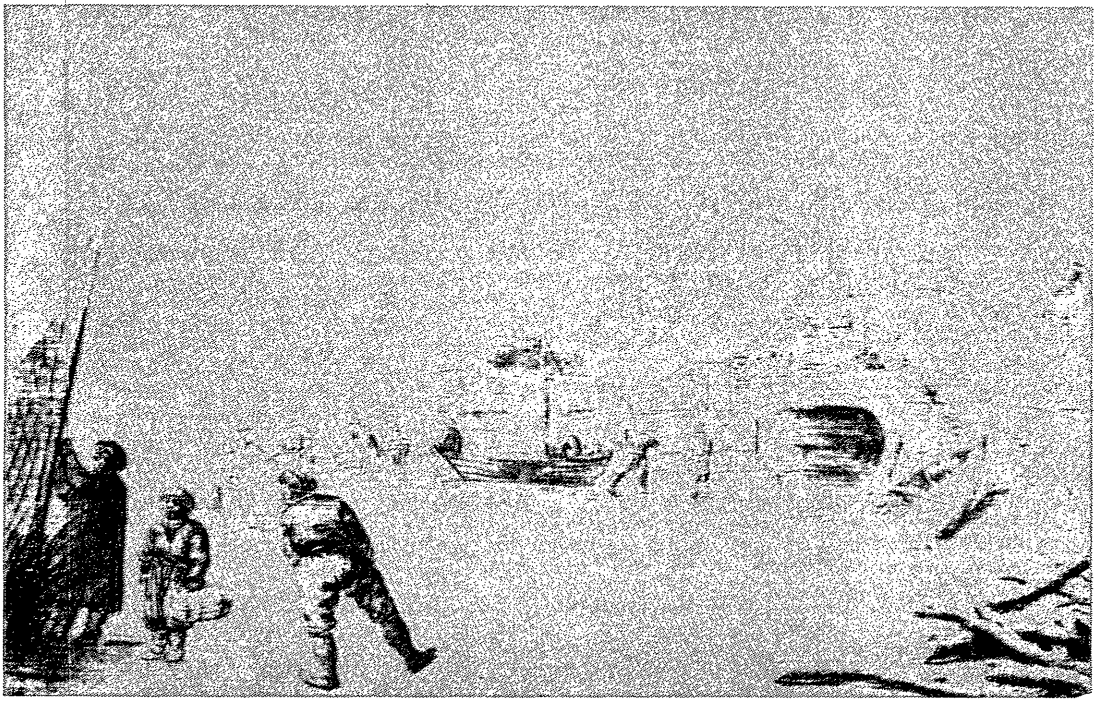

Isaak van Ostade, Winterlandschap (1621 - 1649)

Zoals een ijslaag de vorming van golven op een wateroppervlak tegengaat, zo verhindert een gellaag de vervorming van het grensvlak van een vloeistofmembraan. Hierdoor wordt emulsievorming voorkomen en neemt de stabiliteit van het membraan toe.

Chapter 5

SLM-stabilization by gelation

5.1. Summary

A new method has been developed to increase the stability of supported liquid membranes. By applying a homogeneous gel network in the pores of the support both the mechanical stability (against liquid displacement) and the long term permeability increase substantially. The flux decreases only slightly because of the open structure of the gel network. A second technique, by which a thin dense gel layer is applied to the feed side of the membrane, results in a specific suppression of the formation of emulsion droplets. The stability of the membrane increases by this treatment to values which are very promising.

5.2. Introduction

"A gel is a form of matter intermediate between a solid and a liquid. It consists of polymers or long-chain molecules cross-linked to create a tangled network and immersed in a liquid medium. The liquid prevents the polymer from collapsing into a compact mass; the network prevents the liquid from flowing away".(1)

The last part of this definition has been underlined because that's exactly what we need in order to stabilize SLMs. The idea of "gelled" liquid membranes is not new. Already in 1967 Bloch et al (2) published about the separation of metal ions by dialysis through so called "solvent membranes". This plasticised polymeric type of membrane contained an alkyl-phosphoric ester, which acted as extraction agent and as transport medium for the metal salts. One conclusion of this research was that the stability of this type of membrane had to be extended before the method is of practical value. Further research at the same institute for other systems was described in ref. 3, 4 and 5. However the conclusion remained that the stability was a problem while furthermore the flux was too small (6).

The idea to apply homogeneously swollen polymeric films is also used by other researchers; this type of swollen films is often called "solvent polymeric membranes". Examples of transport studies for different systems, in which often a specific carrier is present, are described particularly by Sugiura et al (7 - 10). Relatively high polymer contents and rather thick membranes are necessary to obtain sufficient mechanical strength. This leads to long diffusion times of the carrier molecules through the membrane which results in a low permeability. The experimentally determined fluxes, which are in the order of magnitude of 10^{-11} mol / cm^2 sec, are a factor 100 lower than the fluxes through our type of SLMs of which the transport of nitrate ions and the fluxes obtained are given in chapter 2 (11).

Swollen polymeric membranes, to which an active component is added, are also frequently used for the development of ion selective electrodes (12 - 14). For these sensor systems it is sufficient that a minute quantity of one component out of a mixture permeates to a detector room. The mobility of the selective component through the film is of minor importance for most applications because these membranes only have an analytical purpose.

To enhance the flux through this type of membranes with relatively high polymer contents, and thus to make them suitable as selective transport medium, "composite solvent swollen membranes" are developed (15, 16). These membranes have a thin gel layer onto a microporous support and they are only suitable for the separation of gas mixtures which exhibit fast diffusion in the open pores. To get an effective transport of a component out of a liquid mixture using such a composite it is necessary that the feed or the stripping phase, which both have to be in contact with the membrane liquid, penetrates into the pores of the support. Because there is no convective flow in these pores, the mass transfer will be liquid diffusion controlled and the flux will be small again.

In our institute the idea arose to enhance the stability of SLMs by gelling the LM-phase <u>in</u> the pores of the support. In this case the inert support does not only immobilize the membrane liquid but also provides mechanical strength to the gel by functioning as a kind of a frame. Only a small amount of polymer in the gel is required, without the risk of deforming the membrane by the aqueous phases which flow parallel to the membrane surface. This can lead to such an open structured gel network that it may be expected that the diffusion rate of the carrier complex through this gelled phase is diminished only to a small extent.

Based on the definition of a gel, it might be expected that the LM-phase is fixed better in the support when a polymer netwerk is present. By gelling the membrane liquid its macroscopic viscosity will increase and thus the resistance against liquid displacement out of the membrane pores will be enhanced. Especially the formation of emulsion droplets, which is the main cause of SLM-degradation (see chapter 4, (17)), will be prevented and so the stability of the membrane will increase.

Except for a study of the influence of the gel network on the permeability and the long term stability behaviour, also the mechanical stability of the gelled SLMs has been tested in this chapter. Again o-nitrophenyloctylether (o-NPOE) was used as a solvent for the various experiments; this solvent was chosen at an early stage because of its capacity to form gel networks with small amounts of polymer, while in previous reasearch (chapter 3 (18)) it appeared that, out of a selection of potential solvents, this solvent gave the most stable SLMs. Tetraoctylammonium bromide (TeOA) was mostly used as carrier, in a system in which nitrate ions were transported, but also experiments using trioctylmethylamonium chloride (TOMA) were carried out. PVC was used as gel forming polymer with o-NPOE as solvent (a number of properties of this type of gel will be mentioned in section 5.2.1); the influence of chemical crosslinking of this polymer in the network has also been studied.

Furthermore the influence of a gel network on the stability of SLMs with the least stable solvent (decanol) has been investigated. Poly(vinylisobutylether) has been used as the polymer for the gelation of LM-phases with decanol; this polymer has been used in ref. 19 for the preparation of a matrix for an ion selective electrode with decanol as solvent.

Finally, apart from these homogeneously gelled SLMs also membranes were developed in which on one side of the membrane a thin gel layer with a dense structure was applied. The formation of emulsion droplets caused by the flow of the feed solution is specifically suppressed in this way. The stability of these membranes is investigated by simulating the long term permeability behaviour to study the effect of the layer in a short period of time. This means that the degradation process of the membrane has been accelerated on purpose.

The expected effect of both types of gel networks on the fixation of the LM-phase in the pores of a support is presented schematically in figure 5.1.

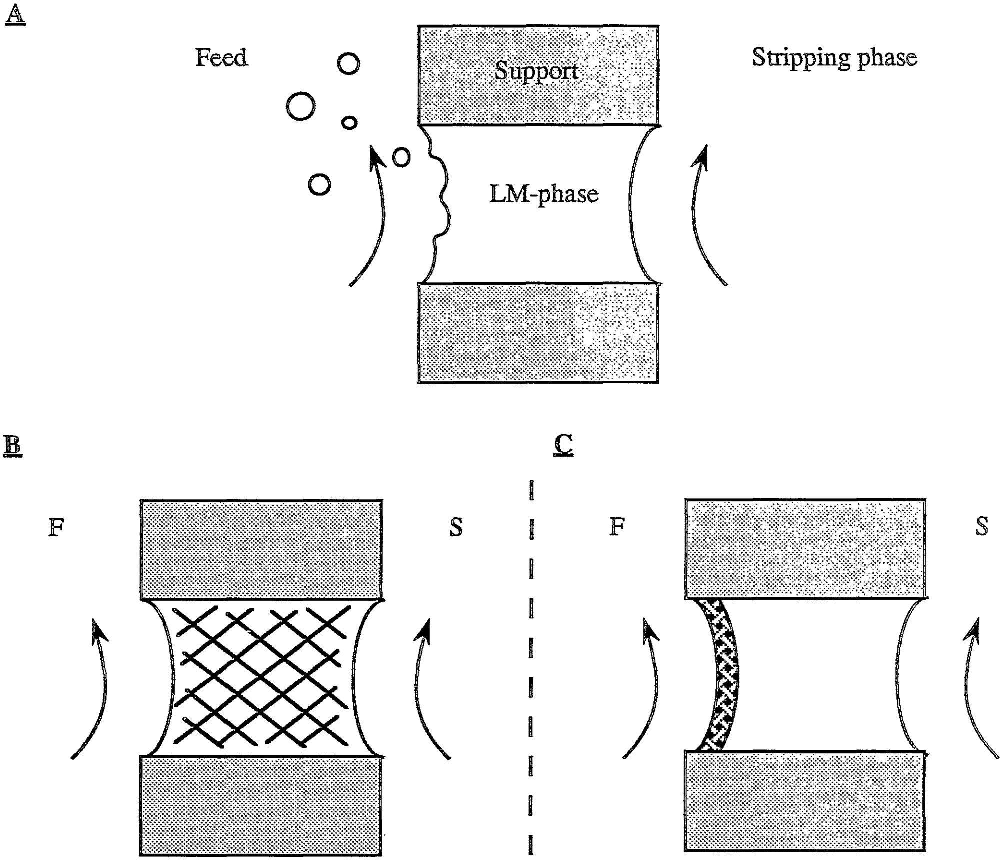

Figure 5.1. *Influence of a gel network on SLM-stability;* ***A*** *; without gel network: SLM-degradation by emulsion formation (due to local deformation of LM-phase in the pores of the support),* ***B / C****: SLM-stabilization by gelation;* ***B****: homogeneous gel network in LM-phase;* ***C****: one thin dense gel layer at the interface with the feed.*

5.2.1. PVC-gels

For the improvement of the stability of SLMs suitable for the removal of components out of an aqueous solution, by means of gelation, a *hydrophobic* gel has to be prepared.

For this purpose the choice of poly(vinylchloride) (PVC) is self-evident because we already obtain a gelled phase at low concentrations of this polymer (from 3 % on; ref. 20). Furthermore this polymer is at present the most frequently used type in related systems like ion selective electrodes (12, 21, 22). For these last mentioned applications, studies have been performed into the usefulness of other polymers like poly(urethane) (23), poly(methylmethacrylate), poly(styrene) and silicone rubber (14). All these membranes were of poorer quality, as far as stability and sensitivity are concerned, than solvent membranes with PVC as polymer.

In spite of numerous investigations, the mechanism of formation and the structure of PVC-gels still have not been fully elucidated (20, 24, 26 - 28). The most accepted hypothesis is that the gel crosslinking points are microcrystalline regions formed from occasional syndiotactic runs in a predominantly atactic polymer (26). Mechanical properties of PVC-gels like the storage modulus and the dynamic viscosity are investigated in a.o. ref. 20, 24 and 25. An important property of this type of gels is that the physical crosslinks formed are thermo reversible.

Physically crosslinked gels can be formed by means of dissolving the polymer in the solvent at increased temperature. The gel network is formed when this solution is cooled. A different preparation method is to dissolve the polymer and the solvent in a suitable volatile second solvent. Gelation takes place by evaporating the volatile solvent. For the preparation of PVC-gels tetrahydrofuran (THF) is mostly used as volatile solvent.

In this chapter we also describe experiments in which a gel network is created with a shorter mesh size by crosslinking the polymer not only physically but also chemically. For this purpose PVC with carboxylic acid groups was used as the starting material and a diamine as the crosslinking agent. The chemical crosslinking reaction, as given in figure 5.2, consists of 2 steps which are performed at room temperature. In the first step the carboxylic groups are "activated" by a di-imide compound (N, N dicyclohexylcarbodi-imide; DCC). The mechanism of this activation reaction, in which an anhydride is formed, is described in more detail in ref. 29. In the next step the reaction with the diamine compound forms chemically stable crosslinks. This reaction runs analogous to the coupling of an amine to an anhydride as described in ref. 30.

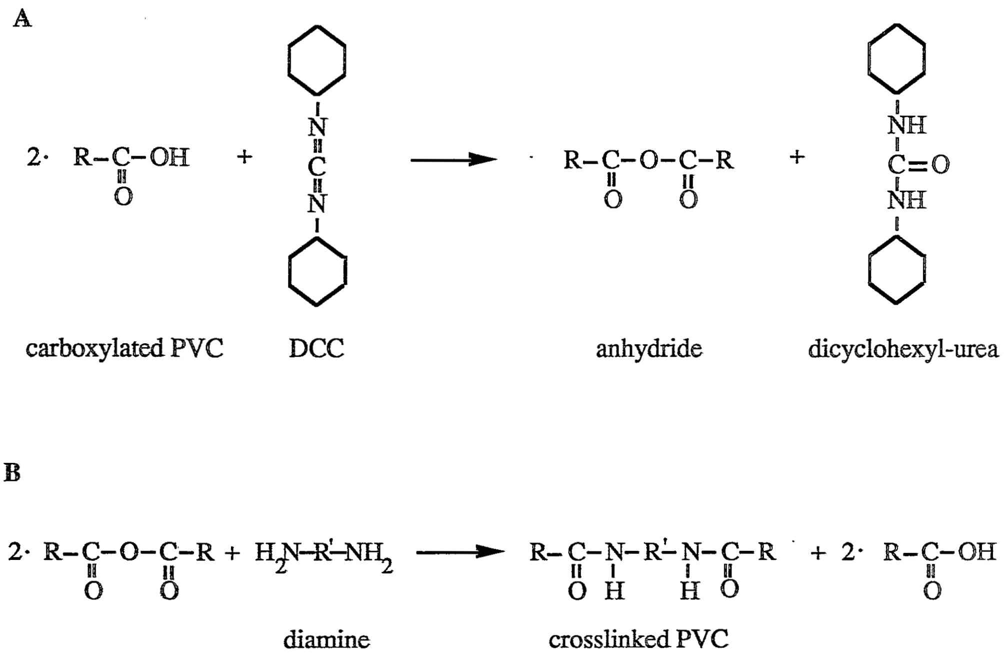

Figure 5.2. *Chemical crosslinking of carboxylated PVC;* ***A****: activation of carboxylated PVC by DCC,* ***B****: reaction of coupled polymeric chains with a diamine.*

5.3. Experimental

5.3.1. SLM-preparation

A: Homogeneously gelled liquid membranes

Two types of PVC were used for the preparation of the various homogeneously gelled SLMs: PVC-Fluka ("high molecular weight") and PVC-BASF ("Vinoflex 531"). The molecular weights of these polymers have been determined by gel permation chromatography leading to Mw values of 91, 000 for PVC-Fluka and of Mw = 80, 000 for PVC-BASF.

Accurel ® (microporous polypropylene from Enka; batch "1E/PP"; thickness: 90 µm; porosity: 73%) and Celgard® (microporous polypropylene from Celanese; thickness: 25 µm; porosity: 45%) were used as supports.

For the preparation of the gelled membranes through a temperature treatment, weighted amounts of LM-phase and polymer were put in a petri-dish. Homogeneous solutions were obtained by placing this mixture in an oven at 120 °C for half an hour while stirring this once in a while. After the supports had been immersed in this solution for three minutes the membranes were taken out of the solution and the extra substance, sticking to the membrane surface, was removed outside the oven with a tissue. Especially the membranes with high polymer contents had to be treated rather quickly, because otherwise the membranes cooled down and gel formation occurred.

When preparing gelled SLMs according to the method of using a volatile solvent the LM-phase and polymer were dissolved in THF by stirring (about 5 ml THF was used on 1 ml of LM-phase). This solution was poured out in a petri-dish and then the support was immersed in the solution. The THF evaporated from the uncovered dish. After one night, when the THF was evaporated entirely, the gel substance attached to the membrane surface was removed with a tissue.

Gelled membranes without support were obtained by pouring out a solution of polymer, LM-phase and THF in a petri-dish and by evaporating the THF. After one night the films were pulled out of the dishes carefully. The thicknesses of these membranes were determined with a Mitutoyo digital thickness meter.

The membranes used for the experiments were always prepared at least three days before.

Gelled membranes in which decanol was used as membrane solvent were prepared by the above mentioned method of using a volatile solvent. In this case poly (vinylisobutylether) (Lutonal® IC K 110 BASF) was used as polymer and again THF as volatile solvent.

B: SLMs with an interfacial dense gel layer

To apply a dense gel layer at the interface of the membrane first a liquid SLM is prepared. This means that the support is soaked in the LM-phase so that the LM-phase can penetrate into the pores. The attached liquid is removed from the surfaces of the membrane with a tissue.

Separately the gel forming polymer and LM-phase are dissolved in THF by stirring (about 10 ml THF per gram of polymer). Activator and crosslinking agent, if any, are added to this solution. The gel layer is applied by wetting a tissue in the gel-forming solution and spreading a layer with this tissue as smoothly as possible over the membrane surface. The THF evaporates during this treatment.

The following polymers were used: PVC-Fluka ("high molecular weight") and PVC-carboxylated (Janssen-Chimica) with $0.3 \cdot 10^{-3}$ equivalent carboxylic groups per gram polymer (31). N, N' dicyclohexyl carbo diimide (DCC) was used as activator and 1, 12 diaminododecaan (DDDA) and 1, 4 phenyldiamine (PDA) were used as crosslinking agents.

The total amount of PVC put on the membrane surface was determined quantitatively by gel permeation chromatography after redissolving the gel mass of a part of the membrane in THF.

5.3.2. Permeability measurements

To determine the permeability of the various SLMs the permeation set up as represented in chapter 2 (11) has been used. The SLMs were clamped in the module and a feed solution of 0.004 M $NaNO_3$ and a stripping phase of 4.0 M NaCl were circulated through the cell halves with a flow rate of 5.5 ml/s. Under these conditions the transport is limited by diffusion of the carrier molecules through the membrane liquid (see chapter 2). The flux was calculated from the slope of the curve for the nitrate concentration in the feed as a function of time.

5.3.3. Mechanical stability (liquid displacement) measurements

A new method has been developed to determine the resistance of the gelled membranes against pressure differences. For these measurements the experimental set up represented in figure 5.3 has been used.

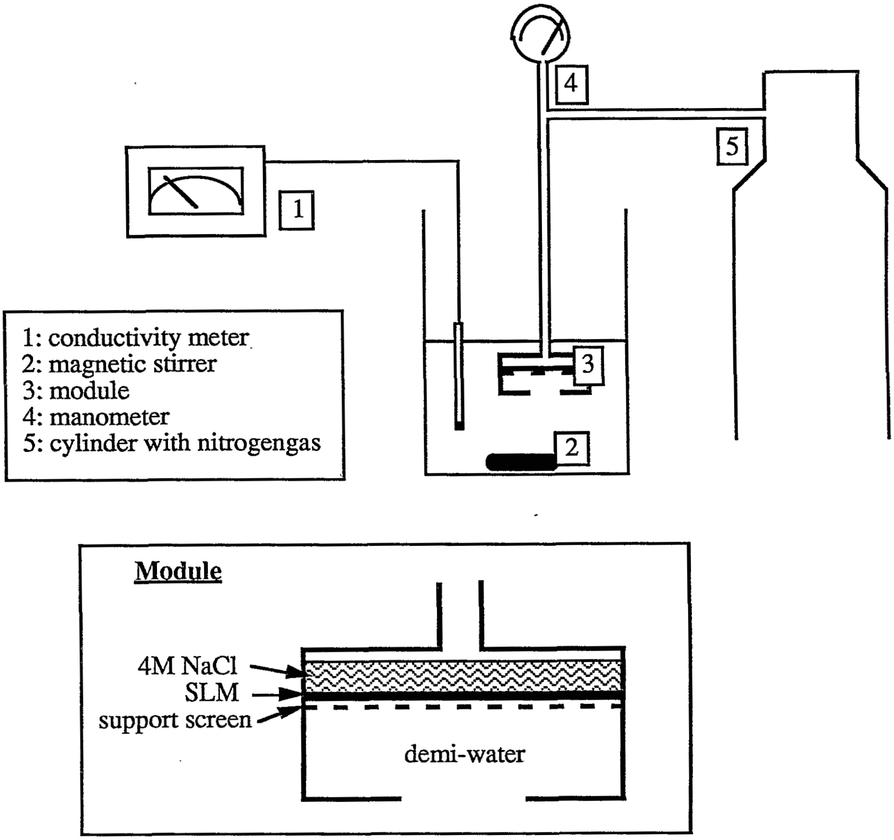

Figure 5.3. Experimental set up to determine the mechanical stability of SLMs

The membrane, supported by a screen (Millipore: xx 4504704), was clamped in a high pressure filter holder (Millipore: xx 4504700). A layer of aqueous solution of 4 M NaCl was put on top of the membrane. The module was placed in a beaker with demi-water. The support screen and thus the lower-surface of the membrane were in direct contact with the demi-water phase. The water was stirred vigorously. A N_2-pressure was put on the upper side of the membrane, after which the pressure difference ove the membrane was increased stepwise. The breakthrough behaviour of the SLMs could be determined by determining the conductivity of the demi-water phase as a function of the pressure difference.

5.3.4. LM-removal by emulsion formation

These experiments were carried out in the same way as described in chapter 4 (17) (section 4.4.3) and thus the feed and stripping phase during these measurements were given exactly the same composition when passing through the cell halves during the measuring time.

Solvent removal; in these measurements no carrier was present in the membrane solvent. The amount of LM-phase removed from the support was calculated by determining the weight of the membranes before the experiment was started and by weighing the centres of the membranes after the measurements were finished.

Carrier removal; the amount of carrier removed from the central area of the membranes was determined spectrophotometrically as described in chapter 3 (18).

5.3.5. Long term permeability

Measurements using homogeneously gelled membranes and Celgard as support.

These experiments were performed in the same way as described in chapter 4 (section 4.4.2), i.e. feed and stripping phases (with equal volumes of 130 ml) were refreshed every 3 or 4 days. The nitrate and chloride contents were measured as a function of time by analyzing samples, which were taken periodically from the feed, using HPLC. From the increase in chloride content in the feed, and the calculation of the counter transport factor as a function of time as described in chapter 3, the occurrence of direct chloride leakage from stripping phase to feed could be determined.

Measurements using homogeneously gelled membranes and Accurel as support.

The performance of these experiments was nearly the same as for the experiments with Celgard as support, except for the large feed volume of 4.1 liter (like in the concentrating experiments as described in chapter 3) that was used and the aqueous phases that were replaced by fresh starting solutions every week. After about 12 weeks the presence of small gas bubbles became visible at the surface of the membranes. These bubbles were removed by tapping.

Simulating long term permeability (by accelerated degradation).

During these measurements the permeability of a membrane was determined in the usual way by analyzing samples, which were taken periodically from the feed. For this purpose a feed solution of $4 \cdot 10^{-3}$ M $NaNO_3$ (130 ml) and a stripping phase of 4 M NaCL (130 ml) were passed parallel to the membrane surface with a flow rate of 5.5 ml/s. The flux was measured. After about 5 hours the "degradation process conditions" were installed by replacing the feed solution by an aqueous solution of 10^{-4} M NaCl, which then was passed along the membrane. The next day the stripping phase was replaced by a fresh solution of 4 M NaCl and the feed by a $4 \cdot 10^{-3}$ M $NaNO_3$ solution and the flux was determined again. The degradation process conditions were reestablished again after the flux measurement. This sequence of actions was repeated during 5 days.

5.4. Results and discussion

5.4.1. Influence of a gel network on permeability

PVC-Fluka could not be used to prepare homogeneously gelled SLMs through the temperature treatment, because of instability problems (discolouration) at 120 °C. A lower temperature could not be used for polymer contents above 5 w/w %. These problems did not occur when using PVC-BASF. Gelled SLMs were prepared with a polymer content of up to 10 % in the pores of Accurel membranes by the temperature treatment method. It appears that from 3 % PVC upwards the cooled polymer-LM solution has an extremely high viscosity indicating that we are dealing with gel formation above this polymer concentration. The influence of the polymer concentration on the permeability is given in figure 5.4.

The permeability at higher polymer content is studied also in order to get more insight in the influence of gel networks on the diffusion rate. However the preparation of these gelled SLMs via the temperature treatment gave problems. Also the PVC-BASF darkened at temperatures above 150 °C, which are needed for dissolution. Furthermore the support shrunk at these high temperatures. Therefore the method using the volatile solvent THF has been used. SLMs were prepared using Accurel as support and PVC-Fluka up to 10 % as polymer. At still higher polymer content it was not possible to remove the attached gel substance from the support with a tissue.

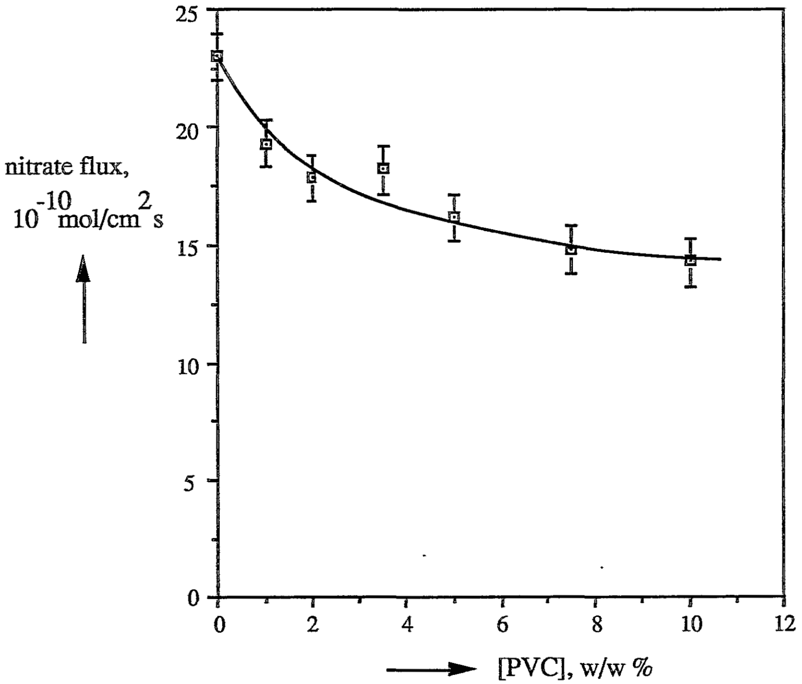

Figure 5.4. *Influence of a homogeneous gel network on SLM-permeability; solvent o-NPOE; carrier TeOA; support Accurel; polymer PVC-BASF; preparation 120 °C, 30 minutes.*

In order to get information on the permeability at very high polymer concentration, gelled membranes without a support were prepared, having polymer contents from 10 % up to 70 % PVC-Fluka, by pouring out the polymer solution and evaporating the THF. These unsupported membranes had to be relatively thick (250 to 300 µm) to be able to handle them. Still the SLMs (without support) containing 10 and 15 % PVC had insufficient mechanical strength in the permeation module. They were dragged along immediately by the aqueous phases which flowed parallel to the membranes, so the flux could not be determined. Eventually it was possible to determine the permeability for a membrane with 15 % PVC by preparing a 400 µm thick membrane, although some membrane deformation could be observed during this measurement.

For a mutual comparison of the permeabilities, the effective diffusion coefficients for the various SLMs have been calculated using the following formula:

$$D_{eff} = J * d_{eff} / \Delta C$$

In this formula J is the measured nitrate-flux through the membrane and d_{eff} (the effective pathlength of the carrier through the membrane) is calculated without making a correction for the actual presence of the gel network; d_{eff} is equal to the measured membrane thickness when no support is present. When a support is present in the membrane this value is obtained by multiplying the membrane thickness with the tortuosity factor of the support. The support tortuosity, as given in chapter 2 (11), is calculated using the formula given by Mackie and Meares and for a porosity of 73 % a value of 1.74 is calculated for this factor.

For the calculation of ΔC (the concentration gradient of carrier over the membrane) we have to be aware that the ΔC value to be used depends on the amount of carrier in chloride form at the stripping side (analogous to chapter 2: 0.96 · 0.2 M), on the porosity of the support (0.73) and on the fraction of polymer in the gel network ([PVC]). The influence of the polymer content on the diffusion rate, determined in this way, is given in figure 5.5.

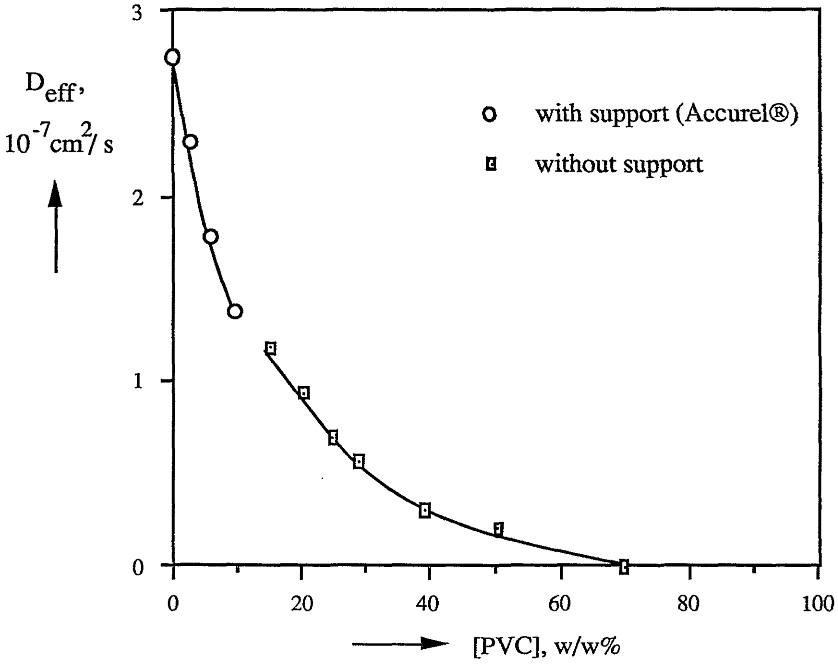

Figure 5.5. Influence of polymer concentration on diffusion rate through gelled liquid membranes; solvent o-NPOE; carrier TeOA; preparation via THF evaporation

Discussion

Figure 5.4 shows that, in spite of the increase of the macroscopic viscosity of the LM-phase with a very large factor when a gel network is present, the permeability decreases only to a small degree in case of low polymer concentrations. This can be explained by the open structure of the gel network so that the microscopic viscosity increases just slightly. This uncoupling of the macroscopic viscosity (which determines the mechanical strength of the membrane) and microscopic viscosity (which determines the diffusion rate through the membrane) can not be realized in liquid membranes without a gel network. The diffusion rate is inversely proportional to the viscosity of the LM-phase of these "conventional" SLMs.

By comparing figures 5.4 and 5.5 we observe the same trend in diffusivity for small PVC contents (up to 10 %) although the decrease in permeability in figure 5.5 being a little larger than for the membranes which are gelled via temperature treatment using lower molecular weigth PVC. It can be seen from figure 5.5 that the permeability decreases drastically for higher polymer contents to vanishingly small transport at 70 % PVC. It is gratifying that the two curves, which are based on membranes with different thicknesses and differing in the presence of a support, link so well. It can be seen as a confirmation for the correctness of the calculation of the tortuosity factor for the support used.

The most important reason for the decline in the effective diffusion rate when increasing the polymer concentration is the increase in tortuosity factor. The carrier molecules have to cover a longer pathlength through the membrane around the polymer chains.

To compare our diffusion coefficients in gelled liquid membranes with a related system, the results of Oetsch and Simon (22) are also plotted in figure 5.6. They performed experiments with an ion-selective electrode using o-NPOE as solvent and PVC as polymer. For polymer contents from 37 to 67 w/w % PVC the diffusion coefficients of a ligand through these solvent polymeric membranes were determined experimentally. For 0 % PVC, D_{eff} was estimated according to the Stokes-Einstein equation.

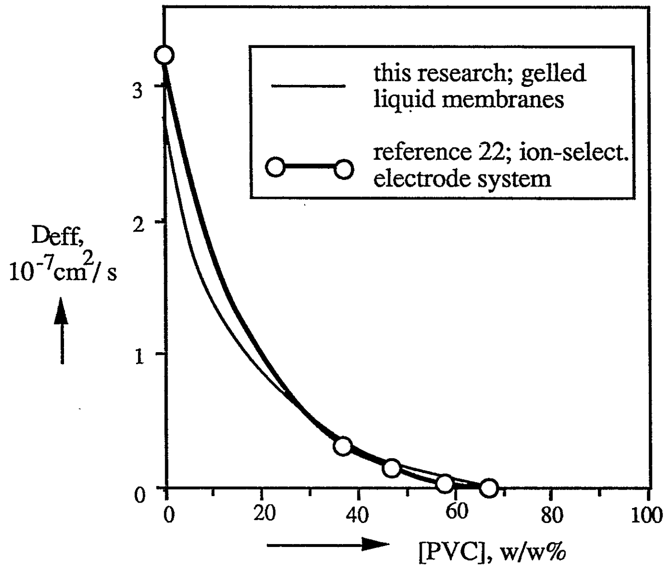

Figure 5.6. *Diffusion rates through gel networks; comparison between gelled liquid membranes and ion-selective electrode system (22).*

Figure 5.6 shows clearly that the experimentally determined diffusion rates through gelled liquid membranes agree quite well with those of a comparable electrode system. An important difference between these two methods is that the diffusion rates through liquid membranes with low polymer contents (from 0 % to 30 % PVC) can actually be determined by using a support and don't have to be estimated. Undoubtedly this method of using a support is also suitable for other systems in which the determination of diffusion coefficients at low polymer concentrations might give problems.

From the strong decrease in permeability at relatively high polymer contents it follows that, for economical reasons, in practical applications only small polymer concentrations (up to ± 10 % PVC) in the membrane will be permissible. Our measurements confirm that such open gel networks can only be handled when they are fixed in the pores of a support. In this way relatively thin membranes with sufficient mechanical strength to withstand the flow of the aqueous phases can be prepared.

5.4.2. Influence of a gel network on mechanical stability (liquid displacement)

The mechanical stability of SLMs with Accurel as support, o-NPOE as solvent, TeOA as carrier and PVC-BASF as polymer has been studied. These membranes (with polymer contents up to 10 %) were prepared via the method of PVC dissolution at 120 °C.

A reproducible method for SLMs without PVC has been developed first. On this basis it was decided to test the membranes starting with a pressure difference of $3 \cdot 10^5$ N/m^2 and increasing the pressure difference every 5 minutes with $0.2 \cdot 10^5$ N/m^2. This increase in pressure was continued till the conductivity of the demi-water phase increased strongly (SLM-breakthrough). The breakthrough curves for the membranes with different polymer concentrations are plotted in figure 5.7.

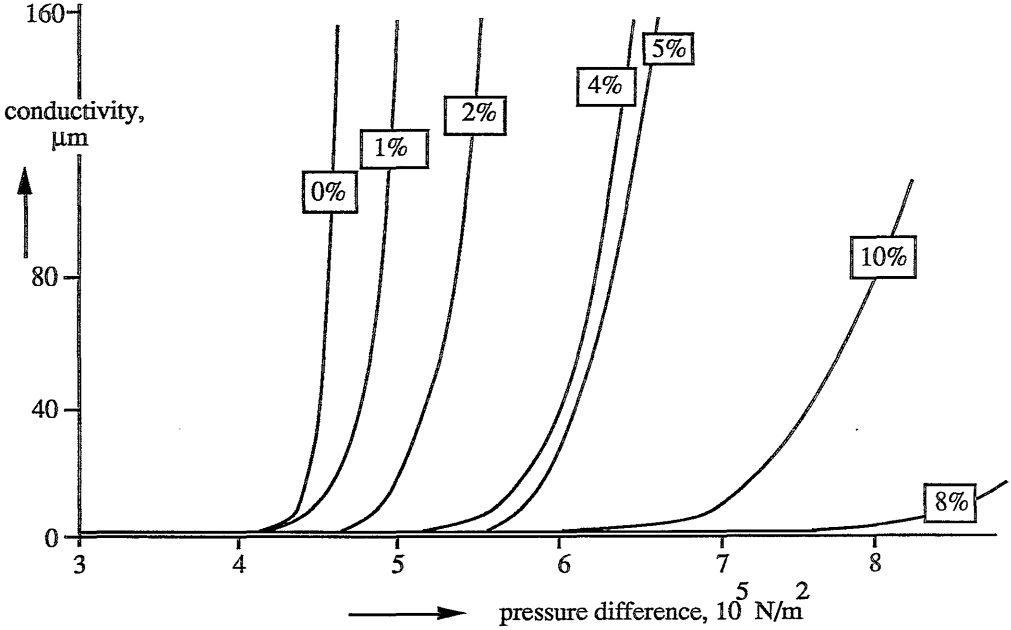

Figure 5.7. Influence of a gel network (with different PVC-concentrations) on the mechanical stability of SLMs; solvent o-NPOE, carrier TeOA (0.2M), support Accurel, polymer PVC-BASF, preparation dissolution at 120 °C (30 minutes).

From figure 5.7 it can be concluded that:

1 An SLM without PVC shows a break through at a pressure difference of a little over $4 * 10^5$ N/m^2. This value is in agreement with expectations. The break-through pressure can be calculated from the Laplace equation because we are dealing with the displacement of a liquid out of a capillary system:

$$\Delta P = 2\,\gamma_{w/LM} * \cos\Theta \,/\, r.$$

At the moment of the removal of the liquid out of the pores, $\cos\Theta$ equals 1 and the interfacial tension ($\gamma_{w/LM}$) between the LM-phase and the aqueous phase is:$16.4 * 10^{-3}$ N/m (chapter 3; table 3.2 (18)), while the pore radius (r) is: 0.1 µm (data obtained from Enka). This gives a ΔP value of: $3.3 \cdot 10^5$ N/m^2, which agrees rather well with the experimentally determined value of $4.2 \cdot 10^5$ N/m^2.

2 Considerably larger pressure differences are needed to remove the LM-phase when the LM-phase is gelled in the pores of the support. This pressure difference increases gradually when increasing the polymer content. The trend is unambiguous despite the fact that the reproducibility of the gels formed has not been verified. An explanation for this behaviour is that when increasing the macroscopic viscosity of the LM-phase (due to gel formation) the resistance against deformation of the LM-phase and thus the resistance against flow through the pores increases.

For the application of SLMs it means that the membranes have a higher resistance against pressure differences. In practice there are always small pressure differences present over the membrane, especially in the performance of the SLM-process in hollow fiber modules. Dworzak c.s. (32) e.g. measured the pressure drop in the lumen over the length of hollow fibers due to the frictional flow of liquid through the fibers. For an inner diameter of 1.8 mm and a length of 2 m. this pressure drop amounted to $0.7 \cdot 10^5$ N/m^2. Furthermore larger pressure differences (e.g. caused by faults in the apparatus) can be withstood better by gelling the LM-phase. The life time of the membranes will be extended by this increase in mechanical stability.

5.4.3. Influence of a gel network on removal of LM-phase from the support, due to emulsion formation

A more important contribution of the gel structure to the stability of liquid membranes results from the suppression of emulsion formation. This is investigated in the following experiments. Allways two aqueous phases with identical compositions were flown parallel to the membrane surface (analogous to the experiments described in chapter 4 (17)) to exclude osmotic pressure differences and the influence of this shearing flow on the composition of the membrane was studied.

solvent removal

To study the effect of a gel network on the removal of solvent from a membrane SLMs with decanol as solvent have been chosen because this compound gave the least stable membranes (see chapter 3). Furthermore Celgard is used as support, analogous to the same type of experiments as described in chapter 4 (section 4.4.3.1). In figure 5.8 the removal of LM-phase resulting from the flow of aqueous phases with 0.5 M NaCl during 7 hours is given as a function of the concentration of poly (vinyl isobutyl ether).

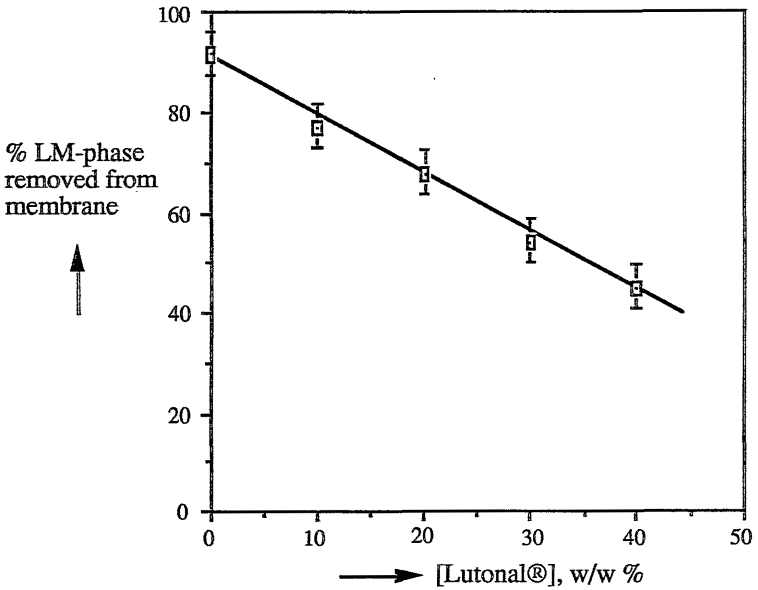

Figure 5.8. Influence of polymer content in homogeneous gel network on removal of decanol from SLM; solvent decanol; carrier:none; polymer poly (vinyl isobutyl ether); support Celgard; preparation method via THF evaporation; composition aqueous phases 0.5 M NaCl; water flow velocity 5.5 ml/s; period 7 hours.

This figure shows that by gelling the LM-phase the removal of decanol out of the membrane due to the formation of emulsion droplets is diminished. But the gel network must have a relatively high polymer content to result in a considerable reduction of the quantity of removed LM-phase when a "bad" solvent (decanol) is used.

carrier removal

To study the effect of a gel network on the removal of carrier from a membrane due to the formation of emulsion droplets, SLMs with o-NPOE as solvent and TeOA as carrier have been chosen because the instability behaviour of this type of membranes has been studied rather intensively in chapter 4. Membranes with a dense gel layer at the interfaces were used during these experiments to prevent, as specifically as possible, the formation of emulsion droplets at the interface. Relatively high polymer concentrations can be used without reducing the flux appreciably because these gel layers are very thin in relation to the total thickness of the membrane. These experiments have an orientational character and they form the basis for the long term permeability measurements which will be discussed in the next paragraph.

The membranes were provided with thin gel layers at both interfaces because identical aqueous phases (with a low salt concentration) were passed at both sides of the membrane. Accurel was chosen as support and gel layers with 40 % polymer and 60 % LM-phase were applied. It appeared, from the GPC- determination, that in all cases the amount of PVC, which was brought on the membranes, was smaller than 2 % of the total amount of LM-phase. This means that, for a total membrane thickness of 90 μm, the gel layers (with a polymer content of 40 %) were thinner than 2 μm.

Apart from gel layers with PVC-Fluka and carboxylated PVC as polymer the influence of the presence of the activator DCC in combination with carboxylated PVC has been investigated. The quantity of DCC (1 equivalent) is based on the amount of carboxylic groups present in the solution. The presence of DCC results in an crosslinking of the polymer indicated by the increase of the viscosity of the solution upon addition of the DCC to the solution of carboxylated PVC in THF. After ± 10 minutes the solution is not fluid any more (despite the presence of THF) and consequently not manageable any longer. Therefore it was necessary to apply the gel layer within a few minutes after adding the DCC to the polymer solution.

The relative amounts of carrier removed from the membrane are given in table 5.1 when aqueous phases with 10^{-4} M NaCl passed during 7.5 hours with a flow rate of 5.5 ml/s parallel to the membrane.

Table 5.1. *Influence of the presence of gel layers on the removal of carrier from the membrane; solvent o-NPOE; carrier TeOA; polymer concentration in gel layer 40 %; thickness gel layers < 2 μm; support Accurel; composition aqueous phases 10^{-4} M NaCl; water flow rate 5.5 ml/s; period 7.5 hours.*

type of polymer in gel layers	% carrier removed from SLM
no gel layer	37 %
PVC - Fluka	30 %
PVC - carboxylated	25 %
PVC - carboxylated + 1 equivalent DCC	21 %

Table 5.1 shows that the removal of carrier out of the membrane is diminished substantially by the presence of a gel network on the surface of the membrane. It can be concluded that the gel network is indeed able to suppress the deformation of the LM-interface by the aqueous phases, so that less LM-phase can be emulsified.

The results also show that this effect is larger for PVC with carboxylic groups, with or without DCC, than for normal PVC. This can be explained by the fact that extra crosslinks due to hydrogen bonding are present between the polymer chains in case of carboxylic groups and by the formation of anhydride bonds when DCC is present, both leading to a network with a shorter mesh size. Special attention will be paid to gel layers based on carboxylated PVC in the following section (in which the long term permeability of this type of membranes is simulated), especially because this polymer can be crosslinked chemically.

5.4.4. Influence of a gel network on long term permeability

The most important stability parameter for SLMs is the long term permeability behaviour. This parameter is investigated in the following experiments for both homogeneously gelled SLMs and membranes with thin dense gel layers at the interface. For the homogeneously gelled SLMs a distinction has been made between membranes using Accurel or Celgard as support. For the membranes with a dense gel layer only Accurel is used as support and the determination of the actual long term permeability has been simulated.

Homogeneously gelled membranes using Celgard as support

First the influence of the presence of a homogeneous gel network on the chloride-leakage behaviour of SLMs is studied. Celgard is used as support in these experiments in order to be able to perform the measurements in a short period of time. Apart from stable systems with o-NPOE as solvent, membranes with decanol as solvent are also investigated in order to study the principle of the effect of a gel network.

The gel networks contained only small amounts of polymer (5 %) in order to reduce the flux as little as possible. The path of the flux as a function of time for the membranes with o-NPOE as solvent and without gel network has already been treated in chapter 4 (section 4.4.2). The flux of the membranes with a gel network showed a similar behaviour. However, the starting values of the permeabilities (in agreement with the results of section 5.4.1) are roughly 20 % lower as compared with the membranes without a gel network.

The first moments at which chloride ion leakage through the membranes was observed (counter transport factor (CTF) larger than 1) are presented in table 5.2.

From table 5.2 it follows that for all systems investigated the presence of a gel network in the membrane results in a considerable increase of the resistance against SLM-failure. These positive effects of a gel network can be explained by the fact that the removal of LM-phase due to emulsion formation is reduced.

Table 5.2. Influence of a homogeneous gel network on permeation stability; support Celgard; 0.2 M carrier; preparation method via THF evaporation; feed 0.004 M $NaNO_3$ stripping phase 4.0 M NaCl.

LM	polymer	SLM-failure (CTF > 1)
decanol - TeOA	none	2 hours
ibid.	5% Lutonal® 110 (polyvinyl isobutyl ether)	> 8 hours
o-NPOE - TOMA	none	7 days
ibid.	5% PVC	> 20 days
o-NPOE - TeOA	none	4 days
ibid.	5% PVC .	11 days

It is remarkable that for the gelled SLMs with decanol as solvent no rapid chloride leakage is taking place in spite of the fact that relatively much LM-phase is being removed (see figure 5.8). Obviously the remaining part of LM-phase in the pores of the support has such a structure, due to the presence of the polymer, that channeling of the membrane is prevented. A possible explanation is that the transport of LM-phase from the pores which are situated deeper in the membrane to the interface of the membrane, where LM-removal takes place in the form of emulsion droplets, (see also chapter 4, section 4.4.5) is hindered. Because this essential step in the degradation process is delayed the moment of chloride leakage is postponed.

Homogeneously gelled liquid membranes using Accurel as support

To get information on *real* long term permeabilities obtainable with SLMs, the stabilities of some stable membranes were determined. Hence o-NPOE was used as solvent, TeOA as carrier and Accurel as support. During these time consuming investigations the influence of the polymer content on the moment of SLM-failure (chloride leakage) and on the flux as a function of time was studied.

In order to approach the practical conditions more closely, concentrating experiments with large feed volumes (4.1 L) were performed. The gelled membranes were prepared in the same way, via the temperature treatment, as the membranes of which the experimentally determined fluxes are given in figure 5.4. The counter transport factor is given as a function of time for 4 membranes with different PVC concentrations in figure 5.9. After 18 weeks the experiments were terminated.

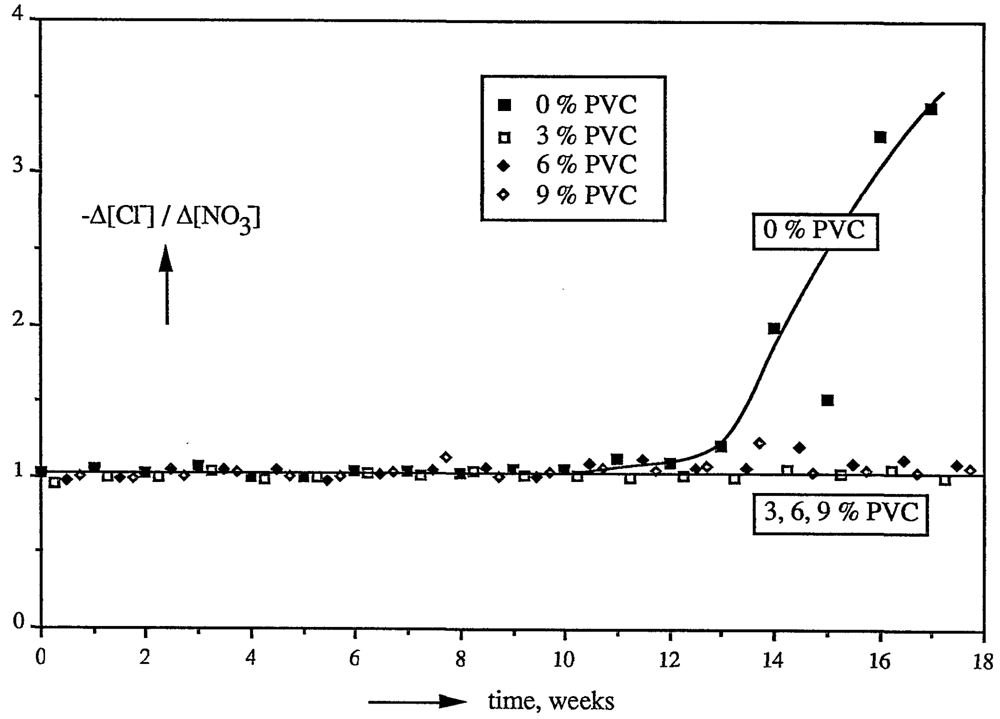

Figure 5.9. Counter transport factor (CTF) as a function of time for homogeneously gelled SLMs with different amounts of PVC; solvent o-NPOE; carrier TeOA; support Accurel; gel-forming polymer PVC-BASF; preparation method 120 °C, 30 minutes; feed 0.00 4 M $NaNO_3$ (4.1 Liter); stripping phase 4.0 M NaCl (130 ml); F & S weekly refreshed.

Figure 5.9 shows that the membrane without gel network starts to leak chloride ions after 13 weeks, while all three gelled membranes remain intact during 18 weeks. Analogous to the results of the long term permeability experiments using Celgard as support (table 5.2) it can be concluded that because of the presence of a gel network in the membrane less LM-phase is removed via the formation of emulsion droplets, leading to a substantial increase in stability.

The course of the flux as a function of time for one of the gelled membranes (with 9 % PVC) is given in figure 5.10. The other three SLMs showed a similar behaviour and are therefore not plotted. The best long term permeability results, known from literature, are also plotted in this figure to compare our results with other measurements.

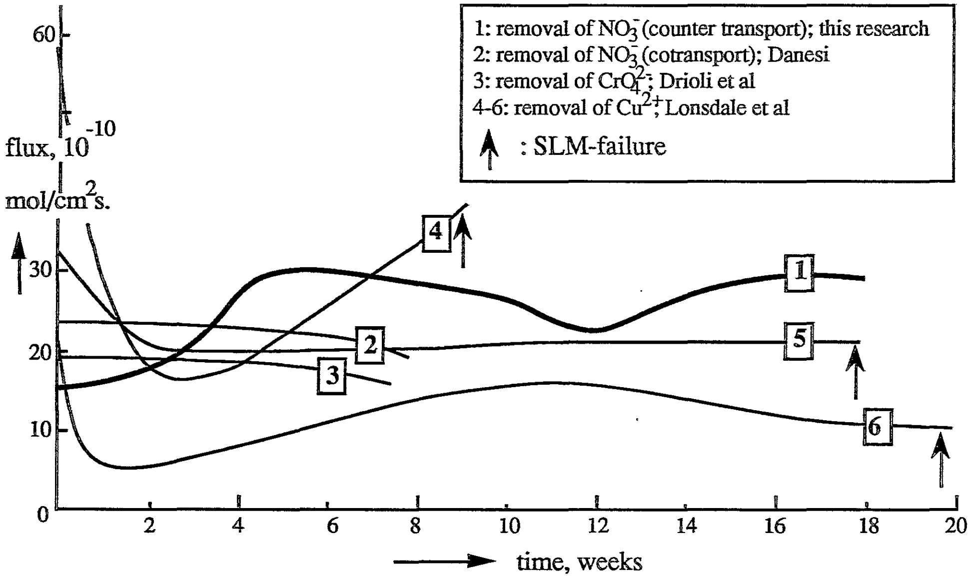

Figure 5.10. *Ion flux as a function of time for long term permeability measurements; 1 this research: 9 % PVC; conditions as in figure 5.9; removal of air bubbles after 12 weeks; 2 - 6 : data from literature; 2: ref. 33; 3 : ref. 34; 4 - 6 : ref. 35.*

Figure 5.10 shows that the flux of the membrane with 9 % PVC first increases as a function of time. This must be caused by the decrease in thickness of the membrane, through which the effective pathlength for the diffusion of the carrier molecules diminishes and consequently the flux increases. After 6 weeks the flux shows a gradual decrease due to the adsorption of air bubbles onto the membrane surface which decrease the contacting area. Removal of these air bubbles (after 12 weeks) leads to an increase in flux again.

Such effects of adhesion of air bubbles and LM-removal by emulsion formation leading to SLM-failure might also be underlying the course of the permeation curves for the other systems taken from literature. Comparing these curves with the results of the gelled membrane it can be concluded that the gelled membrane shows a favourable stability. SLM-failure (chloride leakage) is prevented by applying the gel network, while the permeability remains relatively high because of the open structure of the gel network in the pores of the support.

Simulation of long term permeability measurements for SLMs with a dense interfacial gel layer

In addition to the experiments of section 5.4.3, in which the influence of dense gel layers at the membrane interface on the removal of carrier is studied, the long term permeability of such membranes will be studied in this paragraph. The influence of the presence of the thin interfacial gel layer on the flux will also be determined in these experiments.

Based on previous results, it could be expected that such measurements would require a very long test time. Therefore it was decided to *simulate* the measurement of the long term permeability behaviour. It means that the degradation process of the membrane is accelerated on purpose. This is realized by flowing an aqueous phase with a very low salt content (10^{-4} M NaCl) along the feed side of the membrane instead of a $4 \cdot 10^{-3}$ M $NaNO_3$ solution. In chapter 4 (section 4.4.3.2) it is demonstrated that the membrane degrades much faster for lower salt content in the aqueous phases. Also the usual feed of $4 \cdot 10^{-3}$ M $NaNO_3$ is passed through the measuring cell regularly in order to determine the permeability of the membrane (and consequently the stability) as a function of time.

The *real* long term permeability can be predicted with these results when it is assumed that the instability effects of the different membranes, e.g. the loss of carrier from the LM-phase, are being reflected by the nitrate flux level in a proportional fashion. The stability of a certain membrane can then be estimated by comparing the observed simulated long term permeability with that of a membrane without gel network for which the *real* long term permeability is known.

A 4 M NaCl-solution was constantly passed along the membrane at the stripping side. From earlier work (chapter 4) we know that the membrane does not degrade at that salt concentration by the formation of emulsion droplets. Therefore the membranes were provided with only one dense interfacial gel layer which was always in contact with the feed solution. In addition to the preliminary measurements in section 5.4.3 especially the influence of chemically crosslinked gel networks is studied now. Two types of crosslinking agents and different concentrations of activator DCC were used. Carboxylated PVC is always used as polymer in these measurements and the polymer content in the applied gel layer was 40 %.

The influence of the crosslinking agent on the gel network becomes clear when studying the viscosity of the solutions. As described in section 5.4.3 the solution of carboxylated PVC in THF solidifies by adding DCC to the solution. After a few days, however, the gel becomes fluid again. A solution of carboxylated PVC in THF to which besides DCC also diamine is added also solidifies after some time. But this gel remains solid during at least one month. This means that the anhydride crosslinks formed by adding only DCC are not stable (against hydrolysis) while a chemically stable network is indeed being formed by adding diamine.

In figure 5.11 the flux is plotted as a function of the "degradation time" (that is the time that the 10^{-4} M NaCl solution was in contact with the membrane surface at the feed side) for five different membranes.

Figure 5.11 shows that the flux of the membrane without gel network decreases considerably in a period of 80 hours, under the conditions given. On the contrary this flux reduction is smaller for the membranes with a gel network so that it can be concluded (analogous to section 5.4.3) that the gel network is able to suppress the degradation of the membrane that is caused by the formation of emulsion droplets. Furthermore from the results it can be concluded that the most stable membranes are formed by a gel network with a short mesh size which is built with chemically stable crosslinks.

When comparing the initial flux values it appears that the presence of the gel network has *no measurable influence* on the permeability of the membrane. This means that the thickness of the applied gel layer is very thin in relation to the total thickness of the membrane (in agreement with the determination in section 5.4.3 of the amount of PVC present).

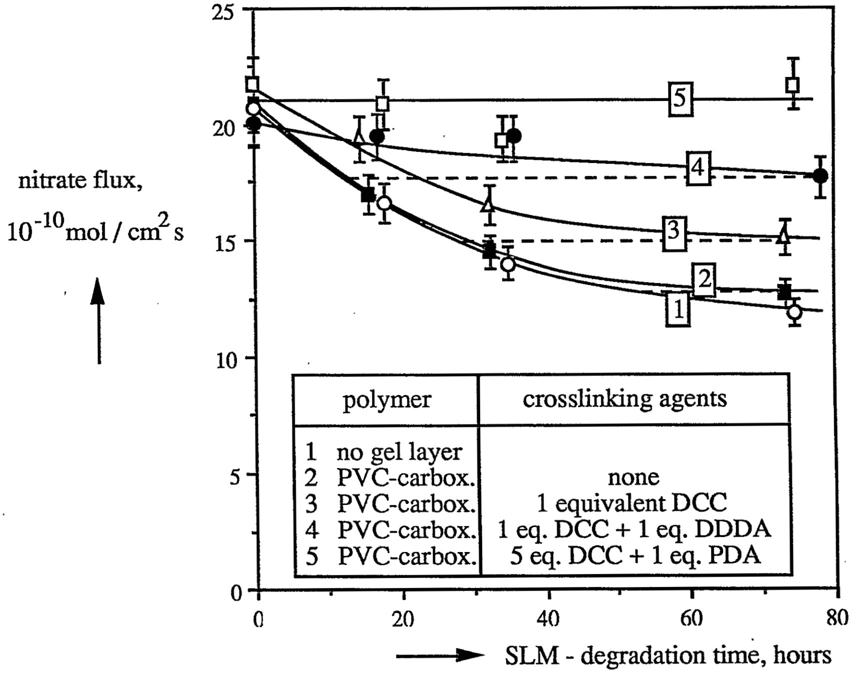

Figure 5.11. *Influence of the presence of one gel layer on simulated long term permeability; solvent o-NPOE; carrier TeOA; polymer concentration in gel layer 40 %; thickness of gel layer < 2 μm; support Accurel; feed solution: alternating* 10^{-4} *M NaCl /* $4 \cdot 10^{-3}$ *M* $NaNO_3$*; stripping phase 4 M NaCl; water flow rate 5.5 ml/s.*

Quite a remarkable effect seen in this figure is that the flux reduces as a function of time at the start of the experiment, while in figure 5.10 (in which also Accurel was used as support) the flux increases substantially during the first period. Obviously the loss of solvent in the present situation is much smaller. These results confirm the conclusion of chapter 4 (table 4.3) that the average size of the removed emulsion droplets decreases with decreasing salt content in the aqueous phases in contact with the membrane surface (10^{-4} M instead of $4 \cdot 10^{-3}$ M in standard long term measurements). The effect of flux reduction (through loss of carrier) dominates the small effect of the decreasing membrane thickness, because the small emulsion droplets that break away contain a relatively high amount of carrier.

So called "proportionality factors" were used to predict the *real* long term stabilities. These factors, which are a quantitative measure for the stability of a gelled membrane as compared to the membrane without a gel layer, are calculated by using the horizontal, dashed lines in figure 5.11. When the proportionality factors found in these series of experiments can be transferred to the practical permeation conditions (in which the removed ions are concentrated in the stripping phase) then we obtain the values as given in table 5.3. The result of previous measurements in which it was found that a membrane without gel network remained intact during 13 weeks (see figure 5.9) is used for these calculations.

Table 5.3. *Predicted long term stabilities of SLMs with one dense gel layer; the numbers 1 to 5 of membranes correspond to those in figure 5.11.*

SLM	proportionality factor	predicted long term stability
1 (no gel layer)	-	13 weeks (experimentally determined)
2	1.4	18 weeks
3	2.7	35 weeks
4	6.2	81 weeks
5	∞	∞

From this table it can be concluded that applying a thin dense crosslinked gel layer at the feed side of the membrane opens new perspectives.

For the sake of completeness it is stated here that results mentioned are a selection of all experiments performed. It is clear that in order to apply a perfect gel layer on the membrane in a reproducible way further reasearch is needed.

5.5. Conclusions

Only gelled liquid membranes with low polymer concentration are interesting for practical application because the diffusion rate of carrier molecules in a gel network decreases drastically when increasing the polymer content to higher values. Such loosely gelled membranes can only be handled when they are immobilized in an inert support because of the mechanical stability.

From the measurements it follows that the resistance of the membrane against a pressure difference increases by applying a homogeneous gel network (with a polymer content smaller than 10 %) in the pores of a support. Furthermore the long term stability increases substantially while the permeability decreases only to a small degree because of the open gel structure.

Another type of gelled membranes, in which a thin crosslinked gel layer with a higher polymer content (40 %) is applied at the feed side of the membrane, very effectively suppresses SLM-degradation caused by emulsion formation. This treatment has no negative influence on the flux because the thickness of the dense gel layer is very small. From experiments in which the determination of the long term permeability is simulated, it appears that this type of asymmetrically gelled membranes have predicted stabilities which look very interesting for practical applications (far over one year).

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SUMMARY

This thesis deals with the stability of supported liquid membranes (SLMs). The use of SLMs, in which an extraction liquid containing a carrier is immobilized in the pores of a microporous support, has recently been introduced as a promising new separation technique. Some advantages ascribed to this method are: the high selectivity, the possibility to concentrate ions by coupled transport and the high diffusion rate through the liquid. Despite these advantages SLMs are, until now, not widely used in practical separation processes. One of the main reasons is the instability of the SLMs.

This thesis describes the results of research into the mechanism of SLM-degradation, with the purpose to provide guide lines for the development of stable liquid membranes. An SLM-system in which nitrate ions are removed from water is used as a model system (with possibilities for practical application) for these measurements. First an inventory of a number of instability effects of SLMs has been made and verified experimentally. Then the correctness of a new hypothesis concerning the mechanism of SLM-degradation has been tested. Finally a new method has been developed by which the stability of SLMs can be improved.

Membranes in general and liquid membranes in special have been described in the first chapter. Special attention has been paid to the various transport mechanisms and advantages of LM-processes and the instability problem of SLMs.

The transport mechanism of a new process for the removal of nitrate from water with SLMs is described in chapter 2. Nitrate ions can be removed completely from the feed solution and transported, against their concentration gradient, to the stripping phase by means of a counter transport of chloride ions. The selectivity of the membrane can be monitored by the choice of the membrane solvent. The results show that the permeability of the membrane is influenced by the compositions of the various phases and the flow rate of the aqueous phases that pass along the surface of the membrane. Under defined standard conditions the overall-flux is limited by the diffusion of the

carrier molecules through the membrane phase. The transport is limited by the diffusion of the nitrate ions through the laminary boundary layer at the feed side only at low flow rates of the aqueous phases or at very low nitrate concentrations in the feed. When lowering the chloride content of the stripping phase the permeability is decreased due to a diminished nitrate desorption, which is determined by the ion exchange equilibrium. The influence of the carrier concentration and the type of carrier can be explained using the diffusion law of Fick and the equation of Stokes-Einstein.

An inventory of a number of SLM-instability effects, like the removal of carrier and solvent from the membrane and the direct transport (leakage) of chloride ions through the membrane, has been made and described in chapter 3, as a set-up for a systematic experimental research. From concentrating experiments it can be concluded that SLM-failure is caused by the removal of LM-phase from the support and that the instability effects depend very much on the type of solvent and the molecular structure of the carrier. These results, however, can not be explained when using the existing theories on this subject. Also an unambiguous relation is absent between the instability effects and physical properties like the viscosity of the LM-phase, the interfacial tensions between the LM-phase and the aqueous phases and the solubility of water in the LM-phase. Furthermore, it is remarkable that in general the stability of the liquid membrane increases when the salt content of the stripping phase is increased.

A clear correlation is found between the instabilities which were observed for the SLMs and the degree of emulsion formation between the same aqueous phases and the LM-phases. This leads to the hypothesis that the instability of SLMs is caused by the formation of emulsions. In chapter 4 this hypothesis is tested by studying the stability behaviour of SLMs when identical aqueous phases pass along both sides of the membranes. The results show that both a decrease in salt concentration in the aqueous phases and an increase in flow velocity of these phases parallel to the membrane surface cause an increase in instability effects. The absolute influence of these variables depends on the molecular structure of the carrier and the type of solvent. When studying the formation of emulsions of the LM-phase in the aqueous phases it was found that the stability of the emulsion droplets is regulated in the same way as the instability of the

SLMs. In view of this significant correlation the conclusion is drawn that instability of SLMs is caused by the loss of emulsion droplets from the LM-phase into the aqueous phases. A mechanism for the degradation of SLMs was proposed in which shear induced break away of emulsion droplets at the feed interface plays the main role.

It can be concluded from these results that for the development of stable SLMs the compositions of the LM-phase and the aqueous phases have to be chosen such that the LM-phase has little capacity for formation of emulsions. Furthermore the stability can be improved by opposing the local deformation of the meniscus of the LM-phase in the pores of the support. This idea has been realized, as described in chapter 5, by applying a gel network in the LM-phase. Only gelled liquid membranes with low polymer concentrations are interesting for practical applications because the diffusion rate of carrier molecules in a gel network decreases drastically when increasing the polymer content. These gelled membranes (with low polymer content) can only be handled when they are immobilized in an inert support because of mechanical stability.

From the measurements it was found that the resistance of the membrane against a pressure difference increases by applying a homogeneous gel network (with a polymer content smaller than 10 %) in the pores of a support. Furthermore the long term permeability increases substantially while the permeability decreases only to a small extent because of the open gel structure. A second type of gelled membranes, in which a thin gel layer with a higher polymer content (40 %) is applied at the feed side of the membrane, is also able to oppose SLM-degradation caused by emulsion formation. This treatment has no measurable influence on the flux because the thickness of the gel layer is very small. Whereas, based on experiments in which the determination of the long term permeability is simulated, it can be concluded that for this type of asymmetrically gelled membranes the stability increases to periods which are highly interesting for practical applications.

SAMENVATTING

Het onderzoek dat beschreven is in dit proefschrift betreft de stabiliteit van geïmmobiliseerde vloeistofmembranen (Supported Liquid Membranes: SLM's). Het gebruik van SLM's, waarbij een extractie vloeistof met een "carrier" geïmmobiliseerd is in de porien van een microporeuze drager, is recentelijk geintroduceerd als een veelbelovende nieuwe scheidingstechniek. Enkele voordelen die aan deze methode worden toegeschreven zijn een hoge selectiviteit, de mogelijkheid ionen te kunnen concentreren door middel van een gekoppeld transport en de hoge diffusiesnelheid door de vloeistof. Ondanks deze voordelen worden SLM's tot nu toe maar op zeer beperkte schaal toegepast bij praktische scheidingsprocessen. Eén van de belangrijkste oorzaak daarvan is de instabiliteit van de SLM's.

Dit proefschrift beschrijft de resultaten van onderzoek naar het mechanisme van SLM-degradatie, op grond waarvan richtlijnen kunnen worden opgesteld voor de ontwikkeling van stabiele vloeistofmembranen. Voor dit onderzoek is, als modelsysteem (met mogelijkheden voor praktische toepassing), gebruik gemaakt van een SLM-systeem waarin nitraationen uit water worden verwijderd. Allereerst zijn een aantal instabiliteitseffecten van SLM's geinventariseerd en experimenteel onderzocht. Vervolgens is een nieuwe hypothese met betrekking tot het mechanisme van SLM-degradatie opgesteld en getoetst op zijn geldigheid. Tenslotte is op grond van de verkregen inzichten een nieuwe methode ontwikkeld waarmee de stabiliteit van SLM's kan worden verbeterd.

In het eerste hoodstuk worden membranen in het algemeen en vloeibare membranen in het bijzonder belicht. Hierin wordt met name aandacht besteed aan de verschillende transportmechanismen, de voordelen van LM-processen en het instabiliteitsprobleem van SLM's.

In hoofdstuk 2 is het transportmechanisme van een nieuw proces voor nitraatverwijdering met SLM's beschreven. Door gebruik te maken van een tegentransport van chloride-ionen kunnen nitraationen volledig uit de voeding verwijderd worden en tegen hun concentratiegradient in naar de stripfase worden getransporteerd. De selectiviteit van het membraan kan gestuurd worden door de keuze van het oplosmiddel in het membraan. Uit de resultaten blijkt dat de permeabiliteit van het membraan wordt beinvloed door de samenstellingen van de verschillende fasen en de snelheden waarmee de waterfasen langs het membraan stromen. Onder gedefinieerde standaardcondities wordt de overall-flux gelimiteerd door de diffusie van de carriermoleculen door de membraanfase. Bij lage langsstroomsnelheden van de waterfasen of bij erg lage nitraatconcentraties in de voeding wordt het transport gelimiteerd door de diffusie van nitraationen door de laminaire grenslaag aan de voedingszijde. Bij een gering zoutgehalte van de stripfase wordt de permeabiliteit gereduceerd vanwege een verminderde nitraatdesorptie die bepaald wordt door het ionen uitwisselingsevenwicht. De invloed van de carrierconcentratie en het type carrier kunnen worden verklaard met behulp van de diffusiewet van Fick en de Stokes-Einstein vergelijking.

In hoofdstuk 3 zijn, als eerste aanzet tot een systematisch onderzoek, een aantal SLM-instabiliteits effecten geïnventariseerd, zoals de verwijdering van carrier en oplosmiddel uit het membraan en het directe transport (lekstroming) van chloride ionen door het membraan. Uit deze concentreringsexperimenten blijkt dat de lekstroming van de membranen het gevolg is van verwijdering van LM-fase uit de drager en dat de instabiliteitseffecten erg afhankelijk zijn van het type oplosmiddel en de structuur van de carrier. De resultaten kunnen echter niet verklaard worden aan de hand van bestaande theorien op dit gebied. Er bestaat ook geen eenduidig verband met fysische grootheden zoals de viscositeit van de LM-fase, de grensvlakspanningen tussen de LM-fase en de waterfasen en de oplosbaarheid van water in de LM-fase. Bovendien is het opmerkelijk dat in het algemeen de stabiliteit van het membraan toeneemt met een toenemend zoutgehalte in de stripfase.

Er blijkt een duidelijk verband te bestaan tussen de waargenomen SLM-instabiliteitseffecten en de mate van emulsievorming tussen dezelfde waterfasen en LM-fasen. Dit leidde tot de hypothese dat de instabiliteit van SLM's wordt veroorzaakt door de vorming van emulsiedruppels. In hoofdstuk 4 is deze hypothese getoetst door bestudering van het stabiliteitsgedrag van SLM's bij langsstroming aan beide zijden van het membraan met identieke waterfasen. Uit de resultaten blijkt dat zowel een verlaging van het zoutgehalte in de waterfasen als een verhoging van de snelheid waarmee de waterfasen langs het membraan stromen leiden tot een toename van de instabiliteitseffecten. De absolute invloed van deze variabelen is afhankelijk van de structuur van de carrier en het type oplosmiddel. Bij bestudering van de vorming van emulsies van de LM-fase in de waterfase blijkt dat de stabiliteit van de emulsiedruppels door dezelfde factoren bepaald wordt als de instabiliteit van de SLM's. Op grond van deze significante correlatie is de conclusie gerechtvaardigd dat de instabiliteit van SLM's wordt veroorzaakt door de verwijdering van emulsiedruppels van de LM-fase naar de waterfasen. Tot slot wordt een mechanisme voor de degradatie van SLM's voorgesteld, waarin de afsplitsing van emulsiedruppels, teweeggebracht door afschuifkrachten aan de voedingszijde van het membraan, de belangrijkste rol speelt.

Uit deze resultaten kan geconcludeerd worden dat voor de ontwikkeling van stabiele SLM's de samenstellingen van de LM-fase en de waterfasen dusdanig gekozen moeten worden dat de LM-fase weinig vermogen heeft tot emulsievorming. Bovendien kan de stabiliteit verbeterd worden door het tegengaan van de locale vervormingen van de meniscus van de LM-fase in de poriën van de drager. Dit idee, beschreven in hoofdstuk 5, is gerealiseerd door het aanbrengen van een gelnetwerk in de LM-fase. Omdat de diffusie snelheid van carriermoleculen door een gelnetwerk drastisch afneemt met toenemend polymeergehalte zijn gegeleerde vloeistof membranen voor praktische toepassing slechts interessant bij geringe polymeer concentratie. Vanwege de te geringe mechanische stabiliteit zijn dergelijke membranen alleen hanteerbaar indien ze geïmmobiliseerd zijn in een inerte drager.

Uit metingen blijkt dat door het aanbrengen van een homogeen gelnetwerk (met een polymeergehalte kleiner dan 10 %) in de dragerporiën, de weerstand van het membraan tegen een drukverschil toeneemt. Bovendien neemt de lange duur permeabiliteit substantieel toe terwijl, vanwege de open gelstructuur, de permeabiliteit slechts in geringe mate afneemt. Een tweede uitvoeringsvorm, waarbij een dunne gellaag met een hoger polymeergehalte (40 %) wordt aangebracht aan de voedingszijde van het membraan, is ook in staat SLM-degradatie door emulsievorming tegen te gaan. Omdat de dikte van het gellaagje zo gering is heeft dit geen meetbare invloed op de flux. Daarentegen kan op grond van experimenten waarin de bepaling van de lange duur permeabiliteit is gesimuleerd, worden geconcludeerd dat de stabiliteit toeneemt tot perioden die voor praktische toepassing zeer interessant zijn.

LEVENSLOOP

Tonny Neplenbroek werd op 13 oktober 1958 geboren te Heino.
In 1977 behaalde hij het Atheneum B diploma aan de Thomas a Kempis-Scholengemeenschap te Zwolle. In datzelfde jaar begon hij met de studie Chemische Technologie aan de Technische Hogeschool Twente, nu Universiteit Twente, te Enschede. Hij behaalde in 1982 het baccalaureaatsdiploma (onderzoekgroep Biomedische Materiaaltechniek) en in 1985 het ingenieursdiploma (onderzoekgroep Membraantechnologie).
Op 1 september 1985 trad hij in dienst van de T.H. Twente als wetenschappelijk assistent in de onderzoekgroep Membraantechnologie van de vakgroep Macromoleculaire Chemie en Materiaalkunde om het beschreven promotie-onderzoek uit te voeren.
Vanaf 1 november 1989 is hij in dienst van de firma Otarès te Enschede.