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Organophilic pervaporation: prospects and performance

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Abstract

Among the different membrane processes, organophilic pervaporation is one of the most promising technologies for environmental applications. The aim of this paper is to give a thorough introduction to organophilic pervaporation in the context of wastewater treatment. The emerging process of organophilic pervaporation is introduced together with other membrane processes relevant for environmental applications. With regard to the performance of pervaporation, an engineering model is presented which will enable ready assessment of process and module design. Sorption and coupled diffusion are covered in the model. Selection criteria for membranes and transport resistances for the mass transport as key process engineering parameters are included. The influences of permeate pressure and temperature upon performance are discussed and a description of commercial pervaporation modules given. Following a brief description of the hierarchy of waste management practice, guidelines for applying and integrating pervaporation into a process are proposed. The importance of considering hybrid processes is highlighted. A case study for phenol recovery with water treatment to 5 ppm is considered. Finally, present restrictions on the use of pervaporation in wastewater treatment such as (a) the unavailability of appropriate membranes and (b) fouling of the membrane are discussed and approaches to overcome the restrictions are presented.

Keywords: Pervaporation; Wastewater; Process design; Module design

1. Introduction

The membrane technologies have become established in recent years as alternatives for environmental applications to conventional mass-exchange technology such as absorption, adsorption or extraction. The focus of this paper is to introduce the emerging process of organophilic pervaporation and to provide sufficient understanding of the process for the successful interpretation of experimental data. However, in a contextual introduction a brief review of other membrane processes with some environmental applications is also given. The first three membrane processes in Table 1 are driven by hydrostatic pressure and involve porous membranes. As the pore sizes decrease from microfiltration to nanofiltration charge interactions become increasingly important.

In the second part of Table 1, the processes are driven by a gradient in chemical potential using the solution-diffusion mechanism. Among these processes reverse osmosis (RO) using dense membranes is well established for the production of potable water by desalination. RO is most prominent in the Middle East and on islands where demand for potable water has exceeded natural supplies. Gas separation is often a cost effective way to separate one gas from another by the use of membranes. The main markets are in the chemical and petroleum industries for hydrogen recovery and for production of moderate purity nitrogen. A possible environmental application is the removal of carbon dioxide from landfill gas in order to produce a stream of sufficient calorific value. This application is commercially used in the Netherlands but uncommon in the UK. Furthermore, a very recent report [1] mentions that the latest generators have engines that need only 32–34% methane whereas older systems needed levels closer to 50%. Thus, the need for methane concentration during gas pre-treatment will be greatly reduced.

Some other membrane processes relevant to environmental management using different driving forces are listed in the final part of Table 1. The most important is electrodialysis, which can be applied for the removal of metals from wastewater streams.

The most successful application of membrane processes is the use of dialysis for medical applications. This can be related to the large number of disposable membrane devices

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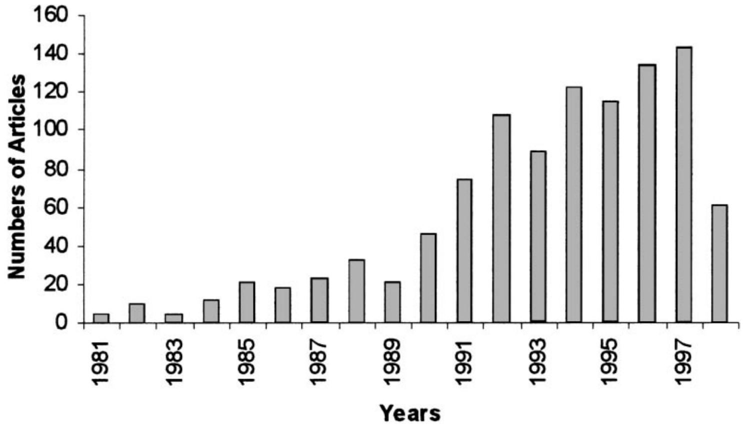
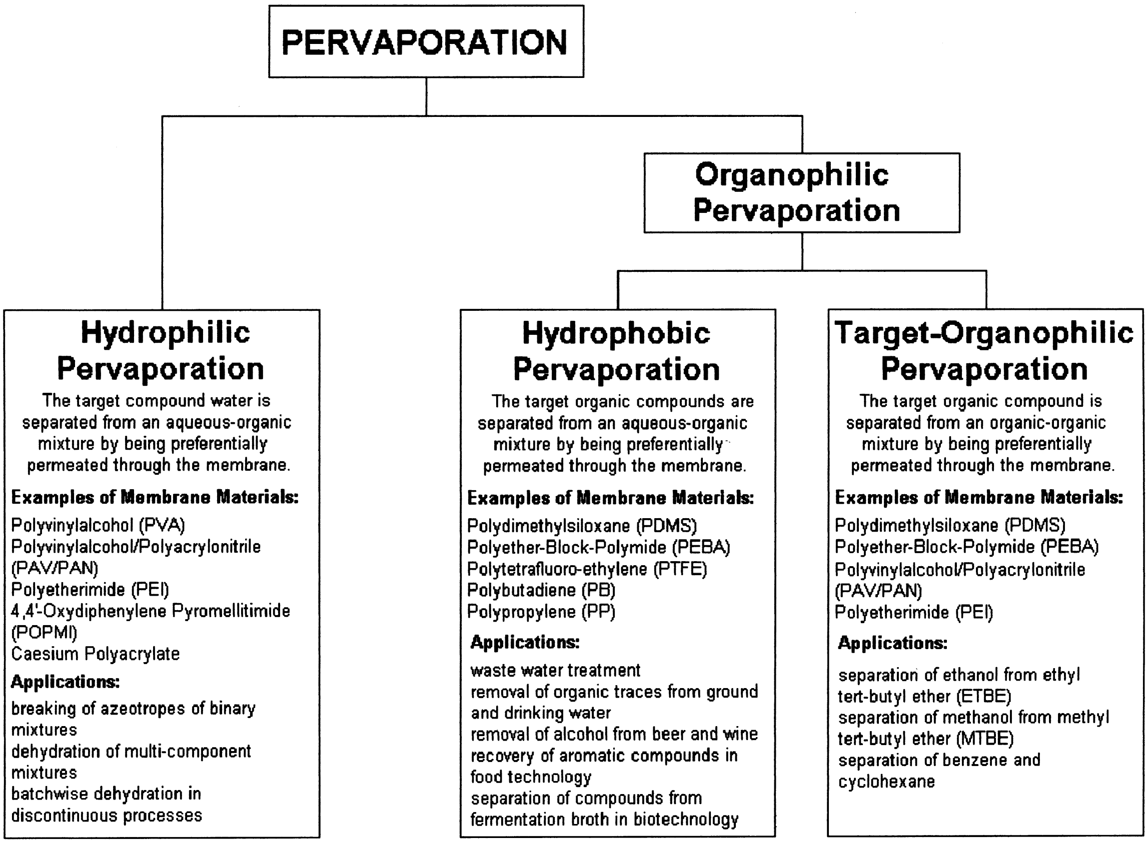


Fig. 1. Number of scientific articles between 1981 and April 1998 [3].

required every day to treat patients who need long-term treatment for loss of renal functions. Compared to the annual sales in the medical sector the market share of membrane process for environmental/wastewater treatment applications is still very small. However, due to the high potential of pervaporation to separate aqueous–organic and organic–organic mixtures it is forecast that the market share of pervaporation will grow at rates even above the market rate for membrane processes [2].

The increasing interest in pervaporation can also be seen in Fig. 1, which shows the number of papers on pervaporation in the last few years. In general, pervaporation (PV) can still be labelled as a new technology. Depending on the permeating component two main areas of pervaporation can be identified: (1) hydrophillic PV, and (2) organophilic PV. Fig. 2 gives an overview of the areas of PV, membranes applied and applications. The first commercial plants for dehydration of alcohol with PV were installed in the late



Hydrophilic Pervaporation

The target compound water is separated from an aqueous-organic mixture by being preferentially permeated through the membrane.

Examples of Membrane Materials:

Polyvinylalcohol (PVA)
Polyvinylalcohol/Polyacrylonitrile (PAV/PAN)
Polyetherimide (PEI)
4,4'-Oxydiphenylene Pyromellitimide (POPMI)
Caesium Polyacrylate

Applications:

breaking of azeotropes of binary mixtures
dehydration of multi-component mixtures
batchwise dehydration in discontinuous processes

Hydrophobic Pervaporation

The target organic compounds are separated from an aqueous-organic mixture by being preferentially permeated through the membrane.

Examples of Membrane Materials:

Polydimethylsiloxane (PDMS)
Polyether-Block-Polymide (PEBA)
Polytetrafluoro-ethylene (PTFE)
Polybutadiene (PB)
Polypropylene (PP)

Applications:

waste water treatment
removal of organic traces from ground and drinking water
removal of alcohol from beer and wine
recovery of aromatic compounds in food technology
separation of compounds from fermentation broth in biotechnology

Target-Organophilic Pervaporation

The target organic compound is separated from an organic-organic mixture by being preferentially permeated through the membrane.

Examples of Membrane Materials:

Polydimethylsiloxane (PDMS)
Polyether-Block-Polymide (PEBA)
Polyvinylalcohol/Polyacrylonitrile (PAV/PAN)
Polyetherimide (PEI)

Applications:

separation of ethanol from ethyl tert-butyl ether (ETBE)
separation of methanol from methyl tert-butyl ether (MTBE)
separation of benzene and cyclohexane

Fig. 2. Areas of pervaporation: membranes and applications.

Table 1
Membrane processes relevant to environmental management

Membrane processes	Definitions[a]	Example of applications
A: Direct pressure driven		
Microfiltration (MF)	process in which particles and dissolved marcomolecules larger than 1 μm are rejected	separation of oil/water emulsions; removal of colloids from waste streams; removal of dust particles from air
Ultrafiltration (UF)	process in which particles are dissolved marcomolecules smaller that 1 μm and larger than about 2 nm are rejected	separation of oil/water emulsions; recovery of proteins from whey and milk; recovery of electrophoretic paints
Nanofiltration (NF)	process in which dissolved molecules smaller than about 2 nm are rejected	treatment of electro-plating rinse water
B: Driven by activity gradient (solution diffusion mechanism applies)		
Reverse osmosis (RO)	liquid-phase process in which applied transmembrane pressure causes selective movement of solvent against its osmotic pressure difference	treatment of leachate from landfill sites removal of nitrate from ground water
Gas separation (GS)	process in which gases are separated from each other with the objective of obtaining one or more of the constituents in purer form [b]	removal of CO_2 and H_2S from landfill gas; removal of condensable solvents
Vapour permeation (VP)	processes in which the feed vaporised before contacting the membrane and the permeate stream emerging from the downstream face of the membrane are vapour phases [c]	removal of condensable solvents from air
Pervaporation (PV)	process in which the feed and retentate streams are both liquid phases while the permeate stream emerges at the downstream face of the membrane as a vapour	dehydration of solvents; removal of organics from wastewater
C: Other driving forces		
Electro-dialysis (electrical potential)	process in which ions are driven through an ion-selective membrane under the influence of an electric field	removal of metals from wastewater; acid recycle from 'pickling' baths; desalination of brackish water
Liquid membranes (gradient in chemical potential based on solubility)	proces in which a liquid phase, existing either in supported or unsupported form, that serves as a membrane barrier	recovery of plating chemicals removal of acid gases from air
Membrane distillation (temperature difference across non-wetting pores)	distillation process in which the liquid and gas phase are separated by a porous membrane, the pores of which are not wetted by the liquid phase	desalination of brine

[a] All definitions based on [5] except gas separation and vapour permeation.
[b] Based on [6].
[c] Based on [7].

1980s. While for environmental applications (Table 1) organophilic PV with hydrophobic membranes has the highest potential by offering the opportunity to efficiently remove low concentrations of organic compounds from wastewater. The first commercial applications of such a process have been reported in 1997 [4].

The aim of this paper is to show the performance and prospects of organophilic pervaporation. After introducing the basic process layouts of pervaporation (Section 1.1), mass transfer in pervaporation is discussed (Section 2) and the influence of process parameters highlighted (Section 3). In a final section of the article a case study is presented (Section 4).

Because of the multi-component nature of many wastewater streams of industrial interest, this area is covered thoroughly (Section 2.2). Fundamental equations to describe the overall mass transfer through the membrane are given in Section 2.2.4. Further, dimensionless numbers as criteria for the selection of membranes for different applications are given (Section 2.3). The significance of transport resistances including concentration boundary layers on the performance of pervaporation is analysed and integrated into the overall mass transfer expression for pervaporation (Section 2.4,). Next, the implications of two key process parameters. temperature (Section 3.1) and permeate pressure (Section 3.2) on process and module design (Section 3.3) are discussed. Finally. organophilic pervaporation is considered in the context of wastewater treatment (Section 4.1) and guidelines are given for the integration of pervaporation into environmental and industrial processes (Section 4.2). The recovery of phenol from wastewater is used as a case study (Section 4.3).

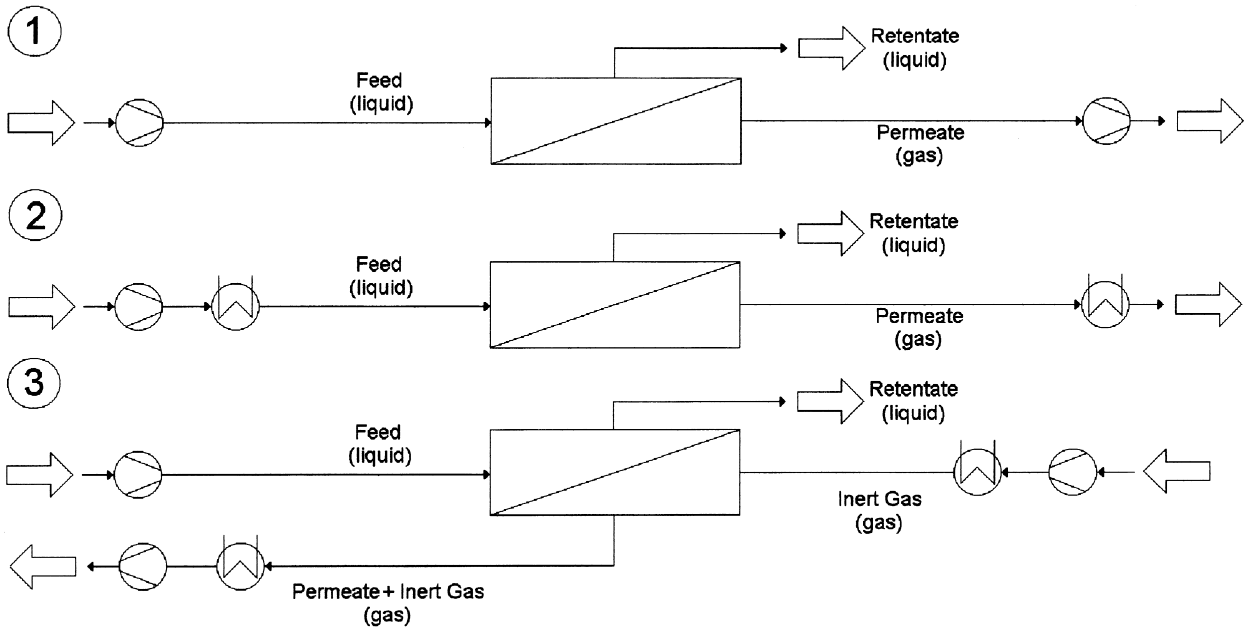


Fig. 3. Basic process layouts for the three forms pervaporation.

It should be noted that each of this article's sections is self-contained and, therefore, can be read independently of each other. The reader is encouraged to move directly to sections of interest.

1.1. Basic process layouts of pervaporation

The key features of pervaporation is the mass transfer of components through a non-porous polymeric membrane combined with a phase change from liquid phase to vapour phase. The driving force in pervaporation is a difference in chemical potential (difference of partial pressure or activity) between feed and permeate side. The separation is achieved by different mass transfer rates of the components through the membrane. Generally, the pervaporation process can be distinguished by the three different layouts of

1. vacuum pervaporation,
2. thermopervaporation, and
3. sweep gas pervaporation.

In vacuum pervaporation (Fig. 3(1)), the driving force is realised by applying vacuum on the permeate side of the membrane. Hence, the partial pressure of evaporated permeate is lowered and a pressure gradient across the membrane is maintained using a vacuum pump.

In the alternative approach of thermopervaporation (Fig. 3(2)) the partial pressure difference between feed and permeate side is created by a temperature gradient across the membrane. The feed temperature has therefore to be increased significantly over the permeate temperature. Similar to vacuum pervaporation the vapour pressure difference, as a result of the temperature gradient between permeate and feed side, is the driving force of the process. This system is supported by a condenser on the permeate side and in some process systems by feed side heat exchange parallel to the membrane surface.

Thirdly, sweep gas pervaporation can be applied. This is driven by a partial pressure difference generated by an inert sweep gas on the permeate side (Fig. 3(3)). As this gas can be heated there is an opportunity to supply the evaporation enthalpy on the permeate side. A condenser on the permeate side removes the permeate from the sweep gas.

Commonly vacuum pervaporation is used in industry with a condenser and separating vessel being placed between the membrane unit and the vacuum pump. This process will have the greatest future impact due to the simplicity of its requirements and process design. Hence, the focus in this paper will on this process layout.

Just as in thermal processes the logarithm of the mean temperature difference and the overall heat transfer coefficient can be misused due to a lack of understanding of their origins, and hence of the restrictions, so a poor understanding of permeability can be misleading. Thus, a thorough introduction to the solution-diffusion model as applied in pervaporation is included.

2. Mass transport in pervaporation

To successfully implement, pervaporation for wastewater treatment and other applications requires a fundamental understanding of mass transfer in pervaporation. A knowledge of mass transport mechanisms in pervaporation will then enable engineers to design and improve membranes, membrane modules and process layouts.

2.1. Solution–diffusion model

For pervaporation, the solution–diffusion model can describe mass transport through the homogenous selective layer of a membrane. This semi-empirical or phenomenological model was originally developed by Graham [8] to describe gas permeation through rubber septa and is used today for both reverse osmosis or gas separation. Binning et al. [9] used the solution–diffusion model to describe pervaporation through a homogenous polymeric film. Based on this model the overall mass transport through the membrane from the feed to the permeate side can be represented by three steps. Firstly, sorption of the component *i* into the membrane polymer on the feed side. The sorption rate of a component is related to its total energy requirement to dissolve into the polymer. Generally, the component in the feed mixture with the lowest energy requirement is preferentially sorbed into the membrane polymer. Hence, the selectivity of the membrane towards a feed mixture will be determined by the sorption step. The second step is the diffusion of the component *i* through the dense polymer film. The diffusion behaviour through the membrane depends on the feed components. Membrane polymer and process parameters. Across the membrane, diffusion will follow the gradient of the chemical potential, the driving force of pervaporation, can be described by Fick's law. The final step is the desorption of component *i* into vapour phase on the permeate side.

Fig. 4 give a schematic overview of the solution–diffusion model showing typical profiles through a membrane. It is assumed that all of the membrane is at the same pressure [10]. For pervaporation the increase in activity at the downstream interface, due to the pressure change, has a negligible effect on mass transfer [11].

The flux J_i of component *i* through the membrane can be described to a first approximation by Fick's Law, which is concentration-based. See, for example, Field [12]. However, the advantage of using an activity rather than a concentration based expression is that thermodynamic equilibrium is assumed at the interfaces. This means that the activities on the membrane surface (a) at the feed side and (b) at the permeate side can be used as boundary conditions for the diffusion equations without having to introduce an additional model for the sorption at the phase boundaries. It should be further that noted that convection can be neglected in the model [13]. The flux can be related to the gradient of the chemical potential as

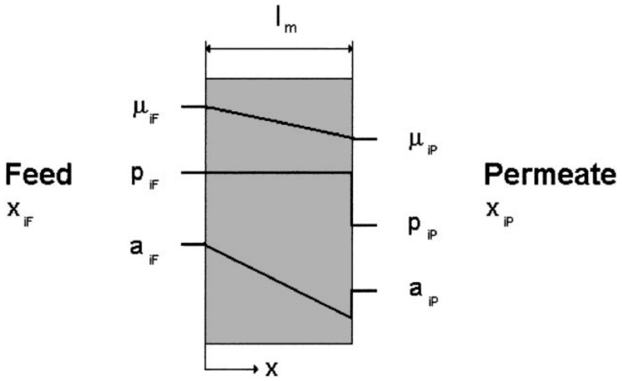


Fig. 4. Schematic diagram of the solution–diffusion model.

$$J_i(x) = \frac{-C_i(x)D_i(x)}{RT}\frac{\mathrm{d}\mu_i}{\mathrm{d}x} \tag{1}$$

The chemical potential can generally be described as a function of temperature, pressure and composition [14]:

$$\mu_i(T) = \mu_i^0(T) + RT\ln a_i^M + \int_{p_i^0}^{P} \tilde{V}_i\,\mathrm{d}p - \int_{T_i^0}^{T} S_i\,\mathrm{d}T \tag{2}$$

For a first approximation of the flux J_i, in pervaporation it can be assumed that $-S_iT < \tilde{V}_i p \ll RT\ln a_i^M$ [15]. Hence, Eq. (1) can be simplified to:

$$J_i = -C_i(x)D_i(x)\frac{\mathrm{d}}{\mathrm{d}x}\left(\ln a_i^M\right) \tag{3}$$

Referring to Fig. 4 the flux through the membrane occurs perpendicular to the membrane in the x direction and, furthermore, assuming a linear variation of the activity in the direction of the flux, Eq. (3) can be rewritten as

$$J_i = \frac{-C_i(x)D_i(x)}{a_i^M}\frac{\Delta a_i^M}{\Delta x} \tag{4}$$

In this equation, a_i^M denotes the average activity in the membrane, while Δa_i^M represents the activity difference of component *i* between feed and permeate side. The difference Δx is the membrane thickness. Under the assumption that there is a very close approach to thermodynamic equilibrium between the liquid feed phase outside the membrane and the feed membrane phase and between the vapour permeate phase and the permeate membrane phase, it follows that

at the feed side

$$a_{i,\mathrm{F}}^M = a_{i,\mathrm{F}} = x_{i,\mathrm{F}}\gamma_{i,\mathrm{F}} \tag{5}$$

at the permeate side

$$a_{i,\mathrm{P}}^M = a_{i,\mathrm{P}} = y_{i,\mathrm{P}}\,\varphi_i\frac{p_\mathrm{P}}{p_i^0} \tag{6}$$

Hence, introducing Eqs. (5) and (6) into Eq. (4) and replacing Δx by the membrane thickness l_M the following expression can be derived:

$$J_i = \frac{D_{i,\mathrm{M}}\,C_{i,\mathrm{M}}}{a_i^\mathrm{M}}\frac{1}{l_\mathrm{M}}\left(a_{i,\mathrm{F}} - a_{i,\mathrm{P}}\right) \tag{7}$$

An experimental estimation of $D_{i,\mathrm{M}}$, $C_{i,\mathrm{M}}$ and $a_{i,\mathrm{M}}$ independent of each other is rather difficult and might lead to highly inaccurate results. To overcome this problem these parameters are summarised in the phenomenological permeability parameter P_i that has to be determined for every system of components through experiments. The permeability of an ideal system can be defined as

$$P_i = \frac{D_{i,\mathrm{M}}\, C_{i,\mathrm{M}}}{a_i^{\mathrm{M}}} = \frac{D_{i,\mathrm{M}}}{\gamma_i^{\mathrm{M}}}\, \frac{\bar{\rho}_{\mathrm{M}}}{M_{\mathrm{M}}} \tag{8}$$

Hence, the following equation for the mass transport through the dense membrane can be obtained for pervaporation:

$$J_i = \frac{P_i}{l_{\mathrm{M}}}\,(a_{i,\mathrm{F}} - a_{i,\mathrm{P}}) \tag{9}$$

The influence of the feed temperature on the permeability parameter P_i will be described by an Arrhenius-type equation:

$$P_i(T_{\mathrm{F}}) = P_i^0 \exp\left[\frac{E_i}{R}\left(\frac{1}{T_0} - \frac{1}{T_{\mathrm{F}}}\right)\right] \tag{10}$$

The two parameters P_i^0 and E_i, are evaluated from measurements at several different temperatures. This ideal approach is suitable for binary aqueous systems with low concentrations of organic components but it might be inadequate for higher organic concentrations or multi-component systems. These real systems are discussed in the following sections.

2.2. Pervaporation mass transfer for real and multi-component systems

The solution–diffusion model, described by Eq. (9), is based on the assumption of ideal conditions, i.e., that the thermodynamic diffusion coefficient is equal to the observed diffusion coefficient and that no further component interactions takes place. In the separation of liquid mixtures, as often found in real wastewater systems, conditions might not be ideal. Real wastewater systems are multi-component mixtures containing different organic compounds, e.g., halogenated hydrocarbons and aromatic compounds as well as inorganic salts. Thus, mass transport may be strongly affected by coupling effects, which reflect interactions of each of the components within the membrane matrix as well as the interactions between the components themselves [16]. Separation capacity and selectivity might decrease dramatically in real solutions, making the separation process much less efficient or even inefficient.

Coupling effects are well known in chemical engineering, e.g, Peltier effects or thermal diffusion were first reported in the field of pervaporation by Heisler et al. [17]. According to the solution–diffusion model, multi-component effects might occur in each of the three steps of the overall mass transport through the membrane, i.e., sorption, diffusion and desorption. In the following, the effects on each of these steps will be discussed in further detail.

2.2.1. Sorption

The so-called preferential sorption is a thermodynamic property, which occurs when the concentration of different components in a mixture differs inside and outside the membrane. It depends on variations in molar volumes of different penetrants, the affinity of respective components towards the polymer and the mutual interaction between the penetrates.

Another cause of non-ideal sorption behaviour might be blocking effects in front of the membrane or inside the membrane itself. In this article, the term blocking is defined as the influence of impermeable solutes on mass transfer of penetrants. The influence is due to the formation of a concentration boundary layer. Wood et al. [18], for example, reported a decrease in permeation rate and selectivity of ethanol when impermeable fructose is added to a ethanol/water feed. A similar effect was observed by Dotremont [19]. Different salts were added to the feed, leading to formation of a so-called depletion layer which hamper the mass transfer of trichlorethylene while not influencing the water mass transfer. A fraction of salts was found even in the membrane top layer, detected by X-ray analysis. Similar results has been observed in our own studies [20].

In the study of Böddeker and Bengtson [21], coupling effects between salts and penetrants in the concentration polarisation region in front of the membrane are explained by salting-out effects. This means that the activity of non-electrolytes in aqueous solution is increased by addition of salts causing the lowering of the activity of the solvent within the membrane. Referring to Eq. (7), salting-out is expected to enhance both organic enrichment and flux density. Thus, salting-out and blocking effects have contrary effects on separation capacity.

2.2.2. Coupled diffusion

Coupled diffusion is a thermodynamic property and means that the permeation rate of one component can be changed by the presence and movement of other components. Several studies are known to describe coupled diffusion on the basis of pure component transport (e.g., by Huang and Yeom [22]) or the free volume theory based on Fujita [23] as well as using phenomenological parameters (e.g., by Drioli et al. [24]). Most of these approaches are developed for binary liquids exclusively or have a strong increase in complexity when the number of penetrants exceeds two. A recent approach based on the thermodynamics of irreversible process (TIP) is the most suitable approach to coupled diffusion. This approach combines a minimum complexity with the opportunity to analyse multi-component mixtures and is therefore discussed in the following.

This theory can be applied to pervaporation. Following Kedem [25], the main assumption is that for a ternary system there are two flows of component i and j in the membrane matrix that may exhibit coupling phenomena. These can be described by the following phenomenological equations:

$$J_i = -L_{ii}\,\mathrm{grad}\,\gamma_{ii} - L_{ij}\,\mathrm{grad}\,\gamma_j \tag{11}$$

$$J_i = -L_{ji}\,\mathrm{grad}\,\gamma_i - L_{jj}\,\mathrm{grad}\,\gamma_j \tag{12}$$

The main coefficients are L_{ii} and L_{jj} and coupling coefficients representing the coupling effects are L_{ij}, and L_{ji}. The number of phenomenological coefficients increase with a rising number of penetrates but due to Onsager's reciprocity relationship

$$L_{ij} = L_{ji} \tag{13}$$

Also according to the thermodynamic principle of entropy production in irreversible systems, the following inequalities must hold:

$$L_{ii} > 0 \quad \text{and} \quad L_{jj} > 0 \tag{14}$$

$$L_{ii}L_{jj} \geq L_{ij}^2 \tag{15}$$

This simplifies the prediction of multi-component coupled diffusion. This approach has been successfully applied by Molinari et al. [26] and Simon et al. [27]. They used the equations based on TIP and obtained a good fitting of these equations to experimental data as well as an evaluation of the degree of coupled diffusion.

2.2.3. Desorption

Desorption means transition of penetrants from the membrane matrix into the permeate side vapour phase. According to Eq. (6), the overall mass transfer is a function of total permeate vapour pressure. For multi-component systems the permeate pressure p_{P} is the sum of the partial pressures of all components. For j components the equation is

$$a_{i,\mathrm{P}}^{\mathrm{M}} = a_{i,\mathrm{P}} = y_{i,\mathrm{P}}\varphi_i \frac{\sum_{n=1}^{j} p_{n,\mathrm{P}}}{p_i^0} \tag{16}$$

For an aqueous binary mixture, total permeate pressure is shared by just two components, one organic and the other water. Now, in multi-component mixtures, total permeate pressure is shared by j different penetrants. Thus, at a constant downstream pressure the existence of additional permeable components reduces the partial vapour pressure of any component i at the permeate side and increases its driving force in accordance with Eq. (7).

2.2.4. Overall mass transfer through the membrane

So far no general model exists including all different coupling effects and phenomena. For engineering aspects this problem might be reduced by the determination of a real permeability parameter P_i^{real} for every multi-component system through experiments. Thus, Eq. (9) for the pervaporation mass transport through dense membranes can be rearranged for multi-component systems to

$$J_i^{\mathrm{real}} = \frac{P_i^{\mathrm{real}}}{l_{\mathrm{M}}} \left(a_{i,\mathrm{F}}^{\mathrm{multi}} - a_{i,\mathrm{P}}^{\mathrm{multi}}\right) \tag{17}$$

The activity of a component in a multi-component mixture can be estimated from binary experiments using activity models, i.e., UNIQUAC, NRTL or WILSON. The advantage of using an equation of the form of Eq. (17) is that permeability and driving force are decoupled. The real permeability of component i in the multi-component mixture P_i^{real} would be calculated using a good estimation of the actual driving force. Thus, if P_i^{real} differs from the binary value of P_i, (the permeability of component i dissolved in water), it is known that the difference is due to changed interactions within the membrane or at its surface.

The temperature dependence can be described by an Arrhenius-type equation as previously given in Eq. (10).

2.3. Transport resistances

Relating the mass transport in pervaporation to only the mass transport through the membrane leads generally to an overestimation of the efficiency of pervaporation. The pervaporation process is further influenced by the concentration boundary layer on the feed side, the structure of the support structure (in case of composite membranes) and the concentration boundary layer on the permeate side. These additional factors have to be taken into account in process design. Among the different resistances influencing the mass transport in pervaporation, the concentration boundary layer on the feed side is one of the key resistances in the overall process and can even dominate the separation process [28]. Several studies [13,29–31] analysing the influence of concentration boundary layer indicated that the influence of this layer is significant especially for volatile organic compounds (VOCs) in real wastewater systems.

To account for this additional effect on the flux, Eq. (9) can be generalised by introducing an overall mass transfer resistance from the bulk of the feed to the permeate side as

$$J_i = \frac{1}{R_{i,\mathrm{ov}}}(a_{i,\mathrm{F}} - a_{i,\mathrm{P}}) \tag{18}$$

Assuming the mass transfer is dominated by the mass transfer through the concentration boundary layer on the feed side and through selective layer of the membrane, the overall mass transfer resistance for a component i can be described by

$$\frac{1}{R_{i,\mathrm{ov}}} = \frac{1}{R_{i,b}} + \frac{1}{R_{i,\mathrm{M}}} = \frac{\gamma_{i,\mathrm{F}}}{k_{i,b}\bar{\rho}_m} + \frac{l_{\mathrm{M}}}{P_i} \tag{19}$$

Introducing Eq. (19) into Eq. (18) the overall mass transfer in pervaporation can be described by

$$J_i = \frac{1}{\left(\gamma_{i,\mathrm{F}}/k_{i,b}\bar{\rho}_m\right) + (l_{\mathrm{M}}/P_i)}\left(a_{i,\mathrm{F}} - a_{i,\mathrm{P}}\right) \tag{20}$$

In general, the overall mass transfer coefficient $k_{\mathrm{ov},i}$ is a series of individual mass transfer resistances for the concentration boundary layer and the membrane. The mass transfer resistance of the homogenous selective layer was described above by the solution–diffusion model. Now the focus will be on the concentration boundary layer.

Since the membrane rejects the less permeable component, this component accumulates at the membrane. At steady state it must be transported back into the bulk of the feed stream, see Fig. 5. This transport has to be diffusive

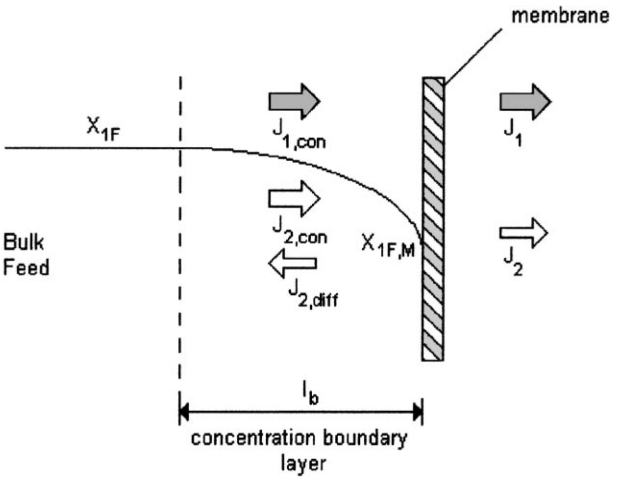


Fig. 5. Concentration polarisation.

since the flow in the mass transfer boundary layer adjacent to the membrane surface is laminar. The driving force is based on a negative concentration gradient, i.e., an enrichment of the less permeable components at the membrane surface compared to the bulk. This layer of higher concentration is described as the concentration boundary layer while the overall phenomenon is called concentration polarisation. The influence of concentration polarisation on the overall process depends on the flux of the components through the membrane as the flow regime on the feed side. To estimate the mass transfer coefficient in the concentration boundary layer the semi-empirical Sherwood correlation can be generally applied. For crossflow pervaporation this correlation can be written as

$$\mathrm{Sh} = a\,\mathrm{Re}^b\,\mathrm{Sc}^c\left(\frac{d}{l}\right)^d \tag{21}$$

The conventional way to describe the Sherwood number is as a relationship between the diffusion coefficient, hydraulic diameter and the mass transfer coefficient for the concentration boundary layer:

$$\mathrm{Sh} = \frac{k_{b,i}\,d_h}{D_{ji}} \tag{22}$$

The adjustment of the variables a, b, c, d in Eq. (22) based on the flow pattern, module types and flow regime applied. Lists of specific adjustment factors can be found in the literature. A review of mass transfer correlations for turbulent flow by Gekas and Hallström [32] gives a general overview of mass transfer correlations that appeared in the literature between 1934 and 1984.

Using these (Eqs. (21) and (22)), the mass transfer coefficient through the boundary layer can be estimated and the overall mass transfer resistance can be obtained using Eq. (19).

The effect of concentration polarisation is of particularly importance if high fluxes through the membrane are combined with laminar or low turbulent flow regime. However, even though the fluxes in organophilic pervaporation are low compared to hydrophilic pervaporation or other membrane processes concentration polarisation is important when the separation factor is large. This is true for a number of volatile organic compounds and so the mass transfer resistance must be included in the design of pervaporation processes applicable for wastewater treatment.

2.4. Dimensionless numbers for membrane selection

The selection of a separation process is generally based on its capability to separate components from each other. In pervaporation there are three interlinked dimensionless numbers that have been used to describe the capability of membranes to separate components from each other – separation factor, enrichment factor and selectivity. It should be noted that these dimensionless numbers used in pervaporation are of a similar nature to ratios used in other separation processes, e.g., distillation. The following equations are generally restricted to binary systems but might be also applied to multi- component systems in wastewater treatment. These dimensionless numbers might give the chemical and environmental engineer a general indication whether the membrane is suitable for particular wastewater separation problem.

The separation factor α_{ij} is essentially similar to the one used in other thermal separation processes; it is the ratio of the permeate compositions to the ratio of feed compositions and can be introduced as a ratio between feed and permeate concentration.

$$\alpha_{ij} = \frac{y_i\,x_j}{x_i\,y_j} = \frac{y_i(1-x_i)}{x_i(1-y_i)} \tag{23}$$

Table 2 gives an overview of selectivities of polydimethylsiloxane (PDMS) membranes, so far the most widely applied organophilic membrane for the recovery organic compounds from wastewater. From this table it can observed that the selectivity is highly dependent on the compound to be recovered.

Another convenient expression for the selectivity is the enrichment factor β_i which is specified as

$$\beta_i = \frac{y_i}{x_i} \tag{24}$$

The quotient of the enrichment factors of the two components can then be used to redefine the separation factor.

$$\alpha_{ij} = \frac{\beta_i}{\beta_j} \tag{25}$$

It should be noted that the separation factor α_{ij} is independent from the measure of concentration applied (e.g., mole fraction, mass fraction) while the enrichment factor β_{ij} is dependent upon the measure of concentration.

For extremely dilute systems such as aqueous solutions of aroma compounds, β_W for the water phase is very close to

Table 2
Selectivities of PDMS membranes for pervaporation of organic compounds from wastewater [33]

Organic compound	Separation factor α_{ij}
Acetic acid	3
Ethanol	7
Phenol	27[a] (18)[b]
Acetaldehyde	48
Acetone	50
Pyridine	70 (56)[b]
Methyl-isobutylketone	705[b]
n-Hexane	1300
Ethyl ether	1600
n-Butyl acetate	2300
1,2-Dichloroethane	4300
Chloroform	6800 (8510)[b]
Vinyl chloride	9000
Cyclohexane	9300
Toluene	10000
Benzene	11000
Styrene	13000

[a] Based on [34].
[b] Based on [13].

unity and the enrichment factor for the aroma compounds are almost identical to their separation factors.

If for Eq. (9) (a) $a_{ip} \ll a_{iF}$ (which is so if the permeate pressure is very low relative to the vapour pressure of the permeable components in the feed) and (b) activity coefficients are close to unity, then:

$$\alpha_{ij} \cong \frac{J_i}{J_j} = \frac{P_i}{P_j} \tag{26}$$

However, the second approximation that is often valid for gas separation is poor for pervaporation because the activity coefficients of the organic compounds in the aqueous feed are often much greater than unity. In absence of feed side boundary layer resistance, the complete expression for a binary system is

$$\alpha_{ij} = \frac{P_i}{P_j}\left[\frac{\gamma_i - y_i p_{\mathrm{P}}/x_i p_i^{\mathrm{sat}}}{\gamma_i - (1-y_i)p_{\mathrm{P}}/(1-x_i)p_i^{\mathrm{sat}}}\right] \tag{27}$$

These dimensionless numbers, combined with the feed concentration, can be related to each other in the following manner [29]:

$$\alpha_{ij} = \frac{1 - x_{i,\mathrm{F}}}{1 - \beta_i x_{i,\mathrm{F}}}\beta_i \tag{28}$$

$$\beta_i = \frac{\alpha_{ij}}{1 + (\alpha_{ij} - 1)x_{i,\mathrm{F}}} \tag{29}$$

$$x_{i,\mathrm{P}} = \frac{\alpha_{ij}\, x_{i,\mathrm{F}}}{1 + \left(\alpha_{ij} - 1\right)x_{i,\mathrm{F}}} \tag{30}$$

It should be noted that in addition to these measures of the separation performance, the flux of the target component through the membrane is an important factor in selecting an appropriate membrane.

3. Influence of process parameters on process design

In the design and operating stage of an organophilic pervaporation unit it is important for the chemical and environmental engineer to understand the key aspects of the process. Apart from the mass transport through the membrane, the other aspects are determined by the process parameters and the module design.

3.1. *Temperature*

In pervaporation, temperature is an important process parameter. According to the solution–diffusion mechanism the effect of temperature can be expressed by an Arrhenius type function. The activation energy required in the exponential function can be dissociated into two parts:

$$E_i = \Delta H_{\mathrm{sorption},i} + E_{\mathrm{diffusion},i} \tag{31}$$

where $\Delta H_{\mathrm{sorption},i}$ is the enthalpy of dissolution for feed molecules of component i to be sorpted into the membrane and $E_{\mathrm{diffusion},i}$ is the activation energy required for the permeating molecules to diffuse through the membrane.

However, in the overall process there is a phase change and the variation of permeating component fluxes as a function of temperature can also be represented generally by the following equation with $\Delta H_{\mathrm{vap},i}$ being the enthalpy of vaporisation:

$$\frac{\mathrm{d}(\ln J_i)}{\mathrm{d}T} = -\frac{E_i + \Delta H_{\mathrm{vap},i}}{RT^2} \tag{32}$$

It can be seen from Eq. (32), that temperature can influence the transport in the membrane in two ways: (i) by modifying the sorption–diffusion step inside the membrane E_i and (ii) by changing the activity driving force across the membrane ΔH_{vap}.

$E_{\mathrm{diffusion},i}$ is commonly positive while $\Delta H_{\mathrm{sorption},i}$ is negative for the exothermic sorption process. When the negative $\Delta H_{\mathrm{sorption},i}$ dominates a negative value of E_i will occur, indicating the permeability parameter P_i will show decreasing trends with increases of temperature [35]. It is, however, observed that the permeation flux increases with an increase in temperature because the effect of temperature on the saturated vapour pressure is more significant.

By definition, pervaporation requires the volatilisation of a portion of the liquid feed. The enthalpy of vaporisation must be supplied by heat from the feed as the liquid feed flows across the membrane and a portion pervaporates. The resulting temperature drop can be significant if the flux is relatively large and particularly if the permeating compound has a high latent heat of vaporisation. A temperature gradient is generally established along the membrane (Fig. 6(1)). As flux is strongly dependent on feed temperature, typical process layouts employ interstage heaters to reheat the feed between membrane modules to compensate for this effect (Fig. 6(2)).

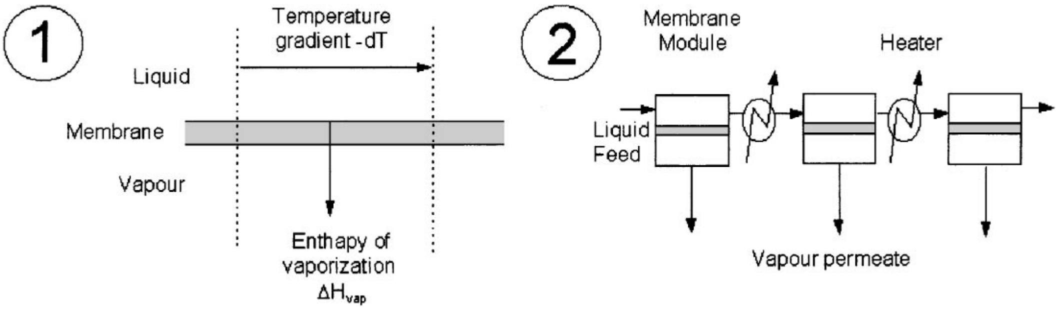


Fig. 6. Temperature in pervaporation: (1) upstream cooling and (2) module interstage heating.

3.2. Permeate pressure

In pervaporation another important parameter is the permeate pressure in the module. Variations in permeate pressure will affect the fluxes across the membrane Eq. (7). The vacuum provides the driving force but the cost of the vacuum system increases rapidly with the quality of the vacuum. However, by knowing the membrane permeabilities and the saturated vapour pressures of the component the effect of permeate pressure upon the performance can be predicted. The response of a pervaporation system towards a change in permeate pressure can be classified into four groups as shown in Fig. 7. In order to locate the system, two terms are required, i.e., E and y_o^*. Both dimensionless terms can be evaluated as follows:

$$E = \frac{K_o\Theta_o}{K_w\Theta_w} \quad \text{where} \quad K_o = \frac{P_o}{p_o^{sat}} \quad \text{and} \quad K_w = \frac{P_w}{p_w^{sat}} \tag{33}$$

$$y_o^* = \frac{1}{(P_w\gamma_w x_w/P_o\gamma_o x_o)+1} \tag{34}$$

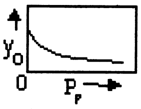
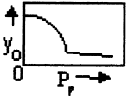
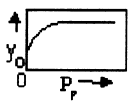
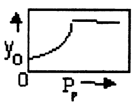
E	y_o^*	Class of system	The profile of y_o in varied P_P
$E>1$	<0.5	A	
	>0.5	B	
$E<1$	<0.5	C	
	>0.5	D	

Fig. 7. Schematic illustration of the variation of permeate composition with permeate pressure for the four possible types of behaviour [36].

The latter term y_o^* is only dependent on upon membrane permeability, feed side composition and activity coefficients, whist the former term E depends on permeabilities, component saturated pressure and the terms Θ which are sorption ratios reflecting the fact that the adsorption isotherms are unlikely to be linear. If they were to be so, then $\Theta_o = \Theta_w = 1$. However, as shown recently [37], the value of Θ_o for high boilers may be significantly greater than unity. When this is so, it is important that the permeate pressure p_P be maintained at a low value.

Clearly y_o^* can be readily evaluated and to a first approximation $\Theta_w \approx \Theta_o \approx 1$ and so E can be estimated readily. Thus, using Fig. 7 a prediction of the sensitivity of the systems towards changes in permeate pressure can rapidly be made.

The different groups in Fig. 7 correspond to the following definitions:

Class A: The relative organic flux at $p_P = 0$ is greater than the relative flux of water but the absolute flux is less than that of water. Also the system exhibits a steeper slope of decrease in permeate concentration as permeate pressure increases from absolute vacuum.

Class B: The relative organic flux at $p_P = 0$ is greater than the relative flux of water and the absolute flux is greater than that of water. The system shows a gentle slope of decrease in permeate concentration as permeate pressure increases from absolute vacuum.

Class C: The relative organic flux at $p_P = 0$ is smaller than the relative flux of water and the absolute flux is less than that of water. The system is defined by a rapid increase in permeate concentration as permeate pressure increases and flattens as permeate pressure approaches the partial pressure of the organic compound in the feed stream.

Class D: The relative organic flux at $p_P = 0$ is smaller than the relative flux of water but the absolute flux is greater than that of water. The system exhibits a gentle slope of increase in permeate concentration as permeate pressure increases from vacuum and a rapid increase as it is close to the partial pressure of organic compound in the feed stream.

The effects of different permeate pressures on the systems in further illustrated in Fig. 7.

3.3. Module design

The key to the successful application of pervaporation lies in the development of both the membrane and the module. The choice of membrane is critical. However, the hydrodynamic mass transfer on the feed side and on the permeate side can also affect the separation quality. Further, the choice of modules also influences the process economics. Generally, the cast membranes can be packaged into modules of several commercially available module geometries (Fig. 8).

The plate-frame module design allows the use of gasket materials that are resistant to corrosion. The hydrodynamic mass transfer resistance can become a limiting factor for the separation in plate-frame modules, thus necessitating a high velocity of feed to enhance feed side mass transfer. For the separation of VOCs from water, a relatively inexpensive spiral wound modules made from plastics can also be used. To increase hydrodynamic mass transfer in the spiral wound modules, feed spacer design needs to be modified. Also the pressure drop on the feed side can be a problem. For the hollow fibre module, a high packing density can be reached. The problems encounter with this module design are longitudinal temperature drop and longitudinal pressure build up on the permeate side [38–40]. However, a novel design that

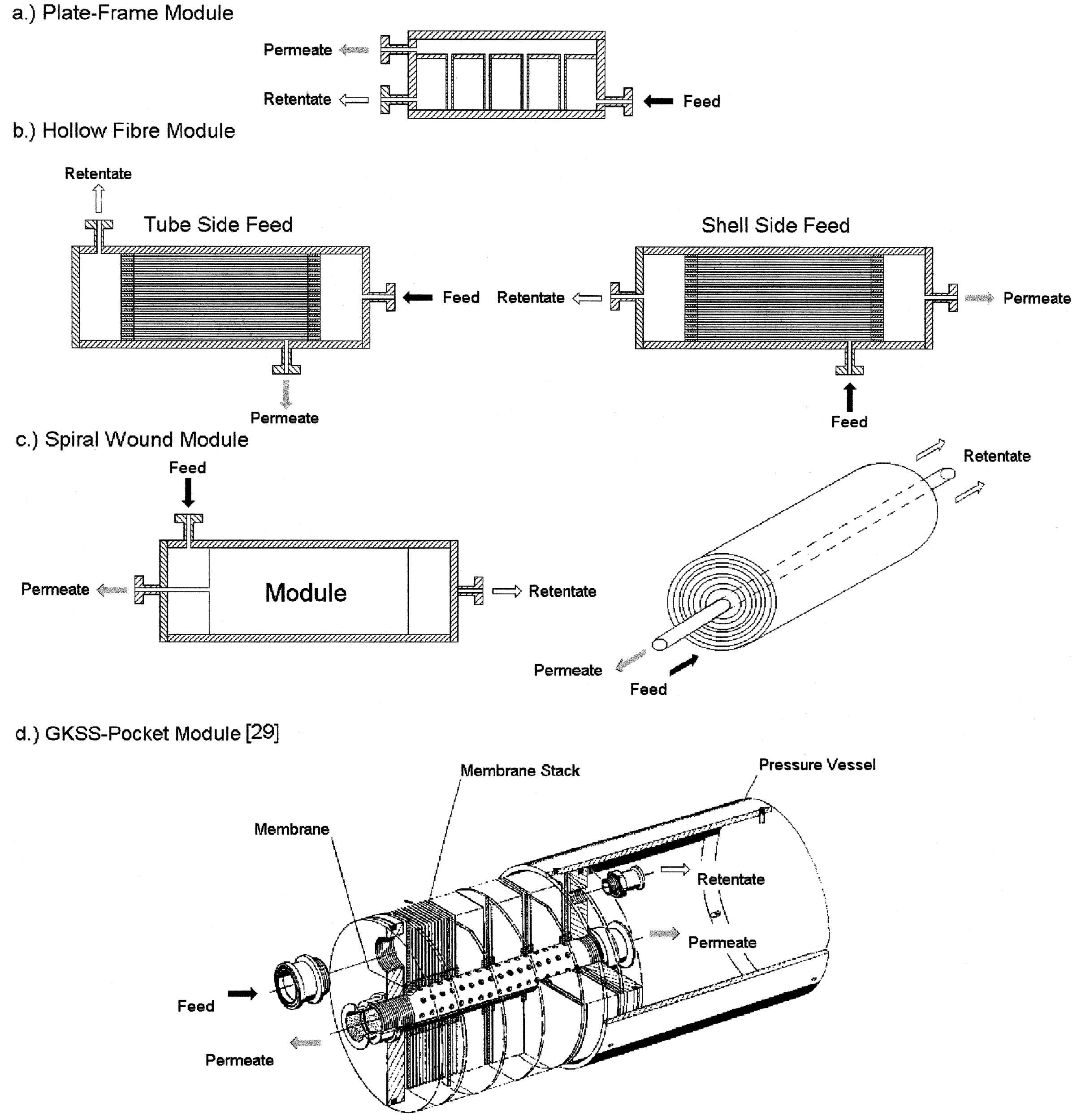


Fig. 8. Commercial pervaporation modules.

gives good mass transfer on the feed side and a low permeate pressure drop is the 'pocket' module of GKSS Research Center Geesthacht GmbH, Germany [29].

4. Environmental applications of organophilic pervaporation

The main environmental application of organophilic pervaporation is in the recovery of organic compounds from industrial wastewater. For various wastewater streams suitable organophilic pervaporation membranes have been developed and successfully tested (see Table 2). To apply pervaporation successfully to wastewater treatment it is necessary to integrate pervaporation into the process design.

4.1. Pervaporation within the framework of wastewater treatment

The hierarchy of waste management practice sets waste prevention as the ultimate target of waste management while disposal without prior treatment is the option with the lowest priority [41]. Since the goal of waste elimination is often not achievable in industry a more practical approach to the waste management hierarchy is generally adopted [40]. Four different strategies can be applied within the framework of wastewater treatment (Fig. 9). Referring to Franken and Fane [42] these strategies are

- no treatment prior to disposal,
- end-of-pipe treatment,
- waste recovery and recycle, and
- new process.

The first two strategies are less favourable since they do not involve integrated pollution prevention and waste minimisation. For improved environmental protection and to meet new environmental legislation, new processes with elimination of waste and reduction at source are the most preferable option followed by waste recovery and recycle. Both approaches are particularly attractive as they give both environmental and economical benefits. If waste elimination is not applicable, the objective is to separate waste from water for recycling and reuse of the valuable chemicals. Additionally, the water itself may often be available for reuse through employment of this method. Overall, whatever approach is employed the strategy will be constrained by both economic and technical boundary conditions.

Various processes can be applied to remove organic compounds from wastewater. The applicability of these processes is commonly restricted to certain concentration range of organic compounds due to technical or economical limitations. Some processes are only applicable if the organic compounds are significantly more volatile than water. Referring to Fig. 10 organophilic pervaporation has to compete against conventional technologies such as adsorption, stripping and extraction. The main advantage of pervaporation in competition with these processes is that it provides the opportunity to recover organic compounds to a standard that both water and organic compounds can be reused without additional processing and no additives are required. Furthermore, pervaporation offers potential energy savings since it works at moderate temperatures and pressures. Consequently, depending on compounds involved and the level of recovery and removal required pervaporation, might offer both environmental and economical benefits to industry.

With reference to Fig. 10 it should be noted that the restriction of pervaporation to a concentration greater than 10 ppm is not due to chemical limitations such as chemical

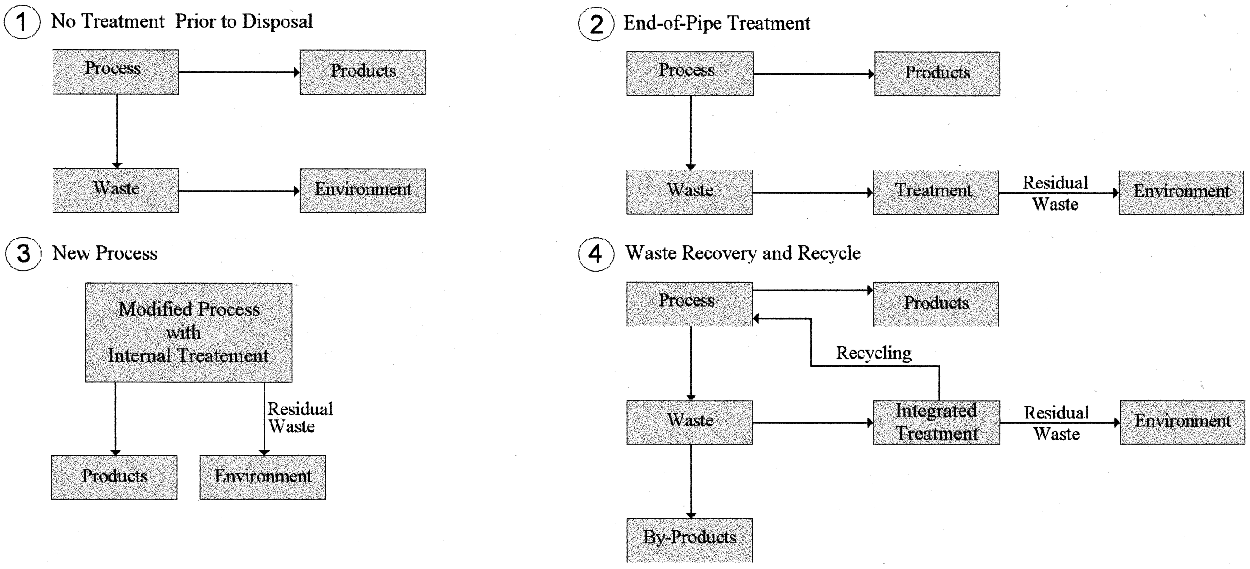


Fig. 9. Different strategies for waste treatment (after [42]).

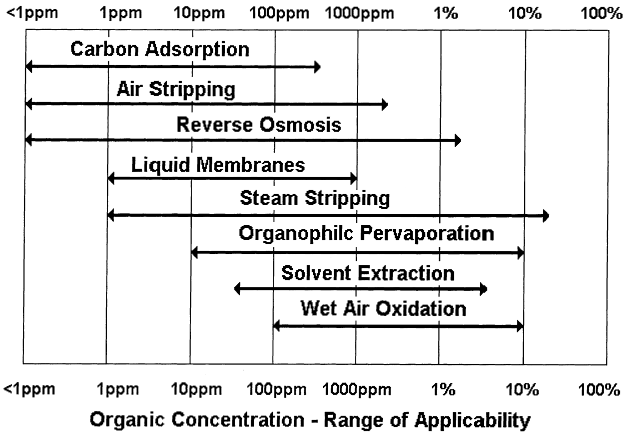


Fig. 10. Organophilic pervaporation within the concept of wastewater treatment (modified after [43]).

equilibrium but due to the exponential increase of membrane area when recovering low concentrations of organic compounds [44] and is, therefore, a result of economic considerations. Further, the application of pervaporation might be limited by the membrane selectivity which might not provide a sufficiently pure permeate stream.

One solution to overcome these limitations is to integrate pervaporation into a package of different processes to form a 'hybrid process'. Virtually every separation process can be combined with a pervaporation process to form a hybrid process as long as it is capable of achieving a predefined task under optimised processes conditions. This hybrid-processes can then achieve separations that are otherwise impractical or economically inefficient [45].

The drying of solvents is not considered in this paper but high concentrations (>99.5 wt.%) of organic compounds can be reached by using hydrophilic pervaporation to remove water. Such a process is applicable to the permeate streams considered in this paper and process combinations of organophilic–hydrophilic have been proposed by others [46,47].

4.2. Guidelines for applying and integrating pervaporation

The following systematic approach for the integration and scale-up of pervaporation units is proposed to give some guidelines for environmental applications of pervaporation. The basic steps of this approach are the following:

1. *Defining the separation problem.* Primarily check that pervaporation is a suitable process to treat the given feed stream.
2. *Initial membrane screening.* In order to decide whether suitable polymers for the task are available, different membrane polymers can be compared (based either on data found in literature, or on experimental solution–diffusion measurements).
3. *Analysis of selectivity and permeability using modifications of the polymer.* Membrane polymers can often be modified by, for example, integrating different functionalised groups into the polymer material. Furthermore, the membrane might be improved by varying the type of support layer (e.g., porosity, thickness) or the thickness of the selective layer. The different membrane polymer modifications are tested with a laboratory test, measuring flux and selectivity under different process conditions. In order to reduce the number of experiments, simulations may be used.
4. *Initial process layout and economical analysis.* After the polymers are tested and modified, an initial process layout can be conducted using the data collected from both experiments and simulations. Based on the initial layout a first economical analysis can be pursued.
5. *Measurements with a pilot unit.* To ensure that the results of the laboratory scale unit are transferable to large-scale units, a pilot unit is used. If the results from the laboratory and the pilot unit are similar it can be assumed that they can be used for the scaling-up process.
6. *Consideration of hybrid process.* From an economical analysis of the variation of recovery with cost, a decision on whether a hybrid process should be investigated has to be made. Such processes allow for a decoupling of recovery and removal objectives.
7. *Simulation and economical analysis of the proposed system.* Following the previous steps, the full-scale unit can be simulated and its economical performance then analysed in detail.
8. *Improvement of the system with focus on plant integration.* To gain the most out of the integration of the unit, the overall process has to be analysed to find the optimum position for the unit.

Applying this step-by-step approach leads to optimised application of pervaporation.

4.3. Case study: the removal of phenol from wastewater

In this case study phenol has been chosen as the organic compound since it represents a family of important chemicals and its production or use commonly involves the production of a contaminated wastewater stream.

Phenol is used in the production of phenol-formaldehyde resin, caprolactam, adipic acid, and aniline which are required for the production of a wide range of consumer goods and product materials. Most of the phenol is produced by using cumene oxidation (Hock process) This process involves the production of a wastewater stream with 1–3 wt.% phenol which is at this concentration miscible with water [48]. The limit for discharging phenol is set to 5 ppm [49].

Referring to Fig. 10 it is obvious that organophilic pervaporation on its own is unable to achieve this target. However, pervaporation can be applied as a pre-treatment

Table 3
Comparison of alternative processes to treat a wastewater steam with 3 wt.% phenol to a final concentration of 5 ppm

Process	Comments
Biological treatment	no recycling of phenol possible large hold up tanks required to provide residence time might be useful to reach very low phenol concentrations of less than 1 ppm
Activated carbon adsorption	no direct recycling of phenol possible regeneration required regeneration might create new waste streams commonly only applied if the waste stream is small or phenol concentration low
Liquid–liquid phase separation	not applicable for phenol concentration of less 10 wt.% in wastewater since aqueous phase saturated with phenol
Incineration	no recycling of phenol possible commonly only applied when waste concentration high or waste stream small
Reverse osmosis	large membrane area required to reach low phenol concentrations phenol concentration in permeate might not be high enough for direct recycling
Solvent extraction	might not achieve low phenol concentrations required for direct disposal of water-rich stream
Oxidation	no recycling of phenol possible commonly only applied when waste concentration low and waste stream small
Pervaporation	large membrane area required to reach low phenol concentration in retentate phenol concentration in permeate might not high enough for direct recycling
Hybrid process Fig. 11	more complex process design required concentration for the recycling of phenol can be achieved required concentration of water for direct disposal can be achieved recycling of liquors from regeneration of activated carbon is integrated

step before a final polishing step. Furthermore, depending on the selectivity of the membrane the concentrated organic permeate stream might be still too dilute for recycling. Depending on the organic concentration in the permeate either liquid–liquid phase separation can be applied or the stream has to be treated by alternatives less favourite alternatives such as incineration or oxidation.

Different alternative processes including a pervaporation-based hybrid process have been screened (Table 3) to treat an aqueous feed stream with a phenol concentration of 3 wt.% a until a final concentration of 5 ppm phenol is has reached. The hybrid process combines pervaporation with adsorption and liquid–liquid phase separation.

Fig. 11 shows a hybrid process design for the removal of phenol from a waste stream of 1000 kg/h. The liquid–liquid

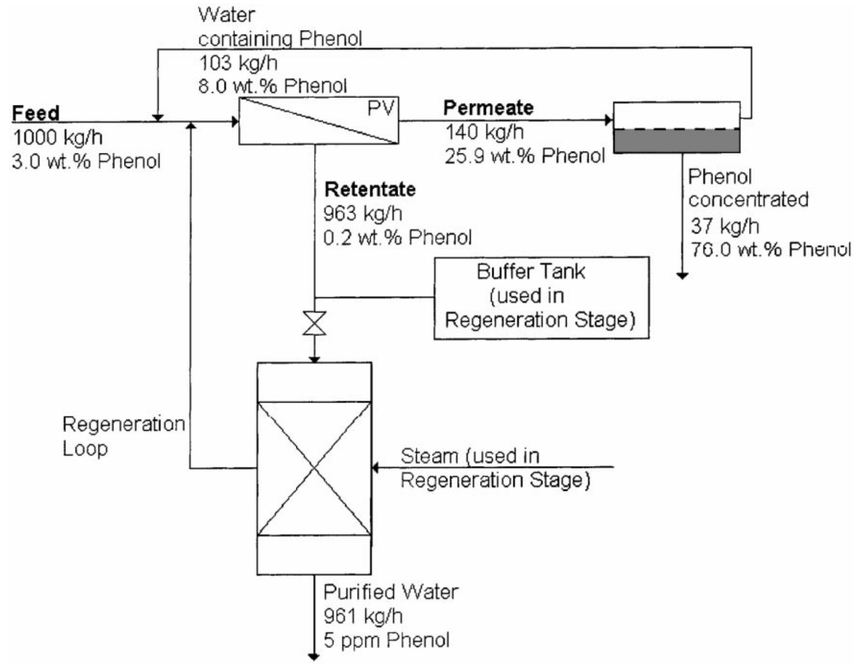


Fig. 11. Hybrid process to recover phenol from wastewater (schematic without heat exchangers). Also note that adsorption column is operated batchwise and has a phenol adsorption rate of 2 kg/h.

phase separation and the pervaporation unit are combined by an internal recycling stream. The hybrid process can produce both a final effluent stream on the water side which meets the environmental standards of less than 5 ppm and a final effluent stream on the organic side which can be recycled in the process.

The change-over concentration of 0.2 wt% between pervaporation and adsorption leads to a reduced membrane area compared to the stand-alone pervaporation. Further, in this case only 2 kg/h of phenol are retained by the adsorption column compared to 50 kg/h in case of adsorption alone, the number of regeneration cycles of the adsorption column is significantly reduced. Hence both processes are running under more ideal process conditions.

From a technical point of view the pervaporation-based hybrid process seems to be an attractive alternative to conventional wastewater processes. However, the economics of the process highly depend on case-specific costs.

4.4. Prospects and restrictions in the use of pervaporation in wastewater applications

Until now, only one industrial-scale application of wastewater treatment using organophilic pervaporation for the recovery of VOCs has been reported in literature by Baker [4]. Since the applications of pervaporation to recover organic compounds is commonly restricted to low concentration and E for VOCs is <1, the system in this application is probably Class D. Hence with reference to Fig. 7 the attainment of low pressure is not essential for this system. Furthermore, as can be seen from Table 2, VOCs have a high separation factor and so easy separation of the permeate into an organic layer and an aqueous layer can be expected to be a feature of the overall process.

In this regard it is important to realise that some of the matters of concern in developing a process for VOCs are different from those involved in developing a pervaporation process for phenolic waste streams. The classification introduced above should therefore provide some clarity.

Even though pervaporation does have advantages against other recycling processes, there are still some restrictions for its application. These restrictions are:

- appropriate membrane material not available,
- fouling of the membrane,
- competition with established processes, and
- lack of understanding pervaporation.

As discussed earlier, flux and selectivity of a membrane are deciding factors in pervaporation mass transport therefore, development of new polymer material is a key research areas in membrane technology. The aim in the development of new pervaporation membranes is either to increase the flux keeping the selectivity constant or aiming for higher selectivities and keeping the flux constant, or both. Three approaches are: (1) functionalisation of membrane polymers [13], (2) integration of adsorber agents into polymer material such as zeolite [50,51] and (3) development of completely new polymers [52].

The suitability of membrane material for a specific separation problem is also limited by possible interaction with aggressive or blocking components in the feed. This can, for example, cause destruction of the membrane material due to insufficient chemical resistance of the polymer against solutes or formation of the deposit layer. The last phenomena is called fouling and means the reversible deposit of impermeable substances on the feed-side polymer. Fouling can be prevented by (1) using a highly turbulent flow regime, (2) cleaning the membrane semi-continuously or (3) the integration of a filtration step before the pervaporation unit, for example, by a microfiltration unit. Furthermore, the membrane life cycle is an important factor in the economic analysis of pervaporation and its replacement must be included, throughout the lifetime of the process, as an additional operation cost.

Membranes are viewed as fragile and sensitive to damage by unexpected conditions. Pervaporation is less familiar to the industry in comparison with well-established mass exchange processes and is perceived to be expensive. To gain a foothold in the industry it is important to analyse and optimise the process design since pervaporation is not only affected by membrane properties but also by module design and process conditions.

The prospects are very dependent upon legislation and the approach of governmental and intergovernmental agencies such as the Environmental Agency of UK. Due to the recent international climate conferences more emphasis is currently being given to the reduction of solvent emissions to the atmosphere and companies offering both pervaporation and vapour permeation technologies have more enquiries with regard to the latter. In the past pervaporation suffered from engineers asking the question: ‘Can pervaporation solve the problem?’, whereas the key question is: ‘Can pervaporation be part of an overall solution?’ Consideration of hybrid processes, as hydrophilic pervaporation [45], will increase the prospects of organophilic pervaporation being adopted. Also if environmental agencies increase their opposition to destruction and emphasise recovery and reuse of solvents from aqueous streams, then organophilic pervaporation will become a significant membrane technology.

5. Concluding remarks

The fundamental aspect of pervaporation is the mass transfer through the membrane based on the solution–diffusion mechanism. This mass transfer is dependent on the compounds in the feed mixture and is influenced by coupling effects. Approaches to the mass transport of binary and multi-component systems are given which seems to be particularly suitable for engineering applications since the number of parameters which have to be obtained from experiments are reduced to a minimum, while all key process parameters like permeate pressure, feed temperature and membrane thickness are integrated and well presented within the model. Furthermore, the model can be extended to include the concentration boundary layer, which can be the main transport resistance in pervaporation. The overall mass transfer in pervaporation can be described by

$$J_i = \frac{1}{(\gamma_{i,\mathrm{F}}/k_{i,b}\bar{\rho}_m) + (l_\mathrm{M}/P_i)}\left(a_{i,\mathrm{F}} - a_{i,\mathrm{P}}\right) \qquad (35)$$

The separation performance due to the mass transport through the membranes, can be easily represented by parameters such as separation factor, enrichment factor and selectivity. The other important parameter is the flux of the target component. Factors such as process parameters and module design can significantly influence the efficiency of pervaporation. Recognition of the class of pervaporation, e.g., Class A or Class B, can be important in anticipating the influence of these factors; for $E < 1$ the concentration boundary layer resistance is expected to influence performance more than the permeate pressure, whilst for $E > 1$ the opposite is true.

Within the framework of wastewater treatment, organophilic pervaporation has to compete against the well-established mass exchange technologies but has the distinctive advantage that it might produce both permeate and feed streams which can be reused in a process without further processing. Even though pervaporation is not limited by thermodynamic constraints when low organic retentate concentrations are targeted, a significant increase of membrane area limits the economical feasibility of applying pervaporation. Therefore, it is often necessary to combine pervaporation with other processes to form a hybrid process. This is supported by the case study which reveals that pervaporation combined with adsorption and liquid–liquid phase separation appears to be superior to alternative processes for the recovery of phenol The future of pervaporation will often be as an integrated and optimised part of a process package which is a so called ‘hybrid process’.

Overall, even though there might be some restrictions to overcome, pervaporation has the potential to be successfully applied in environmental applications as and when legislation on aqueous discharges is strengthened to emphasise recovery and reuse of solvents.

Acknowledgements

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Appendix

Nomenclature

Symbol	*Definition*	*Unit*
a	activity	–
C	mass concentration	kg/m^3
d	diameter	m
D	diffusion coefficient	m^2/s
E	energy	J/mol
E	dimensionless membrane classification term	–
G	Gibbs energy	J/mol
ΔH	enthalpy	J/mol
J	solute flux	kmol/(m^2 s)
k	mass transfer coefficient	m/s
K	overall mass transfer coefficient	kmol/(m^2 s)
l	thickness, length	m
L	coupling coefficient	kmol(m^2 s)
$\tilde{V}$	molecular mass	kg/kmol
p	pressure	Pa, bar
P	phenomenological permeability parameter	kmol/(m s)
R	gas constant	J/(mol K)
Re	Reynolds number ($vd_\mathrm{h}\rho/\eta$)	–
s	molar entropy	J/(mol K)
S	selectivity	–
Sc	Schmidt number (ν/δ)	–
Sh	Sherwood number (kd_h/δ)	–
T	temperature	K
u	convective velocity	m/s
v	velocity	m/s
x	liquid phase molar fraction	–
y	vapour phase molar fraction	–
Greek symbols		
α	separation factor	–
β	enrichment factor	–
δ	solubility parameter	–
χ	interaction parameter	–
Φ	volume fraction	–
γ	activity coefficient	–
η	dynamic viscosity	Pas
φ	fugacity coefficient	–
μ	chemical potential	J/mol
ν	kinematic viscosity	m^2/s
Θ	ratio of permeate to feed-side sorption coefficients	–
ρ	density	kg/m^3
ρ_m	molar density	kmol/m^3
Subscripts		
b	boundary layer	
con	convective	

df	dispersion forces
di	dispersion polar interactions
diff	diffusive
F	feed
h	hydraulic
hb	hydrogen bonds
i	component i
j	component j
M	selective layer of membrane
o	organic compound
ov	overall
P	permeate
p	polymer
vap	vaporisation
w	water

Superscripts

*	at ultimate vacuum
0	standard, reference
M	selective layer of membrane
sat	saturated

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