

Review

# Polymeric membrane pervaporation

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## Abstract

Pervaporation is an efficient membrane process for liquid separation. The past decades had witnessed substantial progress and exciting breakthroughs in both the fundamental and application aspect of pervaporation. This review provided an analytical overview on the potential of pervaporation for separating liquid mixtures in terms of the solubility parameter and the kinetic parameter of solvents. Focus of the review was given to the fundamental understanding of the membrane. Research progress, challenges and opportunities, and the prospect of pervaporation were also discussed. The thermodynamic approach of pervaporation, featuring emphasizing membrane/species interactions, though gained great successes in the past decades, is now facing its toughest challenge in the org–org separation. A kinetic era of pervaporation, featuring emphasizing diffusion selectivity, as well as the synergy between the selective diffusion and sorption, is in the making, and this approach will eventually find solutions to the challenging org–org separation.

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## 1. Introduction

Pervaporation is a membrane process for liquid separation [1,2], a polymeric or zeolite membrane [3–5] usually serves the separating barrier for the process. When a membrane is

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in contact with a liquid mixture, one of the components can be preferentially removed from the mixture due to its higher affinity with, and/or quicker diffusivity in the membrane. As a result, both the more permeable species in the permeate, and the less permeable species in the feed, can be concentrated. In order to ensure the continuous mass transport, very low absolute pressures (e.g., 133.3–400.0 Pa (1–3 mmHg)) are usually maintained at the downstream side of the membrane, removing all the molecules migrating to the face, and thus rendering a concentration difference across the membrane. As a variant, the use of a sweeping gas [6,7] in the downstream side of the membrane is also a feasible alternative for the generally used vacuum operation.

It is well known that the phase change from liquid to vapor takes place in pervaporation. Processes involving phase changes are generally energy-intensive, and distillation is a notorious example of them. Pervaporation cleverly survives the challenge of phase change by two features. (1) Pervaporation deals only with the minor components (usually less than 10 wt.%) of the liquid mixtures, and (2) pervaporation uses the most selective membranes. The first feature effectively reduces the energy consumption of the pervaporation process. Compared with the distillation, because of the characteristics of pervaporation operation, it is essentially true that only the minor component in the feed consumes the latent heat. The second feature generally allows pervaporation the most efficient liquid-separating technology. Take the separation of isopropanol/water mixtures for example, if the water content in the feed is 10 wt.%, the maximum single plate separation factor (isopropanol to water) in distillation is about 2, however, a pervaporation membrane can normally offer an one-through separation factor (water over isopropanol) of 2000–10,000 [8–10]. Furthermore, combination of these two features ranks pervaporation the most cost-effective liquid separation technology [11,12]. In addition, pervaporation also demonstrates incomparable advantages in separating heat-sensitive, close-boiling, and azeotropic mixtures [13–16] due to its mild operating conditions, no emission to the environment, and no involvement of additional species into the feed stream. More recently, the hybrid processes [12,17–19] integrating pervaporation with other viable liquid-separating technologies, and processes are gaining momentum. With these developments, we have more reasons to believe that pervaporation will play even more important roles in the future.

To date, pervaporation has found viable applications [20] in the following three areas: (i) dehydration of organic solvents (e.g., alcohols, ethers, esters, acids); (ii) removal of dilute organic compounds from aqueous streams (e.g., removal of volatile organic compounds, recovery of aroma, and biofuels from fermentation broth); (iii) organic–organic mixtures separation (e.g., methyl *tert*-butyl ether (MTBE)/methanol, dimethyl carbonate (DMC)/methanol). Among them, dehydration of organic solvents is best developed. This resulted from the so-called synergic effect [21]: water is both preferentially dissolved and transported in the hydrophilic membranes due to its much smaller molecular size. When pervaporation is used for removing organic compounds from water, the preferential transport of the organic species cannot be achieved in the organophilic

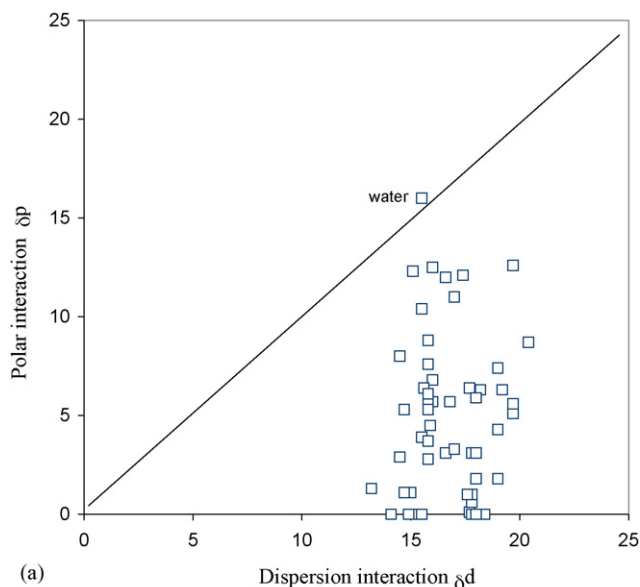
membrane. As a result, the permselectivity of the pervaporation process is reduced, and less than the sorption selectivity. Theoretically speaking, pervaporation in these cases demonstrates no advantage over the adsorption technique. However, when the concentration of organic compounds in water is relatively high, pervaporation tends to be superior to the adsorption technology since pervaporation is a continuous process, it therefore suffers no limitation of the saturated adsorption capacity, which is however an intrinsic weakness of the adsorption process.

Separation of organic–organic mixtures represents the most challenging application for pervaporation [22]. Most liquid pairs in this category are of industrial importance [19], such as polar/non-polar, e.g., methanol/MTBE [23,24], aromatic/aliphatic, e.g., benzene/*n*-hexane [25,26], aromatic/alicyclic, e.g., benzene/cyclohexane [27,28], and isomers, e.g., *p*-xylene, *m*-xylene, and *o*-xylene [29–31]. Research in this category gained some successes in the separation of polar/non-polar liquid mixtures as shown previously, but has not yet seen much significant progress in the other liquid pairs.

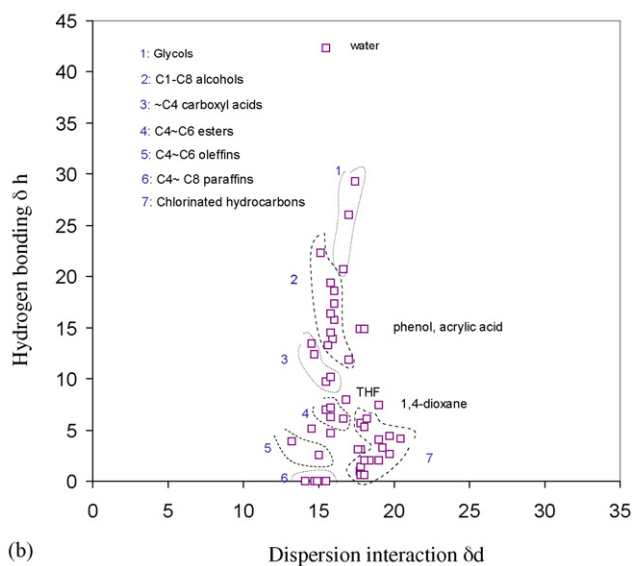
To date, several reviews [2,11,12,17,20,22,32,33] on pervaporation have been available. A detailed review on the zeolite membrane pervaporation had also been conducted by Bowen et al. [11], this review will thus focus on the polymeric membrane pervaporation, with the emphasis given to the fundamental understanding of the membranes, where an analytical overview on the potential of the pervaporation for separating various liquid pairs was presented, the challenges and opportunities, and the prospect of pervaporation was also tentatively discussed.

## 2. Pervaporation in terms of the Hansen solubility parameter and the kinetic diameter

If reviewing the evolution of pervaporation, one may recognize the fact that the Hansen solubility parameter exerted incomparable influence on the development of pervaporation. The Hansen solubility parameter refers to the density of cohesive energy [34], which consists of three components:  $\delta_h$ : the contribution of the hydrogen bonding interaction;  $\delta_p$ : the contribution of the polar interaction;  $\delta_d$ : the contribution of the dispersion interaction. The solubility parameter can thus be represented by a vector in a three-dimensional coordinate. For a binary mixture of components A and B, according to Mulder et al. [35], the end-to-end distance  $\Delta_{AB}$  is an index measuring the dissimilarity of the two species represented by vectors A and B, respectively. By proper selection of a membrane, the obtainable separation factor of the two species could, to some extent, be proportional to this characteristic distance [36]. In order to have an overview of the potential of pervaporation for separating various solvents, the three-dimensional Hansen solubility parameters of over 50 pervaporation-important solvents were collected. Investigation of the solubility parameters shows that for all solvents except water, the component of polar interaction  $\delta_p$  is always smaller than that of the dispersion interaction  $\delta_d$  as shown in Fig. 1(a). So the solubility parameters of all the solvents were plotted in Fig. 1(b) in terms of their two contrasting contributions:  $\delta_h$  and  $\delta_d$ . This treatment allows, though not perfectly, for the solvents to be differentiated into characteristic groups in



(a)



(b)

Table 1

Organic solvents present in the differentiated groups and their typical  $\delta_h$  and  $\delta_d$ 

Group number	Representative solvents	$\delta_h$ (MPa) <sup>0.5a</sup>	$\delta_d$ (MPa) <sup>0.5</sup>
1	Glycols and glycerol	21–29	
2	C <sub>1</sub> –C <sub>8</sub> alcohols	11–23	
3	C <sub>2</sub> –C <sub>4</sub> carboxyl acids <sup>b</sup>	9–13	
4	C <sub>4</sub> –C <sub>6</sub> esters	6–7	
5	C <sub>4</sub> –C <sub>6</sub> olefins	2–4	
6	C <sub>4</sub> –C <sub>8</sub> paraffins	0	
7	C <sub>1</sub> –C <sub>8</sub> chlorinated hydrocarbons <sup>c</sup>	1–7	
Between 4 and 5	Ethers and ketones	5–7	
	Water	43.3	
	Benzene		18.4
	Cyclohexane		16.8
	<i>p</i> -, <i>o</i> -Xylene		17.6

<sup>a</sup> Refer to Appendix A for the accurate range for  $\delta_h$ .<sup>b</sup> Dimethyl carbonate is present in the bottom of the group 3.<sup>c</sup> Aromatics are also present in the group 7.

mercial success accomplished by Sultzer Chemtech [19] in the polar/non-polar mixture separation.

It can be seen in Fig. 1(b) that the dispersion interactions of organics are comparable, and most of them are in the range of 15–20 (MPa)<sup>0.5</sup>. The differences in dispersion interaction are even smaller when the organics are in the same groups, e.g., 1.6 (MPa)<sup>0.5</sup> for benzene/cyclohexane, and there is essentially no difference for isomers (e.g., *p*-, *o*-xylene) as shown in Table 1, suggesting that separation of these species has been out of the reach of the thermodynamic discriminating capability of the membranes. Logically, as pointed out by Koros [37], a complementary approach should be taken in this situation, which emphasizes and relies primarily on the kinetic response of the membranes to the difference in shape and size of the solvents. The kinetic diameters of some of the solvents are illustrated in Fig. 2, and it can be found that substantial differences yet exist between the challenging liquid pairs. For example, there is a

Fig. 1. The comparison of the polar and dispersion contribution of the solvents (a), and the grouped organics in terms of the two-dimensional solubility parameter (b).

terms of their chemical structures or functionalities as shown in Fig. 1(b), and the solvents contained in each group are summarized in Table 1, which include various alcohols, glycols, acids, esters, ethers, ketones, olefins, paraffins, chlorinated hydrocarbons, and some others as specified in Fig. 1(b). Clearly, water possesses the strongest intermolecular hydrogen-bonding interaction, and is followed by glycols, alcohols, esters, chlorinated hydrocarbons, etc. The bigger differences between water and the solvents in  $\delta_h$  suggest that dehydration of organic solvents, and removal of organics, particularly, hydrocarbons and chlorinated hydrocarbons from water, are feasible applications for pervaporation. This has been attested by the worldwide presence of the pervaporation systems for the applications. The substantial difference between methanol (at the top of the group (2) and MTBE in between the groups 4 and 5 also justifies the com-

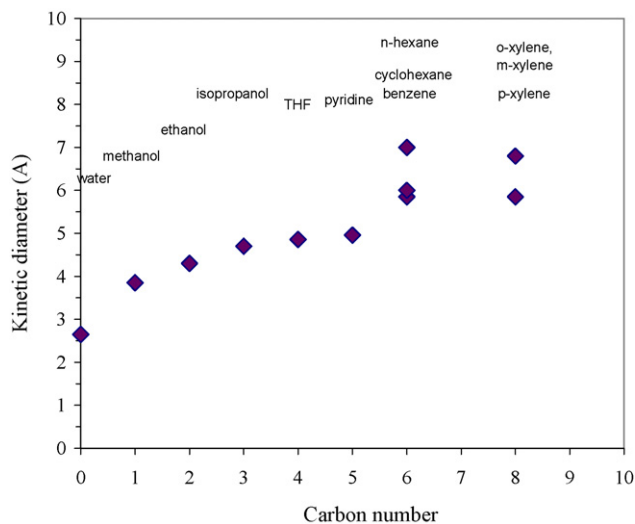


Fig. 2. The kinetic diameters of various organic solvents and water.

0.95 Å difference between *p*-xylene and *m*-xylene, and 1.15 Å between *n*-hexane and benzene. With the continued efforts in developing membranes with proper size-discriminating properties, e.g., highly diffusion-selective polymeric membranes, nanoparticles-incorporated mixed matrix membranes, and single crystalline zeolite membranes, the effective separation of these liquid pairs can be a reality.

### 3. Fundamentals of pervaporation

#### 3.1. Solution-Diffusion theory

Solution-diffusion is the generally accepted mechanism of mass transport through non-porous membranes, which was first proposed by Graham [38] based on his extensive research on gas permeation through homogeneous membranes. It is held that gas permeation through a homogeneous membrane consists of three fundamental processes: (1) solution of gas molecules in the upstream surface of the membrane. (2) Diffusion of the dissolved species across the membrane matrix. (3) Desorption of the dissolved species in the downstream face of the membrane. These three fundamental processes also govern the mass transport across pervaporation membranes [39]. When a pervaporation membrane is in contact with a liquid feed mixture, it is generally believed that the thermodynamic equilibrium reaches instantly at the membrane–feed interface [38,39], therefore:

$$\frac{C_m}{C_{\text{feed}}} = K \quad (1)$$

where  $C_m$  and  $C_{\text{feed}}$  represent the concentrations of a species in the membrane surface and the feed, respectively, and  $K$  is thus the partition coefficient of a species between the membrane and the feed phase, which is a characteristic parameter dependent upon the interaction of the species with the membrane. Membrane transport is a rate-controlling process, which is generally governed by the Fick's first law [38,40,41]:

$$N = -D \frac{dC_m}{d\delta} \quad (2)$$

where  $N$  is the permeation flux of a species through the membrane,  $D$  the diffusion coefficient of the species in the membrane, and  $\delta$  is the position variable. By introducing the partition coefficient  $K$  of the species at the membrane/feed, and membrane/permeate interface, the concentrations of a species in the faces of the membrane can be expressed in its concentrations in the feed and the permeate, respectively, and the Fick's first law thus becomes:

$$N = DK \frac{\Delta C}{\delta} = \frac{DK}{\delta} \Delta C \quad (3)$$

where both the diffusion, and the partition coefficient are treated as constant. If the transmembrane concentration ( $\Delta C$ ) is taken as the driving force for the mass transport, the permeability of the species in the membrane can thus be defined as:

$$P = DK \quad (4)$$

Clearly, the permeability is an index measuring the intrinsic mass transport capability of a membrane for a species. The ideal separation factor of a membrane for species  $i$  and  $j$  can thus be defined as:

$$\alpha_j^i = \frac{P_i}{P_j} = \frac{D_i K_i}{D_{jj} K_j} = (\alpha_j^i)_D (\alpha_j^i)_K \quad (5)$$

Research efforts in pervaporation were thus devoted to seeking the right membrane materials to maximize the differences in these parameters (diffusion coefficient  $D$ , partition coefficient  $K$ , and thus permeability  $P$ ) so that the desired separation can be carried out in an efficient manner. Experimentally, the permeation flux, and the separation factor can be obtained, respectively by:

$$N = \frac{Q}{A \Delta t} \quad (6)$$

$$(\alpha_j^i)^{\text{permselectivity}} = \frac{(Y_i/Y_j)}{(X_i/X_j)} \quad (7)$$

where  $Q$  is the quantity (in gram or mole) of the permeate collected in a time interval  $\Delta t$ ,  $A$  is the effective membrane area used for the test, and  $X$ , and  $Y$  represent the fractions of the components in the feed and the permeate, respectively. Since the downstream pressure in pervaporation operation is negligibly small, the permeation flux of each species through the membrane is essentially proportional to its intrinsic permeability as well as its activity in the feed. As such, the separation factor defined in Eq. (7) is equivalent to the ideal permselectivity as defined in Eq. (5).

It is clear that the classic Solution-Diffusion theory is only valid for governing permeation through essentially non-swollen membranes, e.g., in the case of removal of dilute organics from water [42,43]. When membranes are used for pervaporation dehydration, or organic–organic separation, appreciable membrane swelling usually occurs, and both the partition and diffusion coefficient become concentration-dependent. Therefore, the classic Solution-Diffusion theory should be modified to adapt to the generally swollen pervaporation membranes.

#### 3.2. Modified Solution–Diffusion theories

When a membrane is swollen or plasticized by transporting species, the interactions between polymer chains tend to be diminished, and the membrane matrix will therefore experience an increase in the free volume. The fractional free volume (FFV) of polymers [44,45] is defined as follows:

$$\text{FFV} = \frac{\text{specific free volume}}{\text{polymer specific volume}} \quad (8)$$

It is generally true that in a given membrane, increased free volumes correspond to increased diffusion coefficients of the penetrants. When a membrane is plasticized by more than one species, the diffusion coefficient of a species is facilitated by all the plasticizants. The free volume theory developed by Vrentas and Duda [46–48] offers a perfect background for modeling the mass transport in plasticized membranes. In the case of a

ternary system of [membrane]/[species 1]/[species 2], according to Duda and Vrentas, the diffusion coefficient of the species can be written as:

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \times \exp\left[\frac{\gamma(\omega_1 \widehat{V}_1^* + \omega_2 \widehat{V}_2^* \xi)}{\widehat{V}_{FH}}\right],$$

$$\text{with } V_{FH} = \omega_1 K_{11}(K_{21} - T_{g1} + T) + \omega_2 K_{12}(K_{22} - T_{g2} + T) \quad (9)$$

where  $D_0$  is the diffusion coefficient at infinite dilution,  $E_a$  the diffusion activation energy,  $\widehat{V}_i^*$  the specific critical hole free volume required for a diffusive jump of the component  $i$ ,  $R$  the universal gas constant,  $T$  the absolute temperature,  $\gamma$  is an overlap factor,  $\omega_i$  the weight fraction of the component  $i$  ( $i = 1, 2$ ),  $\xi$  the ratio of the critical volume of the solvent per mole to that of the polymer,  $V_{FH}$  is the specific hole free volume of the polymer–solvent system,  $K_{1i}$  and  $K_{2i}$  the free volume parameters, and  $T_{gi}$  is the glass transition temperature of component  $i$  ( $i = 1, 2$ ). As supports for this theory, many membranologists found that the diffusion coefficient of species  $i$  in a ternary system of [membrane]/[species  $i$ ]/[species  $j$ ] could be generally expressed as [49–54]:

$$D_i = D_{i0} \exp(\alpha_{ii} C_i + \beta_{ij} C_j) \quad (10)$$

where  $D_{i0}$  represents the diffusion coefficients of species  $i$  at infinite dilution,  $C_i$  and  $C_j$  represent the local concentrations of the species of  $i$  and  $j$  in the membrane, respectively, and  $\alpha$  and  $\beta$ , in the membrane science, are usually interpreted as the plasticization coefficients of the two species for the membrane, respectively. Obviously, all of the parameters in Eq. (10) can be correlated to those in Eq. (9). In membrane transport studies, some other relations were also found to be adequate for depicting the concentration-dependent diffusion coefficient. Neel [55] and Greenlaw et al. [56] found that in glassy polymers, the diffusion coefficient took the following form:

$$D_i = D_{i0}(1 + \alpha_i C_i + \beta_j C_j) \quad (11)$$

Albrecht [57] noticed that in some cases, the concentration-dependence of the diffusion coefficient could be well represented by the following function:

$$D_i = D_{i0}(C_i + a C_j) \quad (12)$$

Despite the varieties of the functions found to be eligible for characterizing the concentration-dependence of diffusion coefficient in plasticized membranes, one can perceive that by series expansion of the exponent in Eq. (9), and with some reasonable assumptions for individual cases, the other functions (e.g., Eqs. (11) and (12)) can be generalized with Eq. (10). Therefore, in a ternary system of [membrane]/[species  $i$ ]/[species  $j$ ], the permeation fluxes of the components  $i$  and  $j$  through the membrane can be generally expressed as follows:

$$N_i = -D_{i0} \exp(\alpha_{ii} C_i + \beta_{ij} C_j) \frac{dC_i}{d\delta} \quad (13)$$

$$N_j = -D_{j0} \exp(\alpha_{ij} C_i + \beta_{jj} C_j) \frac{dC_j}{d\delta} \quad (14)$$

Eqs. (13) and (14) are non-linear, and cannot be integrated independently. Dividing  $N_i$  with  $N_j$ , and integrating the ratio by assuming zero concentrations of both the species at the downstream membrane face gives:

$$\frac{N_i}{N_j} = \frac{D_{i0}(\beta_{jj} - \beta_{ij})[\exp((\alpha_{ii} - \alpha_{ij})C_{mi}) - 1]}{D_{j0}(\alpha_{ii} - \alpha_{ij})[\exp((\beta_{jj} - \beta_{ij})C_{mj}) - 1]} \quad (15)$$

Eq. (15) is the so-called “six coefficients” model ( $D_{i0}$ ,  $D_{j0}$ ,  $\alpha_{ii}$ ,  $\alpha_{ij}$ ,  $\beta_{jj}$ ,  $\beta_{ij}$ ) proposed by Brun et al. [51] for describing the binary transport in pervaporation membranes with moderate degrees of swelling. The permeation rate of each species can be numerically obtained provided that the six parameters and the concentrations of the two species in the upstream membrane face are known.

Huang and Shao [58] simplified Brun’s model by ignoring the plasticization effect of the less permeable species in the case of pervaporation dehydration of ethylene glycol. This treatment is reasonable for most of the dehydration membranes, since dehydration membranes generally show overwhelming affinity for water, and the concentration of the less permeable species (e.g., alcohols) in the membrane is negligibly small. The diffusion coefficients of both the species in the membranes are thus dependent on the concentration of water in the membrane phase alone. The ratio of the permeation rate of water  $N_i$  to that of alcohol  $N_j$  can thus be written as:

$$\frac{N_i}{N_j} = \frac{D_{i0} \exp(\alpha_{ii} C_i) dC_i/d\delta}{D_{j0} \exp(\alpha_{ij} C_j) dC_j/d\delta} \quad (16)$$

By integration, Eq. (16) can be expressed as:

$$\frac{N_i}{N_j} = \frac{D_{i0} \exp\{(\alpha_{ii} - \alpha_{ij})C_{Si}\} - 1}{D_{j0} (\alpha_{ii} - \alpha_{ij})C_{Sj}} \quad (17)$$

where  $C_{Si}$  and  $C_{Sj}$  represent concentrations of water and alcohol at the upstream face of the membrane, respectively. By expanding the term  $\exp\{(\alpha_{ii} - \alpha_{ij})C_{Si}\}$  in Eq. (17) into a series, and inserting  $C_{Si} = KC_T X_i$  into the series, where  $K$  is the partition coefficient of water between the membrane and the feed phase,  $C_T$  is the total concentration of the feed, and  $X_i$  is the percentage of water in the feed, Eq. (17) becomes:

$$\frac{N_i}{N_j} = \frac{D_{i0} C_{Si}}{D_{j0} C_{Sj}} \left\{ 1 + \frac{(\alpha_{ii} - \alpha_{ij})KC_T}{2!} X_i + \frac{[(\alpha_{ii} - \alpha_{ij})KC_T]^2}{3!} X_i^2 + \dots \right\} \quad (18)$$

Dividing both sides of Eq. (18) with  $X_i/X_j$  gives:

$$(\alpha)^{\text{perm.}} = (\alpha)^{\text{sorp.}} \frac{D_{i0}}{D_{j0}} \left\{ 1 + \frac{(\alpha_{ii} - \alpha_{ij})KC_T}{2!} X_i + \frac{[(\alpha_{ii} - \alpha_{ij})KC_T]^2}{3!} X_i^2 + \dots \right\} \quad (19)$$

The diffusion selectivity can thus be written as:

$$(\alpha)^{\text{diff.}} = \frac{D_{i0}}{D_{j0}} \left\{ 1 + \frac{(\alpha_{ii} - \alpha_{ij})KC_T}{2!} X_i + \frac{[(\alpha_{ii} - \alpha_{ij})KC_T]^2}{3!} X_i^2 + \dots \right\} \quad (20)$$

As shown in Eq. (20), the overall diffusion selectivity of a membrane is a function of the water content  $X_i$  in the feed. Experiments [58] indicated that the diffusion selectivity decreases as the water content  $X_i$  in the feed increases, and it can thus be judged that  $\alpha_{ii} < \alpha_{ij}$ . The physical meaning of this inequality is that the diffusion coefficient of the more permeable species (e.g., water) is less enhanced by plasticization or membrane swelling than that of the less permeable species (e.g., alcohols). Eq. (20) offers a theoretical interpretation on why a swollen membrane shows reduced overall diffusion selectivity.

Sorption data [58] revealed that the partition coefficient  $K$  of the permeable species (e.g., water) in a swollen membrane is not a constant, and it decreases as the content of the permeable species in the feed increases. It is believed [58] that when the content of the preferentially adsorbed species in the feed is low, the membrane–species interaction dominates the partition selectivity, otherwise the species–species interaction tends to affect the sorption selectivity more, resulting in decreased partition coefficients.

Shao [36] investigated the concentration profiles of water across the thickness of the sulfonated poly(ether ether ketone) membrane, and three water contents in the feed were investigated, which are 93.6, 80.0, and 71.7 wt.%. It was found that the water concentration in the membrane phase decreases slowly in most part of the membrane thickness (see Fig. 3), the quick drop only occurs in a very thin layer adjacent to the downstream membrane surface. In all these three cases, the water content in the membrane reaches 60–80 wt.%. It can be imagined that the water, in this situation, is more like a solvent for the polymer than a solute in the polymeric matrix. It is truly very hard to tell which transport regime (e.g., surface diffusion, viscous flow, slip flow) dominates the water transport in these watery

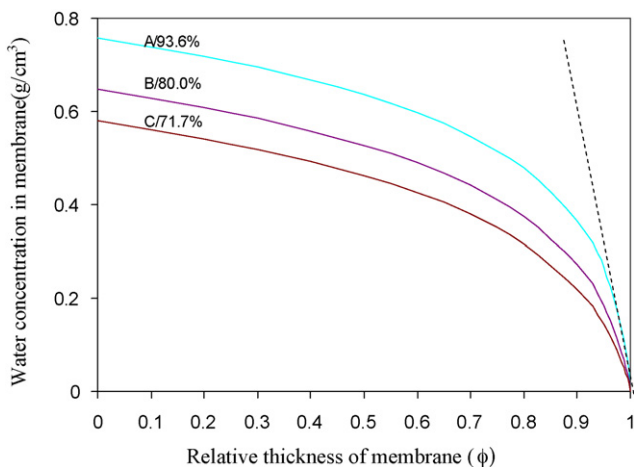


Fig. 3. Water concentration profiles across the membrane thickness.

regions. This ambiguity, to some degrees, justifies the reasonableness of some other transport theories [59–61]. For example, Okada et al. [60,61] proposed a pore-flow model for describing the mass transfer in pervaporation membranes. In this model, the membrane was treated as a medium containing an array of uniform capillary pores, where the mass transport takes place. A liquid–vapor boundary was also assumed to be present in the capillary pores, and the membrane is thus divided into two sections, i.e., the liquid, and the vapor section. The viscous flow takes place in the liquid section, while diffusion occurs in the vapor section. This model offers a very good insight for understanding the modified Solution-Diffusion theory, since it retains the most-striking features of the modified solution-diffusion model. However, this model oversimplified the complex progressive change in the state/phase of the transporting species in the membrane as implied in the modified solution-diffusion model. And as a transport theory, the pore-flow model lacks precision for understanding the actual mass transport in pervaporation membranes.

#### 4. A closer view of the pervaporation membranes

Generally speaking, because of the presence of strong membrane–species interactions, the pervaporation membrane can no longer be treated as a uniform medium for permeation. Shimidzu and co-workers [62–64] believed that the polar groups in the membrane matrix, responsible for the membrane hydrophilicity, act as the fixed carriers for mass transport in the membrane. In the case of dehydration of organic solvents, it is believed that water transport in the membrane proceeds in a special manner. Unlike the random walk of the less polar species  $S_j$  as shown in Fig. 4, the water molecule ( $S_i$ ) jumps from one polar site to another. The fixed carrier theory implies that water and the less polar species in the liquid mixture take different path while diffusing through the membrane. Gierke et al. [65] investigated the morphology of the Nafion perfluorinated membrane by using the wide and small-angle X-ray scattering technique. They believed that the sulfonic groups in the membrane matrix were aggregated due to the electrostatic interaction, and water molecules were trapped inside these aggregates when the membrane was exposed to water. The estimated diameter of the water globule crusted with the sulfonic groups aggregate varied from 2 to about 5 nm, depending upon the ion exchange capacity of the Nafion membranes, which ranged from 0.5 to about 1.1 meq/g.

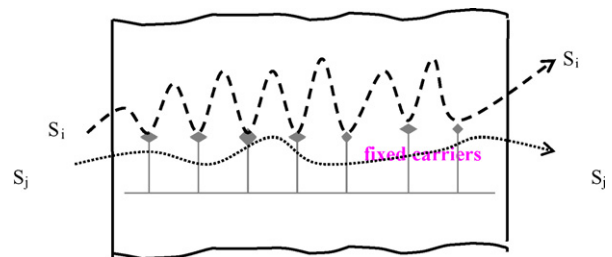


Fig. 4. Schematic representation of the diffusion of the polar species  $S_i$  and the less polar species  $S_j$  in the membrane matrix with the fixed carriers represented by the diamond (◆).

The water globules were interconnected to form a globules string, which extended across the membrane thickness, and acted as the water transport channel. Cabasso and Liu [66] studied the sorption and transport behaviors of water and isopropanol in the Nafion hollow fiber membrane with an ion exchange capacity of 0.879 meq/g. The hollow fibers were elongated with swelling, and the highest degree of swelling occurred when the fibers was in contact with a feed mixture with a water content around 50 wt.%, and the pure component feeds were found to correspond to much lower degrees of membrane swelling. They believed that water preferentially interacts with the sulfonic groups, while isopropanol interacts better with the  $-O-CF_2-$  in the side chains. Indicating that water and isopropanol transport in the membrane through different channels. It was also found that the permeation activation energies of water and isopropanol through the membrane were essentially the same, this finding was analyzed based on the above-mentioned Gierke aggregate model, and it was concluded that the water channel in the Nafion membrane used is discrete, since otherwise water would have a much smaller permeation activation energy than isopropanol. Huang and Shao [36,67] investigated the sorption and transport of water and isopropanol in the sulfonated poly(ether ether ketone) membranes with the ion exchange capacity varying from 1.37 to 2.15 meq/g. The sorption experiments showed that the water content in the absorbates of the sulfonated poly(ether ether ketone) membranes in various feeds was essentially independent of the ion exchange capacity of the membrane, implying that the sorption behavior of water and isopropanol is shaped essentially by the individual presence of the sulfonic groups, and independent of the density of the sulfonic groups in the membranes. Based on this result, Huang and Shao [36,67] proposed that there are two environments present in the sulfonated poly(ether ether ketone) membranes, i.e., the hydrophilic environment (the environment A) consisting of the polar sulfonic groups, and the hydrophobic environment (the environment B) consisting of the rest of the membrane matrix. Because of the hydrophobicity of the environment B, it can be assumed that water dissolves only in the environment A, where water molecules adsorb around the sulfonic groups to form so-called water clusters as shown in Fig. 5. Isopropanol is amphiphilic, it can thus dissolve in both the environments A and B as illustrated in Fig. 5. The concentrations of isopropanol in the two environments are in thermodynamic equilibrium. The ratio of these two concentrations is determined by the difference in the standard Gibbs free energies of the species in the two environments, namely,  $C_{\text{isopropanol}}^A / C_{\text{isopropanol}}^B = e^{-(G_A^\circ - G_B^\circ)/RT}$ . As mentioned previously, the content of isopropanol in the adsorbate is essentially independent of the ion-exchange capacity of the membrane, the concentration of isopropanol in the environment B is thus negligibly small compared with that in the environment A. It can thus be concluded that both the water and isopropanol share the same diffusion channel in the sulfonated poly(ether ether ketone) membranes.

It is shown that the transport behavior of the species in a membrane can be species-specific, and for a same species, the transport behavior can also be membrane-specific. This reflects the complexity of mass transport in pervaporation membranes,

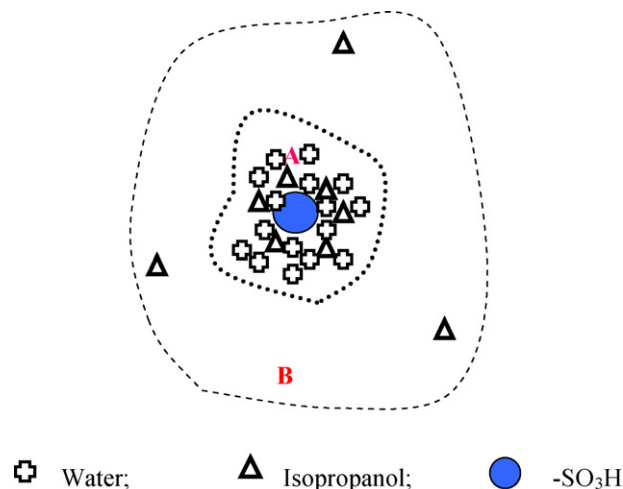


Fig. 5. Dissolution of water and isopropanol in both the hydrophilic (A), and hydrophobic environment (B). Reprinted from Ref. [67] with permission from Elsevier.

which results from the intricate interactions among a membrane and the penetrants in the membrane. In this sense, it is true that there exists no such a universal model, which can characterize every detail of mass transport in pervaporation membranes, and transport models for pervaporation membranes are system-specific.

## 5. The coupled transport in pervaporation membranes

The coupled transport is a frequently observed mass transport phenomenon in pervaporation membranes [68–71]. According to Mulder et al. [72], there are generally two types of coupled transport, i.e., the thermodynamic, and kinetic coupling. The thermodynamic coupling results from the interaction between the dissolved species in the membrane. As is well known that the Gibbs free energy of one species can be changed by the presence of other species, and the changes in the free energy can bring about changes in the partition/sorption behaviors of the species in the membrane. This is the background of the thermodynamic coupling. The background of kinetic coupling is relatively complicated in terms of the coupling mechanisms. A well-known example for the kinetic coupling is the plasticization effect of the dissolved species on the diffusion coefficient of the transporting species in the plasticized membrane. Because it is the combined effect of all the plasticizants in the membrane that changes the free volume of the polymer, the diffusion of the transporting species in the polymer matrix thus becomes interdependent. The mechanism of the kinetic coupling of this kind is implied in the free volume theory developed by Vrentas and Duda [46–48], so the kinetic coupling of this kind is of general sense. It should be noted that mechanisms of the kinetic coupling might be differing, since the membrane/species is a very complex system, which involves a large variety of fundamental interactions. Huang and Shao [36,67] proposed a novel transport mechanism and interpreted the coupled transport observed in the pervaporation dehydration of isopropanol using the sulfonated poly(ether ether ketone) membranes. In this mechanism, both

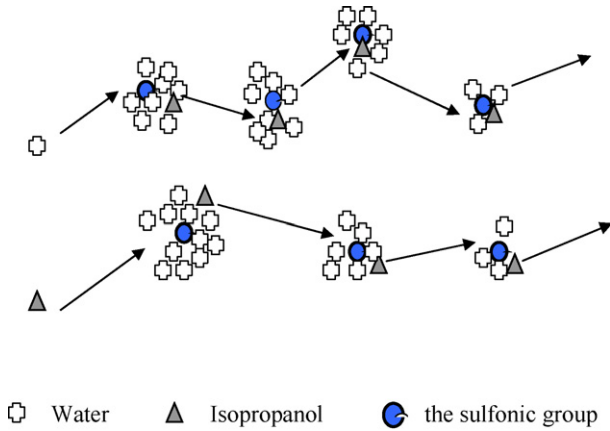


Fig. 6. The simplified species transport in the sulfonated PEEK membrane. Reprinted from Ref. [67] with permission from Elsevier.

water and isopropanol are believed to adsorb around the sulfonic group, and form the so-called water clusters as shown in Fig. 6. Water and isopropanol molecules transport across the membrane by jumping from one cluster to another. The coupled transport is very likely to occur in this situation. For example, when a water molecule jumps from one cluster to another, the vacancy left in the cluster can be filled by either one water molecule or one isopropanol molecule in the previous neighboring cluster. This means the filling of the vacancy is non-selective, and the total concentration difference between the two neighboring clusters acts as the driving force for transport of both water and isopropanol. This composite driving force forms the basis of the coupled transport of the non-general type. For a specific vacancy in a cluster, the probability that the vacancy will be filled by a species (water or isopropanol) was assumed to be proportional to its local concentration  $C_i$  or  $C_j$ . Therefore, the local diffusion coefficients of water and isopropanol should be corrected by their respective jump probability, and the apparent local diffusion coefficient, and the permeation flux of water or isopropanol can be written, respectively as:

$$D_i^{\text{app.}} = D_i \frac{C_i}{C_i + C_j} \quad (21)$$

$$N_i = -D_i \frac{C_i}{C_i + C_j} \frac{d(C_i + C_j)}{d\delta} \quad (22)$$

Experiments [67] show that this model provides a reasonable explanation for the coupled transport.

Kedem [68,69] introduced several methods for dealing with the coupled transport between transporting species, and the phenomenological equation based on the non-equilibrium thermodynamics may have been the most-frequently used equation for describing these complex transport phenomena, where the chemical potentials  $\mu_i$  ( $i=1, \dots, k$ ) are treated as the driving force for the coupled transport as shown below:

$$N_i = -L_{ii} \nabla \mu_i - \sum_{j=1 \neq i}^k L_{ij} \nabla \mu_j \quad (23)$$

where  $L$  is the phenomenological coefficient, the subscripts  $i$  and  $j$  represent the different species in the membrane,  $k$  is the total number of the transporting species in a membrane. The phenomenological equation system provides a versatile correlation between the permeation data and the chemical potential gradients. However, it cannot offer a picture on how the coupled transport takes place in the membranes, and the physical meaning of the coupled transport is thus not well defined.

## 6. Structural stability of composite pervaporation membranes

Pervaporation membranes fall into two categories, the homogeneous membrane and the composite membrane. The composite membrane can offer a higher permeation flux than the homogeneous one due to the much thinner thickness of the homogeneous membrane supported on a porous substrate. The composite membrane is thus suitable for industrial use. Ideally, the porous substrate of a composite membrane presents negligible resistance to mass transport [73]. Otherwise, the substrate resistance leads to decreased membrane productivity and selectivity [74]. As such, tailoring the microstructure of the substrate is important in achieving high performance composite membranes.

Apart from the selectivity and productivity, attention should also be given to the structural integrity of the composite membrane. It is well known that high degrees of swelling occur in pervaporation membranes, and in some particular cases (e.g., separation of high boiling point components), very high temperature operation is necessary [75–77]. If the active skin layer and the underneath support do not swell in a coordinated manner, a big stress can be produced at the interface. And if the interfacial stress surpassed a “critical point”, which depends on the overall complex interaction between the two neighboring materials, the composite structure could be disintegrated, and the membrane would become useless.

Some methods have been adopted to improve the structural stability of the composite membrane, which include the cross-linking of the top layer [78–84], the multi-layer structure strategy [85–87], and the integrally skinned structure approach [88]. The cross-linking treatment suppresses the top layer membrane swelling by reducing the mobility of the polymer chains, and therefore a better compatibility between the two “unlike” materials can be achieved. The multi-layer approach is to coat the support with one or multiple additional material(s) showing compatibility for both the skin and support materials. Huang et al. [85] inserted a slightly cross-linked hydroxyethylcellulose layer between the chitosan top layer and the readily available but relatively hydrophobic polysulfone substrate. The inserted layer was found to serve as a buffer, which smoothens the difference in the degree of the skin layer and the substrate swelling, the structural stability of the resulting composite membrane was considerably improved. In the case of the integrally skinned membrane, because the skin layer and the substrate are made of the same material, the structural stability is no longer a problem. In order to obtain a defect-free skin layer, a high polymer concentration in the cast solution is generally used, and a less porous



substrate is usually produced, which could present a substantial resistance for vapor transport in pervaporation applications.

As an effort to enhance the structural stability of composite membranes, a novel composite membrane with integrated skin layer was developed by Shao et al. [89]. Unlike the conventional procedures for making composite membranes, the skin layer of the composite membrane in this approach is pre-fabricated, and a polymer solution is then cast onto the surface of the pre-fabricated skin layer for preparing the porous substrate by the immersion and precipitation technique. The integration of the skin layer into the substrate is achieved by adding a small quantity of the common solvent, which is capable of dissolving both the skin layer, and the substrate material, to the polymer solution for making the substrate. The cross-sectional morphology of the composite membrane shows that the integration region is more like an integral matrix than a composite structure. The pervaporation tests showed that the skin layer of the novel composite membrane received more reinforcement from the support due to the skin-support integration. This novel composite membrane also demonstrated better anti-swelling property and better separating performance in pervaporation dehydration of ethylene glycol.

## 7. Pervaporation research progress, challenges and opportunities

### 7.1. Organic solvent dehydration

Dehydration of organic solvents (e.g., alcohols, ethers, acids, and ketones) largely represents the applications of the pervaporation [90–94]. The materials used in earlier dehydration research were the naturally occurring polymers, e.g., cellulose and cellulose derivatives [1]. Synthetic polymers [95,96], e.g., poly(acrylic acid) (PAA), poly(vinyl alcohol) (PVA), polyacrylonitrile (PAN), and nylon 6, were subsequently investigated, with a focus mainly on ethanol dehydration [96]. This endeavor did not gain success until the breakthrough achieved by GFT in 1980s. According to Neel [1], the first industry scale pervaporation plant was put into operation in 1988 in France with a daily capacity of 15 M<sup>3</sup> refined ethanol. According to the incomplete statistics [17,19], there have been more than 60 pervaporation units operating around the world so far.

After the success of GFT membranes based on the cross-linked PVA coated on the PAN substrate, many other hydrophilic materials were studied, and some of which includes sodium alginate, chitosan, nylon 6, polyethyleneimine (PEI), cellulose sulfate (CS), synthetic zeolites [97–99], etc. Uragami and Saito [100] and Mochizuki et al. [101] were among the pioneers using sodium alginate membranes for alcohol dehydration. Sodium alginate is a polysaccharide obtained from seaweeds, and it shows excellent affinity for water. As a membrane material, it however lacks mechanical strength and stability in aqueous solutions. Yoem and co-workers [79,81,82] improved the membrane strength and stability by cross-linking using glutaraldehyde, or alternatively by thermal treatment of the membrane at 100 °C for hours. Huang et al. [78] also obtained stabilized sodium alginate membranes by using a relatively simple but quite effective

method of ionic cross-linking, which results from the interaction between the multivalent metal ions (e.g., Ca<sup>2+</sup>, Al<sup>3+</sup>) and the carboxyl groups of the polymer. It is well known that cross-linking limits mobility of the polymer chains, and thus excessive membrane swelling can be suppressed. However, the density of cross-linking should be well controlled, otherwise, membranes will become too brittle to be used.

Blending is also an effective approach for modifying membrane properties. It was found that blending of alginate with other polymers could increase both the mechanical strength and stability of the membrane in aqueous solutions. Zhang et al. [102] blended alginate with cellulose cuoxam, the increased mechanical strength of the blended membranes was attributed to the hydrogen bonding interactions between the hydroxyl groups of the two polymers. Yang et al. [103] blended alginate with cellulose, and further cross-linked the alginate using Ca<sup>2+</sup>. It was found that the tensile strength of the membrane was enhanced 12 folds, and more importantly, the good separating performance of alginate was retained.

Ethanol dehydration using chitosan membranes was first reported by Masaru et al [104], Matsuda et al. [105], and Mochizuki et al. [106], and the continued research [107–111] indicated that chitosan is a very promising material for solvent dehydration, and it demonstrated better separating performance than the cross-linked PVA. Dehydration of isopropanol and ethylene glycol using chitosan membranes was subsequently attempted by Lee et al. [112], Feng and Huang [113], and many others [114–116], aimed at upgrading ethylene glycol used as the airport anti-freeze, and enriching the diluted process isopropanol in chip industry [116].

Like sodium alginate, the chitosan membrane is extremely hydrophilic, and can lose membrane integrity in aqueous solutions. Accordingly, cross-linking and blending strategies [117,118] were employed to suppress the excessive membrane swelling and achieve the enhanced membrane stability. Generally speaking, the cross-linked, or blended chitosan membranes exhibit lower permeation flux, and higher selectivity. As it is known an amine group is present in each repeat unit of chitosan, and chitosan is thus a polycation. Therefore, the polyanion–polycation interaction was also utilized for improving the separating properties of the chitosan membranes. When chitosan is blended with other polyanions (e.g., polyacrylic acid, cellulose sulfate) in homogeneous solutions, the amine groups in chitosan can form very stable complex linkages with the protons or other cations in the polyanions, and the resulting polyelectrolyte complex linkages act as the “ionic cross-linking” for the membranes. Shieh and Huang [119] mixed a chitosan solution with that of polyacrylic acid, and very stable separating performance of the membrane was obtained. Earlier work in this regard was carried out by Richau et al. [120] using cellulose sulfate as a polyanion, which was mixed with various polycations, e.g., polyethyleneimine (PEI), poly(dimethyldiallyl ammonium chloride) (PDMDAAC), and poly(*N,N*-dimethyl-3,5-dimethylene-piperidinium chloride) (PPIP). Pervaporation tests revealed that all these membranes demonstrated excellent membrane stability and dehydration performance.

Table 2  
Pervaporation dehydration performance of some post-GFT membranes with the feed water content at 10 wt.%

Membrane	Solvent	Temp. (°C)	Flux (g/m <sup>2</sup> h)	Selectivity	Ref.
GA <sup>a</sup> cross-linked sodium alginate	Ethanol	60	300	1000	[82]
Al <sup>3+</sup> , Cr <sup>3+</sup> cross-linked sodium alginate	Ethanol	70	942	2750	[121]
	Isopropanol	70	2815	4521	
GA cross-linked sodium alginates	Acetic acid	30	70	5	[122]
	Isopropanol	30	50	3591	
GA-urea-formadehyde-sulfuric acid cross-linked sodium alginate/5 wt.% hydroxyethylcellulose blend	Dioxane	30	111	36	[123]
	Tetrahydrofuran	30	162	543	
GA cross-linked sodium alginate/chitosan blends	Ethanol	60	300	200	[124]
Sulfuric acid surface cross-linked chitosan	Ethylene glycol	35	300	103	[115]
		80	1130	796	
GA cross-linked chitosan	Ethanol	50	1100	6000	[83]
HMDI <sup>b</sup> cross-linked chitosan	Isopropanol	30	300	500	[116]
GA cross-linked two-ply chitosan/sodium alginate	Ethanol	60	210	1000	[125]
	Isopropanol	60	600	1030	
Chitosan/polyacrylic acid complex	Ethanol	60	2000	1000	[119]
CS/PEI complex CS/PDMAAC <sup>c</sup> complex	Ethanol <sup>d</sup>	50	650	208	[120]
	Isopropanol <sup>d</sup>	50	1800	2100	
GFT cross-linked PVA/PAN	Ethanol	50	90	150	[31]
	Isopropanol	60	100	450	

<sup>a</sup> GA: glutaraldehyde.

<sup>b</sup> HMDI: hexamethylene diisocyanate.

<sup>c</sup> PDMDAAC: poly(dimethyldiallyl ammonium chloride).

<sup>d</sup> The feed water content is 20 wt.%.

The separating performance of various dehydration membranes is summarized in Table 2. It can be seen that in some cases, based on the same materials, the membranes displayed quite different separating performance. This suggests that enhanced membrane performance can be obtained by optimizing the modification strategies, and particular attention should be given to membrane cross-linking in terms of cross-linking agent selection, cross-linking density characterization, and cross-linking solution chemistry tuning so that new generations of pervaporation membranes can be obtained based on these promising materials. Table 2 also shows that that GFT membrane exhibited relatively lower flux, and this may be attributed to its double layer structure. According to the characterization results of Koops et al. [73], the surface porosity of the asymmetric PAN substrates is on the level of 10<sup>-4</sup>. Since PVA and PAN have comparable permeability for water, it can be concluded that the PAN support of the GFT composite membrane also acts as a separating layer in this situation.

### 7.2. Dilute organics removal from water

Removal of organics from water is long-standing topic for environmental protection, and the adsorption technology plays a key role in this area. As pointed out previously, pervaporation demonstrates a competitive gap over the adsorption technology when multiple, or relatively high concentrations of organics are present in water, since pervaporation is a continuous pro-

cess, and can offer the incomparable operation convenience than the intermittent process. According to the literature, the cross-linked polydimethylsiloxane membrane has found wide use in this application [126–128], since it shows high affinity and low transport resistance for organics, and is also very stable in the streams. Other rubbery materials were also attempted for the application, some of which are summarized in Table 3, and it can be seen that all the materials demonstrated high selectivity for their respective organic(s).

Table 3  
Typical membrane materials for organic removal from water and their performance

Polymer	Organics	Selectivity	Reference
Poly(dimethyl siloxane)	Chloroform	6,800	[126]
	Toluene	25,000	[42]
	Methylene chloride	19,000	
	Trichloroethane	5,000	
	Benzene	11,000	[135]
	Styrene	13,000	
Polyurethane	Cyclohexane	9,300	
	Toluene	10,000	[42]
Poly(ether- <i>block</i> -amide)	Trichloroethane	2,600	
	Methylene chloride	4,300	[42]
Nitrile-butadiene rubber	Methylene chloride	6,000	
	Chloroform	18,000	[136]
Styrene-butadiene rubber	Chloroform	17,000	[136]

The concentration polarization is the most-striking phenomenon involved in this separation. As it is known that rubbery membranes show both high permeation flux and selectivity for organics, and when the concentration of the organics in water is dilute, the organics in the feed can be depleted much faster than provided, and a diffusion layer or the concentration-polarized layer can be easily induced in the vicinity of the membrane surface [126,129–132]. Many researchers [130–134] have investigated this phenomenon based on the classic transport theory or the resistance-in-series model. It was found that the concentration polarization led to both decreased membrane selectivity and permeation flux for the organics.

Clearly, the challenge facing the pervaporation in this category is not how to find the right material for specific applications, but how to fight against the concentration polarization to make full use of the good separating properties of the available membranes. Based on this understanding, some attempts have been directed to the concentration depolarization [137,138]. The use of turbulence-promoting spacer in the membrane systems, and the introduction of the Dean vortices to the feed flow represent the two main strategies for coping with the challenge, the others also include two-phase feeding [139], and vibrating pervaporation modules [140]. Different from the turbulence-promoting spacer, which abates the boundary layer resistance by promoting turbulent flow in the membrane surface, the Dean flow technique relies on the centrifugal force to induce a secondary flow/eddy flow (Fig. 7) in the feed by using the coiled feed channel. The resulting eddy flow mixes the diffusion layer with the bulk feed and thus facilitates the overall mass transport. In the work of Schnabe et al. [138], the centrifugal force was produced by arranging the hollow fibers in a spiral manner on the surface of a perforated partition tube, and it was found that the permeation flux of the membrane for the organic was enhanced by a factor of 2–3, suggesting that the resistance of the diffusion layer is much higher than that of the membrane itself, and the concentration polarization has severely limited the mass transport through the pervaporation membrane. It can thus be concluded the hydrodynamics of the system should be well improved before pervaporation can play a better role in the area.

### 7.3. Org–org separations

The org–org separation attracted lots of research interest from the very beginning of pervaporation [49], researchers have been motivated by the huge industrial needs of efficient methods for separating mixtures like benzene/cyclohexane, benzene/hexane, toluene/heptane, ethylbenzene/xylene, *p*-xylene/*o*-xylene, etc. As it is known that the components in these pairs have similar physicochemical properties, and effective separation of these mixtures could be very difficult according to the solubility parameter theory. Even so, some attempts have been proved to be promising.

Ho et al. [141,142] separated aromatics/saturate mixtures using the polyimide copolymer membranes, which contain both soft and hard segments. It is believed that the soft segments show preferential affinity for aromatics, are thus responsible for the selective performance of the mem-

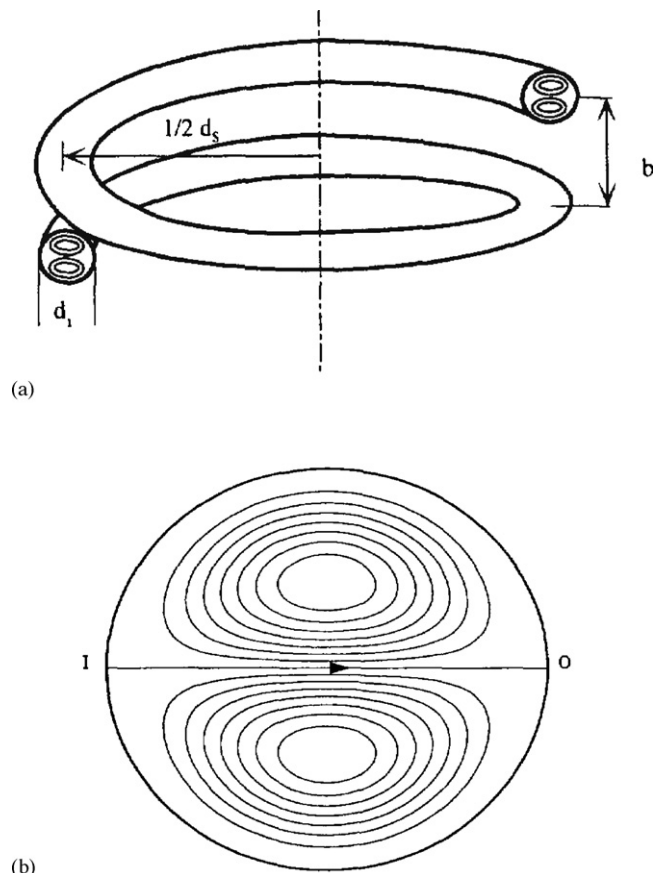


Fig. 7. The secondary flow produced in the spiral-wound hollow fiber. (a) The spiral-wound hollow fiber, and (b) the schematic representation of the dean flow in the bore of the hollow fiber. Reprinted from Ref. [137] with permission from Elsevier.

brane, while the hard segments provides mechanical integrity for the membrane. Based on this approach, Tanihara et al. [143,144] used the polyetherimide segmented copolymer, and polyimide-*co*-polyphenylenediamine membranes for separating benzene/cyclohexane, benzene/heptane, and acetone/cyclohexane mixtures. The achieved separation factor of benzene to cyclohexane varied from 9 to 27, and the permeation rate varied from 0.4 to 2.7 kg/m<sup>2</sup> h.

Polymer blending was attempted by Neel et al. [145], Cabasso et al. [146,147] for the separation of benzene/cyclohexane and other mixtures like methanol/hexane and styrene/ethylbenzene. The blended polymers are expected to demonstrate superior separating performance to the single materials. The difference is made by the resulting optimization in the blended polymer architectures through polymer chain entanglement and intermolecular interactions. The blended membranes showed very good balance between the permeation flux and the separation factor, while single polymers usually give either high permeation rate (e.g., polyphosphonates, polyethylene, polypropylene), but low separation factor, or fairly good separation factor, but very low productivity (e.g., cellulose acetate, poly(vinyl fluoride)) [146]. Cabasso et al. [146,147] blended cellulose acetate and polyphosphonates, and the achieved separation factors of benzene/cyclohexane ranged from 12 to 40, and the perme-

ation rates varied from 800 to 1000 ml/m<sup>2</sup> h. Similar results for the separation were also obtained by Acharya et al. [148] by using the blended membranes based on cellulose acetate and polybromophenylene oxide dimethylphosphonate ester. More recently, blending polymers with nanoparticles, or fine powders with nanostructures have been attempted by some researchers [149,150] for the separations, and the preliminary results were quite encouraging. It is expected that nanotechnology will play an increased role in the near future.

The complex interaction between olefins and silver ions (Ag<sup>+</sup>) was also utilized for separating olefin/paraffin mixtures. Koval et al. [151,152] used the perfluorosulfonate-Ag<sup>+</sup> for the separation of styrene/ethylbenzene. The membrane was styrene-selective, and a selectivity of 36 was obtained while the permeation flux of the membrane was quite low, at the level of 10<sup>-10</sup> mol/s cm<sup>2</sup>. The lower permeability was attributed to the low solubility and diffusivity of styrene in the membrane, since the membrane used is intrinsically hydrophilic, and the size of the resulting complex between the silver ion and styrene is quite large.

Although some promising results have been achieved by using the above-mentioned approaches (e.g., copolymer, blending, and the complex interaction), the separating performance of the membranes is still below the standards expected by the industry. It can be seen in Table 4 that research progress in this area advanced very slowly over the past decades, and more innovative efforts are thus needed to change this situation.

Based on the Solution-Diffusion theory, Koros [37] pointed out that the advantage of the mobility difference of the organic species should also be taken for the efficient separation of the organic mixtures. For doing this, rigid glassy polymers or copolymers with cross-linkable segments should be selected since glassy polymers are generally more shape and size-selective, and in order to suppress the plasticization effects of the penetrants for retaining or even improving the intrinsic mobility selectivity of the membrane, an appropriate degree of cross-linking of the glassy polymer should be performed. Xu, Paul, and Koros [75] employed the rigid polyimide copolymer

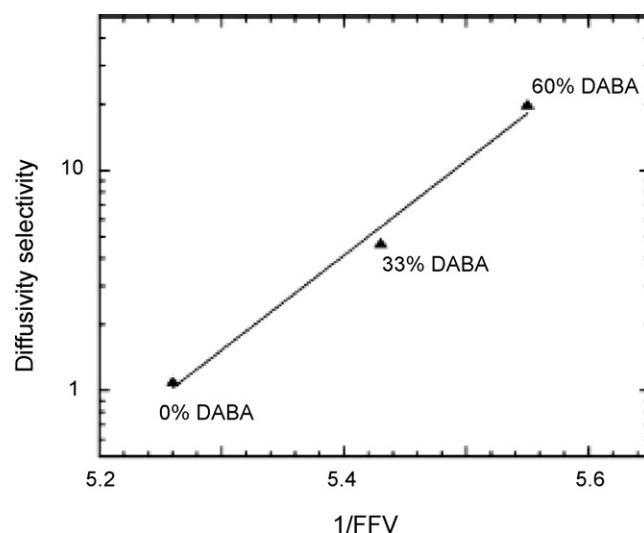


Fig. 8. Diffusivity selectivity correlated with fractional free volume at 100 °C for a 50/50 toluene/*iso*-octane mixture. Reprinted from Ref. [75] with permission from Elsevier.

containing the cross-linkable functionality: 3,5-diaminobenzoic acid, for separating toluene/*iso*-octane. The separating performance of the membranes was analyzed in terms of the sorption, and diffusion contribution. It was shown that there is a robust correlation between the mobility selectivity and the fractional free volume of the cross-linked membranes, and suppression of FFV of the membrane can effectively improve the diffusion selectivity. The potential of this approach was demonstrated by the significantly enhanced mobility selectivity (from 1 to 20 in Fig. 8). The synergy between sorption and diffusion was also observed in membrane permeation, the sorption selectivity was increased from 3.5 to about 5.0 by introducing the cross-linkable segment into the polyimide chain, and a permselectivity higher than 100 was achieved with the mobility selectivity being the main separation contributor.

The zeolite membrane represents another innovative approach for the organic–organic separation [11]. Compared

Table 4  
Membranes used for benzene/cyclohexane separation and their performance

Membrane	Benzene (wt.%)	Temp. (°C)	Permeance (g/m <sup>2</sup> h)	Selectivity	Year	Reference
PP	55	25	54400	1.3	1967	[153]
LDPE	50	25	10800	1.6	1968	[154]
PVDF	53	60	1600	6.2	1973	[155]
CA/PPN	50	78	13600	40.0	1983	[146]
BP-PEO	60	70	2100	9.1	1995	[144]
PMMA-EGDM	10	40	8700	6.7	1997	[156]
DSDA-DDBT	60	78	930	32.0	1997	[157]
Nylon 6-g-PBMA	50	50	1120	2.2	1999	[158]
Nafion-Ag <sup>+</sup>	50	50	2	12.7	2002	[159]
Nafion-Cu <sup>2+</sup>	50	30	0.8	3.4	2004	[160]
PU	54	25	325	2.7	2006	[161]
PVAc-PVA	50	25	500	7.5	2006	[162]

BP: biphenyltetracarboxylic dianhydride; DDBT: dimethyl-3,7-diaminobenzothioiophene-5,5'-dioxide; DSDA: 3,3',4,4'-diphenylsulphone tetracarboxylic dianhydride; Nafion: sulfonated poly(perfluorinated ethylene); EGDM ethylene glycol dimethacrylate; LDPE: low density polyethylene; PBMA: polybutylmethacrylate; PEO: polyethylene oxide; PP: polypropylene; PPN: polyphosphonates; CA: cellulose acetate; PVDF: poly(vinylidene fluoride); PMMA: poly(methyl methacrylate); PU: poly(urethane); PVA: poly(vinyl alcohol); PVAc: poly(vinyl acetate).

with polymeric membranes, zeolite membranes can provide essentially non-swollen, well-defined, and molecular-sized pore structures. As such, zeolite membranes are particularly suited to separate organic mixtures with appreciable size differences although preferential sorption also plays an important role in the zeolite-resulting separations [11]. For the separation of organic mixtures like benzene/*p*-xylene, *p*-xylene/*o*-xylene, the uniform pore structures of silicalite-1 [163], Mordenite [164], and Ferrierite [165] zeolite membranes have demonstrated very good potential. At 303 K, with the 50/50 (mol) feed composition, the Ferrierite zeolite membrane [165] exhibited a selectivity (benzene to *p*-xylene) of 100, and a benzene flux of 12 g/m<sup>2</sup> h. Although synthesis of a thin yet perfect zeolite layer on support to ensure a satisfactory membrane flux is still a very complex process, with continued research efforts, the zeolite membrane will surely be able to play an important role in the organic–organic separation.

## 8. Commercial and engineering aspects of pervaporation

Since the commercialization of pervaporation for ethanol dehydration launched by GFT in 1980s based on the cross-linked PVA/PAN composite membrane, both the scope of application and the types of the pervaporation membranes were extensively enlarged [166]. According to the website of Sulzer Chemtech, a wide array of solvents have been covered in its dehydration market, which includes various alcohols, ethers, ketones, acids, and some polymer solvents like THF, dioxane, etc. The SULTZER PERVAP<sup>®</sup> membranes also succeeded in Methanol/MTBE, and Ethanol/ETBE separation. GKSS developed complex polyelectrolytes composite membranes for dehydration of various solvents. Mitsui Engineering & Shipbuilding Co. also succeeded in rolling out their high flux, high-temperature-resisting NaA zeolite dehydration membranes [11,99]. MTR has been very successful in vapor permeation, and the removal of organics from wastewater also saw some progress in MTR.

The plate-and-frame is still the dominating module configuration employed in pervaporation since this configuration can provide low resistance channels in both the permeate and feed side, the ease in manufacturing is also one of the factors accounting for the dominance. It should be noted that ensuring low transport resistance in the permeate side is a critical consideration in pervaporation module design, this is because the efficient evaporation of the permeate molecules in the downstream face of the membrane needs an extremely low absolute pressure, presence of resistance in the permeate channel can very sensitively affect the pervaporation separation process. Because of this characteristic requirement, the compactness of the membrane modules is no longer a preferential consideration for pervaporation modules. Generally speaking, it is impossible for a hollow fiber module to be employed in pervaporation unless the fiber length is improperly short, or the fiber diameter is big enough, e.g., 5–25 mm [167,168]. As a result, the tubular membrane is also a feasible module configuration for pervaporation, such as the tubular zeolite membranes developed by Mitsui Engineering & Shipbuilding Co. The configurations of various pervapora-

tion membrane modules were not included in this review, since a good summary can be found in a review by Smitha et al. [20], which illustrated the plate-and-frame, spiral wound, hollow fiber, and tubular modules.

## 9. Concluding remarks

Pervaporation has played an important role in solvent dehydration, and this application can be further extended by integrating pervaporation with other viable liquid-separating technologies, and by finding right materials for dehydrating some caustic solvents (e.g., nitric acid). Higher membrane productivity and selectivity is always a concern for application, and this was conventionally accomplished by operating the pervaporation membranes at higher temperatures. The improved membrane flux can also be achieved by conducting optimized membrane cross-linking, particularly when membranes are used for dehydrating solvents of lower water contents. And the improved separating performance of the membrane can also be anticipated by incorporating various active nanostructure in the polymeric membrane matrix. Removal of organic compounds from water is a very promising application for pervaporation, however, continued research need to be done to improve the hydrodynamics of the pervaporation system to reduce the mass transport resistance in the diffusion layer so that the concentration polarization can be effectively suppressed. Compared with the solvent dehydration and the removal of organics from water, pervaporation saw least advance in the org–org separation over the past decades. However, encouraging results were achieved more recently by three innovative approaches:

- (1) using cross-linkable glassy polymers (e.g., polyimide copolymer);
- (2) using supported zeolite membranes (e.g., silicalite-1, Mordenite, and Ferrierite);
- (3) using nanocomposite membranes (e.g. zeolite-incorporated mixed matrix membranes).

All these approaches originate from the same consideration, namely, the selective diffusion properties of the membranes should be preferentially relied on, and the synergy between the diffusion and sorption should be simultaneously sought. This novel approach emphasizes taking the advantage of the mobility difference of the species in the membrane, and can thus be called as the kinetic approach. It is a complementary approach for the well-known thermodynamic one that emphasizes the membrane/species interaction, and had been proven to be infeasible in dealing with the org–org separation over the past decades.

The huge markets in the chemical and petrochemical industries justify the importance of the org–org separation. The org–org separation will surely be one of the focuses of the future pervaporation research. Research in the following aspects will be helpful for creating final solutions to this challenging problem.

- Synthesize more-diffusion-selective copolymers, and maximize the synergy between diffusion and sorption properties of the polymers.

- Develop fundamental understanding on the FFV of polymers to conduct molecular design of the polymers which gives ideally low FFV.
- Investigate the FFV of polymer alloys in view of obtaining the suppressed FFV of the blended systems.
- Investigate the interactions between the diffusion-selective polymer and the zeolite nanoparticles to synthesize bettered separating performance of the hybrids.
- Develop theoretical understanding on the transport phenomena of the species in the complex composite membrane materials.
- Develop technologies for making supported ultra-thin membranes to compensate for the reduced membrane productivity due to the suppressed FFV of the pursued more-diffusion-selective polymeric materials.

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### Appendix A. The Hansen solubility parameters of various pervaporation-important solvents

Solvent	Dispersion	Polar	Hydrogen
1,2-Diethyl benzene	17.7	0.1	1
1,4-Dioxane	19	1.8	7.4
1-Butanol	16	5.7	15.8
1-Butene	13.2	1.3	3.9
1-Heptene	15	1.1	2.6
1-Hexene	14.7	1.1	0
1-Pentanol	15.9	4.5	13.9
1-Propanol	16	6.8	17.4
2,3-Dichlorobeneze	19.7	12.6	4.4
2,4-Dichlorobenzene	20.4	8.7	4.2
2-Butanol	15.8	5.7	14.5
2-Pentanol	15.6	6.4	13.3
2-Propanol	15.8	6.1	16.4
Acetic acid	14.5	8	13.5
Acetone	15.5	10.4	7
Acrylic acid	17.7	6.4	14.9
Benzene	18.4	0	2
Butane	14.1	0	0
Carbon tetrachloride	17.8	0	0.6
Chlorobeneze	19	4.3	2
Chloroform	17.8	3.1	5.7
Cyclohexane	16.8	0	0.2
Diethyl carbonate	16.6	3.1	6.1
Diethyl ether	14.5	2.9	5.1
Diethyl ketone	15.8	7.6	4.7
Diethylene glycol	16.6	12	20.7
Dimethyl carbonate	15.5	3.9	9.7
Ethanol	15.8	8.8	19.4
Ethyl acetate	15.8	5.3	7.2
Ethyl benzene	17.8	0.6	1.4
Ethylene dichloride	19	7.4	4.1
Ethylene glycol	17	11	26
Glycerol	17.4	12.1	29.3
Heptane	15.3	0	0

### Appendix A (Continued)

Solvent	Dispersion	Polar	Hydrogen
Hexane	14.9	0	0
<i>m</i> -Dichlorobenzene	19.7	5.1	2.7
Methanol	15.1	12.3	22.3
Methylacrylic acid	15.8	2.8	10.2
Methylene dichloride	18.2	6.3	6.1
<i>n</i> -Butyl acetate	15.8	3.7	6.3
Octane	15.5	0	0
Octanol	17	3.3	11.9
<i>o</i> -Dichlorobenzene	19.2	6.3	3.3
<i>o</i> -Xylene	17.8	1	3.1
<i>p</i> -Dichlorobenzene	19.7	5.6	2.7
<i>p</i> -Diethyl benzene	18	0	0.6
Phenol	18	5.9	14.9
Propionic acid	14.7	5.3	12.4
Tetrahydrofuran	16.8	5.7	8
Toluene	18	1.8	2
Trichloroethylene	18	3.1	5.3
Triethylene glycol	16	12.5	18.6
Water	15.5	16	42.3
Xylene	17.6	1	3.1

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