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PERVAPORATION: PRINCIPLES AND APPLICATIONS

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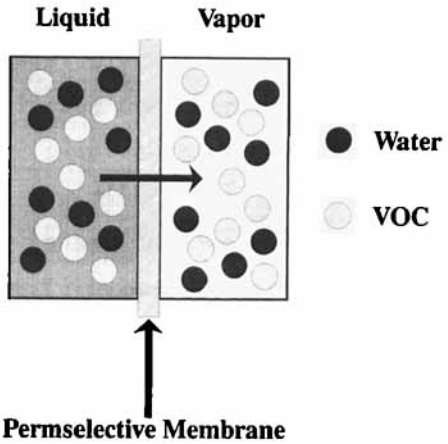
1. Introduction

The method of pervaporation combines, in a single unit operation, selective membrane permeation of species with their subsequent evaporation -- i.e., it concentrates as it separates. Pervaporation is being seriously considered for wider commercial applications as a means of separating volatile liquids. Laboratory experiments on pervaporation with liquid mixtures started more than seventy years ago.[1] Binning and coworkers[2] first identified its commercial potential. Since then numerous laboratory investigations have been directed to separating a variety of liquid mixtures. In recent times many pervaporation membranes have been developed and tested in the laboratory. Commercial success has also been attained in several cases such as drying of aqueous ethanol.[3] More than 90 industrial solvent dehydration units using pervaporation process have been installed worldwide.[4]

In the pervaporation process (a diagrammatic illustration is given in Figure 1), one or more components in a liquid mixture preferentially absorb on one side of a dense polymeric membrane, diffuse through the membrane thickness, and desorb and evaporate at the opposite membrane surface. This sequence of preferential sorption, diffusion and evaporation is the basis for the separation of species by pervaporation. Wherever applicable, pervaporation can be an alternative to fractional distillation, which is relatively energy-intensive. The following are the major advantages pervaporation offers when compared with the dominant methods of liquid separation, particularly distillation.



1. The pervaporation process illustrated.

1. It is energy-efficient because only the fraction of the feed that diffuses through the membrane is vaporized. The remainder does not undergo any phase change.
2. Unlike distillation, pervaporation does not require energy-consuming reflux.
3. The required equipment is small, hence it takes less space.
4. Simple operation and control, and low maintenance cost.
5. Small to large scale of operation.

Pervaporation, however, cannot be considered a common alternative to conventional processes like distillation or extraction for separating liquid mixtures. The reason is that pervaporation is generally a diffusion-controlled process, and hence inherently slow. Also the right membrane that would provide high flux and a satisfactory separation factor is not always available. As a result the application of this potentially important technique has so far been limited to the separation of mixtures that are not easily amenable to treatment by conventional methods. But the growth of research interest in this emerging separation technique in recent years has been very significant. New membranes are now available to cover broader applications ranging from the recovery of high-value ingredients from complex mixtures to environmental applications such as removal of volatile organic compounds (VOC's) from waste water. Tables I to III[5-110] list laboratory and pilot scale demonstrations of pervaporation with a variety of membranes for the separation of a wide range of liquid mixtures.

Finding a suitable membrane is the most important hurdle to devising a pervaporation system. A large number of membranes have been developed and their efficacy demonstrated, at least in the laboratory, in separating liquid mixtures. These include (i) polymeric membranes; (ii) organic/inorganic composite membranes, e.g., zeolite-filled polymeric membranes; (iii) inorganic membranes, e.g., zeolite membranes; and (iv) liquid membranes. A partial list of these laboratory demonstrations is presented in Tables I to III.

Although several authors have reviewed different aspects of the pervaporation process,[111-113] this review focuses on the principles involved in each step of pervaporation from feed liquid phase to permeate vapor phase. Mass transport resistances in both feed and permeate sides, thermodynamic theories governing the membrane/feed interface properties and diffusion of species through the membrane are reviewed. Operating variables affecting pervaporation process are identified and discussed. Commercial membrane modules, process design and economics are discussed critically. Several commercial applications of pervaporation process are also described.

2. Laboratory Apparatus for Pervaporation

A typical laboratory test cell for pervaporation consists of two compartments separated by a membrane. The feed flows through one compartment while the other is maintained at a desired vacuum or is swept by an inert gas. The feed temperature is maintained by continuously pumping it through a heat exchanger. The permeate vapor is condensed in a cold trap. Downstream pressure is maintained by a vacuum

TABLE I. Important Membranes Used for Dehydration of Organic Solvents

Membrane	Organic	References
cellulose acetate	ethanol	5-11
regenerated cellulose	ethanol	5, 12, 13
grafted PTFE	organics	14, 15
polysulfone	ethanol	5, 6, 8, 9, 16
polyvinyl acetate	ethanol	3, 9, 16, 17
ion exchange	ethanol	18-21
polyacrylonitrile	ethanol	6, 9, 17, 22
grafted PTFE	ethanol	23
cross-linked polymethyl acrylate	ethanol	24
polyvinylidene fluorides	ethanol	22
substituted polyimides	ethanol	25
substituted polyacetylene	ethanol	26, 27
ceramic silica	alcohols	28
PSS/Al_2O_3	ethanol	29
zeolite	ethanol	30
	butanol	30
acrylonitrile-butyl acrylate Latex	ethanol	31
PAN	pyridine	32
PVA Cation-exchange	pyridine	33
zeolite-filled	ethanol	34, 35
ionomer (PVA based)	amines	36
sodium alginate	THF dioxane acetone	37

TABLE II. Organophilic Membranes for Extracting Organics from Aqueous Solutions

Membrane	Organic	References
natural and synthetic rubber	toluene & trichloroethylene	38
NBR and SBR	chloroform & benzene	39, 40
silicon rubber	hydrocarbon & chlorinated solvents	41-51, 52
	ethanol	8, 11, 16, 53-58
	pyridine	33, 59
	acetone	60
	benzyl alcohol	61
PDMS-zeolite	ethanol	55, 62, 63
filled	aniline and ethanol	64
	1-octene-3-ol	65
PEBA-adsorbent	aromatic & chlorinated	
filled	hydrocarbon	66
PTMSP	chlorinated solvents	48
PVDMS&PVDF	chlorinated solvents	16
PE	chlorinated solvent	41, 67, 68
PVAc	chlorinated solvent	69

pump and a pressure controller. The membrane is supported on a porous metal disk held between two flanges. A typical laboratory set-up for vacuum pervaporation is shown by Ji et al (Figure 2).[51] The feed side mass transfer resistance may be reduced by increasing the cross-flow feed velocity. Alternatively, the feed compartment may be provided with a stirrer to create adequate turbulence in order to reduce the diffusional resistance.[93, 114-116] In a sweep gas pervaporation apparatus, in which the permeate is continuously carried away by a flowing noncondensing gas, a bypass can be provided to inject small amounts of the product stream to a gas chromatograph to

TABLE II - Continued

Membrane	Organic	References
PEBA	hydrocarbon, chlorinated solvent, phenol, ethanol & isomeric butanols	49-51, 70-72
	acetone	60
synthetic ion-exchange	phenol	73
polyacrylic acid ester-co-acrylic acid	chlorinated solvents	74
PB	ethanol	75, 76
	aniline and methylene chloride	77
PUR	alcohols	71
PTFE	ethanol	72
	chlorinated solvents	43, 69
liquid membrane	TCE & toluene	78-80
silicalite membrane	ethanol	81, 82
	alcohols	83, 84

continuously monitor the rate of pervaporation and product composition simultaneously.[117]

In commercial installations, spiral wound and hollow fiber membranes are used. A brief description of some commercial modules will be given later.

3. Physicochemical Principles and Transport Mechanisms

The technology of pervaporation is one of conveniently and effectively exploiting the principles of molecular interactions in polymer-solute systems and of

TABLE III. Membranes Used for Organic/Organic Separations

Membrane	Mixture	References
polypropylene	benzene/cyclohexane	85
	m-xylene/p-xylene	86
polymer alloy of CA and PPO	benzene/cyclohexane	87, 88
HEMA-MA graft copolymer	benzene/cyclohexane	89
polysulfone		5
grafter PTFE	alcohol/alkane	90, 91
cellulose acetate and Nylon		92
QPPO		88
PFSA ionomer	polar/apolar solvents	93
	methanol/MTBE	94
silicalite	methanol/MTBE	95
PVA-PAA blend	methanol/MTBE	96
PSS/Al_2O_3	methanol/MTBE	97
PEBA	DCE/TCE	98
silica	methanol/MTBE	28
polypyrrole	ethanol / cyclohexane	99
	methanol/solvents	100
polyimides	benzene/cyclohexane acetone/cyclohexane	101
polyethylene	aromatic C_8-isomers	102

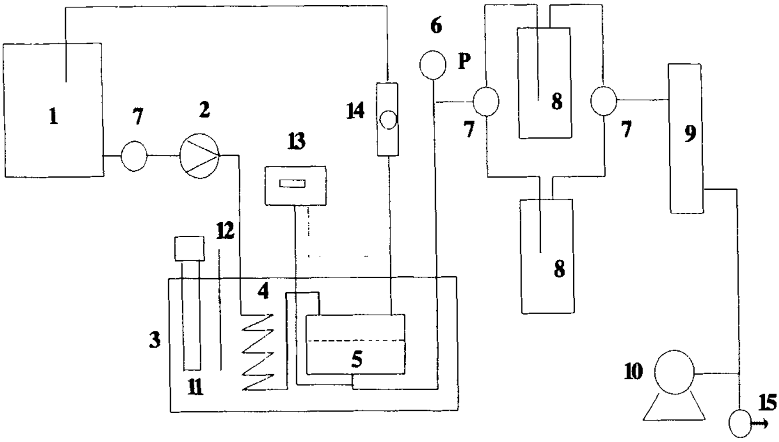
TABLE III - Continued

Membrane	Mixture	References
NBR & SBR	benzene/n-heptane	103
ethyl cellulose polypropylen5	propane/propylene	104
cellulose acetate	methanol/MTBE/C_4	105
PDMS	butanol/butanol-oleyl alcohol	106
polyoxyethylene grafting nylon 6	cyclohexane/cyclohexanone /cyclohexanol	107
PS/SBS	benzene/ethanol	108
poly(ether imide) segmented copolymer	benzene/cyclohexane benzene/n-hexane acetone/cyclohexane	109
adsorbent-filled	toluene/ethanol	110

diffusion of solutes in a swollen polymer. Such interactions are usually multicomponent in nature.

3.1 Pervaporation Flux and Selectivity

The effectiveness of a polymeric membrane in separating a liquid mixture is characterized by two parameters - flux and separation factor (or selectivity). While flux is expressed as the amount of permeate collected per unit time per unit membrane area (kg/m^2-hr or kgmol/m^2-hr), selectivity of the permeation process to a particular solute is expressed in terms of either of the separation factor, α, or the enhancement factor, β, given by



2. Test unit for pervaporation process. 1. feed tank, 2.feed pump, 3. isothermal bath, 4. heating coil. 5. membrane cell, 6. pressure meter, 7. valve, 8. cold trap, 9. dryer, 10. vacuum pump, 11. immersion circulator-heater-controller, 12. thermocouple, 13. thermometer, 14. flowmeter, 15. needle valve

$$\alpha = \frac{w_i' / (1 - w_i')}{w_i / (1 - w_i)} \tag{1}$$

$$\beta = \frac{w_i'}{w_i} \tag{2}$$

where w_i' and w_i are the weight fractions of the solute i in the permeate and feed respectively. The relation between these parameters is readily obtained as

$$\alpha = \frac{\beta(1 - w_i)}{1 - \beta w_i} \tag{3}$$

The parameter α is more commonly used because it fits the general definition of separation factor.

3.2 Basic Steps of the Pervaporation Process

The overall process of enrichment of one or more components of a feed solution by pervaporation can be considered as the sequential combination of the following steps.

(i) Convective transport of solutes from the bulk of the feed solution to the feed-membrane interface (i.e., the upstream membrane surface).
(ii) Sorption of the solutes at the upstream membrane surface.
(iii) Molecular diffusion through the membrane.
(iv) Desorption of the solutes from the downstream side of the membrane.
(v) Transport of the vapor to the condensing surface.

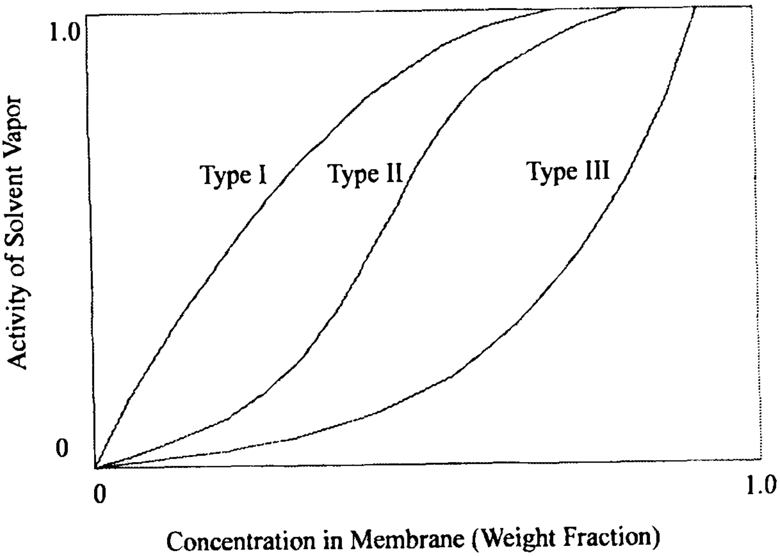
A dense polymer film of suitable thickness is commonly used for laboratory pervaporation studies. Commercial membranes are usually composite membranes, consisting of a thin dense polymeric film on a porous support. In the latter case, step (v) is again a combination of two consecutive steps — poreflow of the permeate vapor through the support layer followed by vapor transport from the surface of the backing to the condensing surface. In most practical situations steps (ii) and (iii) determine the flux and the separation factor, although for enrichment of a very dilute solution, step (i) may play the dominating role, as established by some (Psaume et al.[42] Ji et al.[51] see also section 4.4). The relative importance of steps (ii) and (iii) depends on the particular polymer-solute system. While in one situation, preferential sorption of a solute at the feed side of the membrane may control the process as in the case of highly swollen membranes,[5, 71, 72, 118] variant species diffusivities may be controlling in some other situations.[21] As a result sound understanding of multicomponent sorption and diffusion in a polymer is extremely important in the selection of a polymeric material for a pervaporation membrane and also in analyzing its performance.

3.3 Sorption Equilibria

Equilibrium sorption data indicate the affinity of a membrane towards the species in solution. Preferential sorption has sometimes been found to dominate pervaporation selectivity.[16] Sorption data are necessary for testing pervaporation models that are generally based on the solution-diffusion mechanism, and for calculating the interaction parameters required for thermodynamic modeling of polymer-solute equilibria. Also sorption rate data for pure liquids (or vapors) can be used to calculate single component diffusivity values.[119-121]

3.3.1 Sorption Experiments

One side of a pervaporation membrane contacts the feed solution and the other side contacts the permeate vapor. Sorption measurements of species present in both liquid and vapor are, therefore, important. Total liquid sorption is usually measured by equilibrating a piece of dry membrane with the feed solution for sufficient time, and weighing the membrane after quickly blotting out the surface liquid using a tissue paper. The equilibrated membrane, after surface drying, is put in a flask, the sorbed liquid is pulled out by applying vacuum, and is collected in a cold trap. The analysis of the condensate gives the composition of the sorbed liquid (see, for example, Terada et al.[89] Dutta and Sikdar;[93] Sun and Ruckenstein[112]). Alternatively the composition of the sorbed liquid can be determined indirectly from an analysis of the supernatant liquid after equilibration with the membrane.[16] This latter method, however, does not appear to provide good accuracy,[9] except for dilute solutions. The "purge and trap" method, was developed by Ji et al.[66] to measure the sorption of volatile organic compounds from water. After equilibrating with a dilute aqueous VOC solution, the membrane sample is placed in a sparge tube. VOC's are removed from the membrane sample by a heated inert gas (e.g., He), and are collected by an adsorbent trap. The trap is heated to release the VOC's, which are brought by a carrier gas (e.g. He) into a GC which determines the amount of



3. Types of sorption isotherms in polymeric membrane systems

organics. This technique has advantages of high sensitivity and automatic operation. The accuracy of this measurement is improved by minimizing exposure of VOC samples to air. Several other methods of measuring preferential sorption have been cited by Pouchy and Zinvy[123] and Brun et al.[39]

Measurement of vapor sorption is usually done by using an electrobalance.[124, 125] It is similar to sorption measurements done for gas permeation membranes.

3.3.2 Flory-Huggins Theory

Three types of sorption isotherms are generally encountered in penetrant-polymer systems: type I normally observed in a rubbery polymer, type III for gas sorption in a glassy polymer, while type II shows an intermediate behavior (Figure 3). Because pervaporation membranes are mostly rubbery or elastomeric (some may have a degree of crystallinity), sorption of solvents in such membranes show mostly exclusively type I isotherm. Of the various thermodynamic theories proposed and applied to interpret sorption equilibria in an elastomer, the Flory-Huggins theory and its extensions have been quite successful[126] and most widely used. For a binary mixture-polymer membrane system, the free enthalpy of mixing ΔG_m is given by the following equation[127]:

$$\Delta G_m = RT(n_i \ln\phi_i + n_j \ln\phi_j + \chi_{ij} n_i \phi_j + \chi_{ip} n_i \phi_p + \chi_{jp} n_j \phi_p) \tag{4}$$

where n and ϕ are the mole fraction and volume fraction, respectively, and χ's are adjustable parameters. Subscripts "i", "j" and "p" denote penetrant i, j and polymer, respectively. Differentiation of eqn.(4) with respect to n_i and n_j, respectively, gives Eqs.(5) and (6):

$$\ln a_i^m = \ln\phi_i + \phi_j(1-\frac{V_i}{V_j}) + \phi_p(1-\frac{V_i}{V_p}) + (\chi_{ij}\phi_j + \chi_{ip}\phi_p)(\phi_j+\phi_p) - \chi_{jp}\phi_j\phi_p\frac{V_i}{V_j} \tag{5}$$

$$\ln a_j^m = \ln\phi_j + \phi_i(1-\frac{V_j}{V_i}) + \phi_p(1-\frac{V_j}{V_p}) + (\chi_{ij}\phi_i\frac{V_j}{V_i} + \chi_{jp}\phi_p)(\phi_i+\phi_p) - \chi_{ip}\phi_i\phi_p\frac{V_j}{V_i} \tag{6}$$

where V_i and V_j are molar volumes, a^m is activity in the membrane, and χ_{ij}, χ_{ip}, and χ_{jp} are the Flory-Huggins interaction parameters. If the swelling of the polymer is slight, the elastic contribution can be neglected. At equilibrium,

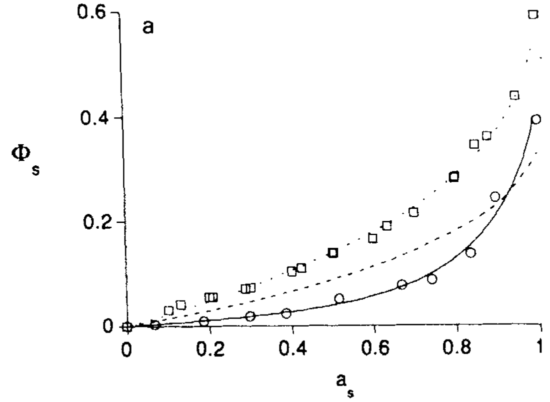
$$a = a^m \tag{7}$$

Here, a is activity in the feed. Equations 5 to 7, which would be considerably simplified if one puts $V_i/V_p = 0 = V_j/V_p$ (because the polymer is a much larger molecule than the solutes), can be used to predict the penetrant concentration in membranes and preferential sorption selectivity.[5, 6, 128-130] In the original Flory-Huggins theory and the derivation of Eq. 5 and 6, the interaction parameters are assumed to be constant. However, concentration dependent interaction parameters have to be used in most penetrant-membrane systems.[5, 6, 130] A procedure of estimating each of these interaction parameters was given by Mulder et al.[5]

A large number of modifications were made to the original Flory-Huggins Equations were developed. For example, the Flory-Rehner equation[131] introduced an additional term in Eq. 4 to account for contributions due to elastic forces in case of equilibrium swelling of a crossed-linked polymer. Other modifications include entropic contributions[132, 133] and enthalpic contributions.[134, 135] A simple example of the applicability of the F-H theory to interpret sorption isotherms of chloroform and of 2-butanol in polydimethyl siloxane is shown in Figure 4. It is seen that sorption of the good solvent, chloroform, can be interpreted well using this theory, but the deviation is significant for sorption of 2-butanol, which, however, fits the Koningsveld-Kleinjtens modifications of the F-H theory.[136] The Flory-Huggins equations and its modifications, however, frequently fail to predict solubility in polymers because the interaction parameters are essentially empirical and adjustable.[137] Recently Favre et al.[138] have observed that the Flory-Huggins theory is moderately good for predicting multicomponent equilibria in an elastomer-apolar solute system, but not suitable for predicting sorption equilibria in thermoplastics, while in the case of polar solutes the prediction was rather poor.

3.3.3 UNIQUAC Model

The UNIQUAC[139] and UNIFAC[140, 141] models have been widely used to predict vapor-liquid and liquid-liquid equilibrium. Oishi and Prausnitz[142] introduced a free volume correction to the UNIFAC model and applied it to polymer solutions. For 13 binary solvent-polymer systems they studied, errors for activity calculation were within 10%. Oishi and Prausnitz's UNIFAC model was evaluated by Goydan et al.[143] for estimating the solubility of organic compounds in solid polymers. Fairly accurate results were obtained. Stephan and Heintz.[144] used the UNIQUAC model to predict penetrant concentrations in polymeric membranes for binary mixtures based



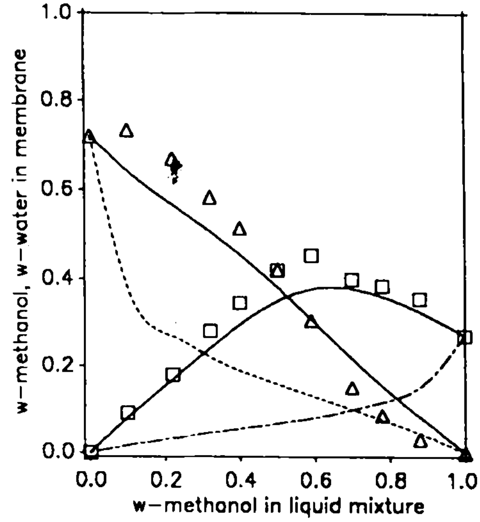
4. Sorption isotherms of chloroform (□) and 2-butanol (O) in PDMS at 40°C. F-H equation (----), Koningsveld and Kleinjtens modification (—)[136]

on data available from single component sorption isotherms. According to the UNIQUAC model, the activity, a_i, of the component i in a binary liquid mixture of i and j can be expressed as:

$$\ln a_i(w_i, w_j, \tau_{ij}, \tau_{ji}) = \ln \phi_i + \frac{z}{2} q_i \ln \frac{\Theta_i}{\phi_i} + \phi_j \left(l_i - \frac{r_i}{r_j} l_j\right)$$
$$-q'_i \ln(\Theta'_i + \Theta'_j \tau_{ji}) + \Theta'_j q'_i \left(\frac{\tau_{ji}}{\Theta'_i + \Theta'_j \tau_{ji}} - \frac{\tau_{ij}}{\Theta'_j + \Theta'_i \tau_{ij}}\right) \quad (8)$$

where w is the weight fraction of a component in the binary mixture, and $w_i + w_j = 1.0$. ϕ is volume fraction; Θ, Θ' are surface fractions which are functions of w; r, q, q' and l are parameters related to the geometrical data of the molecular shape of the components, z is the coordination number. τ_{ij} and τ_{ji} are parameters describing exchange energies of the intramolecular interaction of the different molecular components, which can be obtained by fitting the Eq. 8 to vapor-liquid equilibrium data of the binary mixture.

For a ternary system containing a binary mixture and the membrane, the activity of component i in the membrane can be described by Eq. 9:



5. Experimental and calculated mixture solubilities (weight fractions w) in PVA at 333 K. Experiments: (Δ) water; (□) methanol. Calculation: (—) UNIQUAC model; (----) ideal model, water; (-•-) ideal model, methanol.[146]

$$\ln a_i(w_i, w_j, w_m, \tau_{ij}, \tau_{ji}, \tau_{im}, \tau_{mi}, \tau_{jm}, \tau_{mj}) = \ln\phi_i + \frac{z}{2}q_i \ln\frac{\Theta_i}{\phi_i} + l_i - \phi_i l_i - \phi_j l_j \frac{r_i}{r_j}$$
$$-r_i\phi_m\left[\frac{z}{2}\left(1-\frac{q_m}{r_m}\right)-1\right] - q_i^{'}\ln(\Theta_i^{'} + \Theta_j^{'}\tau_{ji} + \Theta_m^{'}\tau_{mi}) + q_i^{'}$$
$$-q_i^{'}\left(\frac{\Theta_i^{'}}{\Theta_i^{'} + \Theta_j^{'}\tau_{ji} + \Theta_m^{'}\tau_{mi}} + \frac{\Theta_j^{'}\tau_{ij}}{\Theta_i^{'}\tau_{ij} + \Theta_j^{'} + \Theta_m^{'}\tau_{mj}} + \frac{\Theta_m^{'}\tau_{im}}{\Theta_i^{'}\tau_{im} + \Theta_j^{'}\tau_{jm} + \Theta_m^{'}}\right) \qquad (9)$$

where w_m is the weight fraction of polymer, $w_i + w_j + w_m = 1.0$. Four additional parameters, i.e., τ_{im}, τ_{jm}, τ_{mi}, and τ_{mj}, of this model can be obtained from single component-membrane sorption isotherms, given by the following equation, subject to $w_i + w_m = 1.0$.

$$\ln a_i(w_i, w_m, \tau_{im}, \tau_{mi}) = \ln\phi_i + \frac{z}{2}q_i \ln\frac{\Theta_i}{\phi_i} + l_i - \phi_i l_i$$
$$-r_i\phi_m\left[\frac{z}{2}\left(1-\frac{q_m}{r_m}\right)-1\right] - q_i^{'}\ln(\Theta_i^{'} + \Theta_m^{'}\tau_{mi}) + q_i^{'}$$

$$-q'_i\left(\frac{\Theta'_i}{\Theta'_i+\Theta'_m\tau_{mi}}+\frac{\Theta'_m\tau_{im}}{\Theta'_m+\Theta'_i\tau_{im}}\right) \tag{10}$$

The UNIQUAC model has been used to predict the solubilities of cyclohexane/benzene and cyclohexane/toluene mixtures in a polyurethane membrane[144, 145] and six-component aqueous/organic mixtures in poly(vinyl alcohol) membranes.[146, 147] Good agreement between experimental data and the prediction results was reported. Application of the UNIQUAC model to the ternary water-methanol-PVA membrane system is shown in Figure 5. The UNIQUAC model appears to have better predictive ability for highly non ideal multicomponent mixtures. Moreover, the parameters can be evaluated from vapor-liquid equilibrium data of the components in the feed solution and single-component vapor sorption isotherms.

3.3.4 Doong and Ho's Model

Doong and Ho[148] recently developed a thermodynamic model for multicomponent solubility in a polymer (membrane) by combining three frequently used theories. This model was first tested in a single component-polymer system[148] and later extended to a multicomponent penetrant-membrane system to predict the pervaporation flux and selectivity of organic mixtures through polyethylene membrane.[149] Good agreements between experimental data and the model occured in both cases. The activity of a component dissolved in the polymer was expressed by the fundamental thermodynamic equation.

$$RT\ln a_i = \left(\frac{\partial \Delta G}{\partial n_i}\right)_{n_j, j\neq i} \tag{11}$$

Doong and Ho expressed the Gibbs free energy change for sorption, ΔG as the sum of combinatorial entropy, free-volume, interactional enthalpy, and elastic factors,

$$\Delta G = \Delta G^{c} + \Delta G^{fv} + \Delta G^{\text{int}} + \Delta G^{el} \tag{12}$$

The Flory-Huggins lattice theory was used to calculate the combinatorial-entropy.[127] The equation-of-state theory developed by Flory[150] was adopted to account for the free-volume effect. The UNIFAC method[140, 142] was applied to calculate interactional activity. Finally, the elastic factor was determined by the Michaels-Hausslein theory.[151] Doong and Ho tested their model for sorption of pure liquids in polymers. They also used it for testing a multicomponent pervaporation model they developed. But the model was not tested explicitly for multicomponent polymer-solute equilibria. However, because the model combines all the major factors, it seems to have much potential for application.

3.4. Modeling Pervaporation

Several attempts have been made to develop pervaporation models that relate the flux of a component in a feed mixture to a measurable driving force and the component's transport parameters. Modeling the process of pervaporation is important not only for a quantitative understanding of the dependence of fluxes on the process parameters, but is also useful in design calculations for a pervaporation module. The solution-diffusion transport mechanism has been the basis of most pervaporation models. The simplest approach is to describe the relation between flux and driving force by Fick's law.

$$J_i = uC_i - D_i \frac{dC_i}{dz} \tag{13}$$

Where J_i, is the permeation flux, u is the molar average velocity of the components; D_i, is the diffusion coefficient, and C_i the local concentration of the species in the membrane. The convective contribution to the total flux, uC_i, can be neglected if the diffusional process dominates. Thus,

$$J_i = -D_i \frac{dC_i}{dz} \tag{14}$$

However, swelling of the membrane and its consequences on transport are important factors to be taken into account before an attempt is made to solve the above equation for a multicomponent system. The membrane undergoes maximum swelling on the face that is in contact with the feed solution. The concentrations of the permeating components decrease across the membrane reaching a minimum at its downstream side. This concentration gradient causes a swelling gradient in the membrane. The diffusion coefficients depend on local concentrations of the permeants leading to an interdependence of the fluxes. Thermodynamic equilibrium between the membrane and the feed side is assumed in the solution-diffusion model. An experimental verification of this assumption was provided by te Hennepe et al.[152] who observed that the diffusion through the membrane determined the transport rate in the pervaporation of propanol/water mixture using a silicalite-filled silicone rubber membrane. The propanol concentration in the membrane at the feed side was measured to be the same as the value obtained from the equilibrium sorption. However, significant sorption resistances have been reported by Mulder et al.[6] in ethanol/water/cellulose acetate membrane system. The resistances resulted in lower concentrations of permeant in membrane at the feed side than would be expected from the equilibrium sorption measurements.

Theoretical aspects of the solution-diffusion model for liquids permeating through membranes have been investigated.[7, 9, 13, 15, 40, 93, 153-160, 161, 162] Thermodynamic interactions among solute, solvent and polymer membrane, and flow coupling between solute and solvent complicate multicomponent transport through a pervaporation membrane[163]. The crux of the solution-diffusion model is to express the diffusivities as functions of concentration and to quantitatively account for the swelling gradient. It is pertinent to give here an overview of concentration dependence of diffusivity in a swollen polymer.

3.4.1 Concentration-Dependent Diffusivities

The “free volume theory”[164] provides a good theoretical framework for steady state permeation of sorbed molecules through a polymer matrix. Diffusion rates of small molecules through a nonporous polymer depend on the ease with which the polymer chain can exchange positions with diffusing molecules. The diffusion coefficient of a permeant can be expressed as a function of fractional free volume of the polymer (which includes the volume fraction of the sorbed molecules) and two adjustable parameters that are characteristic of a particular polymer permeant pair. The free volume theory was extended to the diffusion of gases and liquid mixtures by Fang et al.[165] The diffusion coefficients in a binary mixture are given by

$$D_1 = RTA_{d1}\exp(-\frac{B_{d1}}{v_f}) \tag{15}$$

$$D_2 = RTA_{d2}\exp(-\frac{B_{d2}}{v_f}) \tag{16}$$

where D, is the diffusivity of the components, A_{di} and B_{di} are the corresponding adjustable parameters. The free volume, v_f depends on the concentrations of the liquids in the polymer and on the free volume of the “dry” polymers.

Yeom and Huang[160] proposed an equation for diffusion coefficients based on Fujita’s free volume theory. For a ternary system consisting of a binary mixture and a membrane, they assumed that the total free volume is the sum of the free volume of the polymer itself and the increase in free volume due to the plasticizing actions of the two components. The thermodynamic diffusivity of component i [see Eq. 26] can then be expressed as:

$$(D_T)_i = RTA_{di}\exp\left\{-\left[\frac{f(0,T)}{B_{di}}+\frac{\beta_i(T)}{B_{di}}\phi_i+\frac{\beta_j(T)B_{dj}}{B_{di}}\phi_j\right]\right\}^{-1} \tag{17}$$

where *f(0,T)* is the free volume fraction of the polymer itself and *β(T)* is a proportionality constant. The property data of penetrant and polymer and the single component permeation data or diffusivity data at zero concentration were used to determine the free volume parameters in eqn. (17).[130, 160, 166-168] A basic assumption used in this calculation is that the free volume parameters A_{di}, B_{di}, B_{dj}, $\beta(T)$ and $f(0,T)$ are the same for single component-membrane systems as for binary mixture-membrane systems.

Recently, Doong and Ho[169] developed a hybrid model that combined Pace and Datyner's molecular model[170, 171] and Vrentas and Duda's free volume model[172, 173] to describe single penetrant diffusivity in a polymer:

$$D = \frac{1}{6} L^2 v \exp\left(-\frac{\omega_1 v_1^* + \omega_2 v_2^* \xi}{v_{fp} + \beta \omega_1} \right) \tag{18}$$

where L is the jumping distance of the permeant, and v is the average jumping frequency. ξ is the ratio of the molar volume of the penetrant V_1* at 0 K to the molar volume of the polymer jumping unit V_2* at 0 K, v_{fp} is the free volume of the penetrant-polymer system, and w_i is the weight fraction of species i in the polymer-penetrant system. Three adjustable parameters (L, V_2* or ξ , and β) can be determined from single component diffusion data measured by vapor sorption experiments.[169] Equation 18 was later generalized by Doon et al.[149] to a multicomponent system,

$$D_{im} = \frac{1}{6} L_i^2 v_i \exp\left(-\frac{v_i^* M_i \sum_{j=1}^{p} \omega_j / M_j}{v_{fp} + \sum_{j=1}^{q} \beta_j \omega_j} \right) \tag{19}$$

Equation 19 coupled with Doong and Ho's thermodynamic model and a generalized Fick's equation successfully predicted flux and selectivity in the pervaporation of a mixture of toluene, p-xylene, and mesitylene through a polyethylene membrane at various temperatures and permeate pressures.[149] No permeation experiments were required in the model calculation, and the model parameters were determined from single component vapor sorption experiments.

Although the free volume theory has a satisfactory theoretical basis and has been successful in interpreting diffusion data of simple molecules, it is inadequate to explain diffusion in highly swollen polymers. Moreover, extensive experimental work is often required to determine those free volume parameters in the model. As a result, this theory is yet to gain much acceptance. A semi-empirical approach of describing concentration dependent diffusivity has been more popular. Greenlaw et al.[162] proposed a linear dependence of diffusivity on the concentrations of the individual components.

$$D_i = D_i^0(C_i + K_{ji}C_j) \qquad \text{i,j=1,2 for a binary mixture} \tag{20}$$

These expressions, however, do not satisfy the limiting conditions as C_i and C_j tend to zero.

For pure component permeation an exponential dependence of diffusivity on concentration (sometimes called the "Long model") has proved to be useful.[15, 40, 117, 120, 170]

$$D_i = D_i^0 \exp(\gamma_i C_i) \tag{21}$$

where γ is an adjustable parameter, called the "plasticization parameter". The exponential expression is consistent with the predictions of the free-volume theory for molecular diffusion in polymers. For the permeation of a binary mixture Suzuki and Onozato[117, 120] proposed the following functional forms:

$$D_i = D_i^0 \exp(\gamma_i C_i + \gamma_j C_j) \tag{22}$$

Here the exponential parts of the expressions for D_i and D_j are identical. Although the limiting conditions at vanishingly low concentrations are satisfied by the above expression, it is more reasonable and general to assume relations of the forms:[39, 40]

$$D_i = D_i^0 \exp(\gamma_{ii} C_i + \gamma_{ij} C_j) \tag{23}$$

This "six-coefficient" model has been widely used in modeling complex ternary pervaporation systems which exhibit a large deviation from ideality.[9, 171-174]

Bitter[133, 175] proposed another approach to calculate the diffusivity of species in the membrane. He treated a swollen membrane as a homogeneous liquid mixture consisting of polymer and permeant. A modified Vigne equation[133] was used to calculate the self-diffusion coefficient of component i in the mixture, D^*_{im}, as shown in Eq. 24:

$$\ln D^*_{im} = \phi_i \ln D^*_{ii} + \sum_{j=1}^{n} \phi_j \ln D^\infty_{ij} \tag{25}$$

where D^*_{ii} is the self-diffusivity of component i; D_{ij}^∞ is the binary diffusivity of i in j at infinite dilution of i. Both D^*_{ii} and D_{ij}^∞ can be obtained from empirical equations for calculating diffusion coefficients, and from desorption experiments.[133]

All these expressions involve adjustable constants whose values have to be determined by fitting experimental data.

3.4.2 Transport Equations and Pervaporation Models

Eq. 13, or Eq. 14, if the convective effects can be neglected, can be integrated for a multicomponent system after incorporating suitable expressions for D_i and D_j, and specifying the boundary conditions at both ends. Direct measurements of equilibrium sorption may provide these conditions. Alternatively these data may be estimated by equating the activities of the components in a fluid phase with the corresponding activities in the polymer.[40] Activities in the membrane may be computed using a suitable thermodynamic model as discussed in the previous section.[127, 140, 149]

In the case of moderate to highly swollen membranes, the Hittorf system has been preferred to the Fick's system in which the membrane material is considered stationary with respect to the frame of reference.[126, 176]

$$J_i = -D_i \left(\frac{1}{1-\phi_i} \right) \frac{dC_i}{dz} \tag{25}$$

Eq.26 has been used by a number of authors for predicting the permeation flux.[119, 177] However, if the swelling is low, i.e. $1-\phi_i \approx 1.0$, then Eq. 25 becomes Eq. 14, and the difference between these two frames becomes negligible.

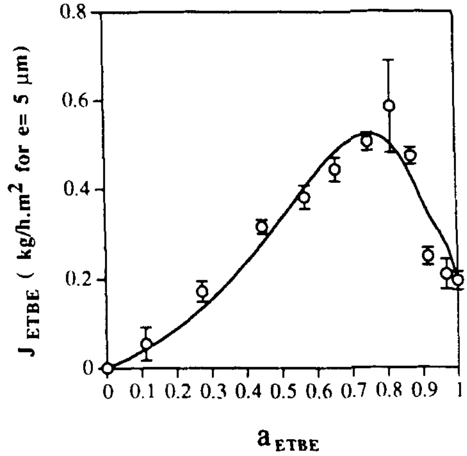
A more rigorous approach considers the flux of a species to be proportional to the gradient of chemical potential rather than to the gradient of concentration. This is a more accurate expression according to modern diffusion theory.[155]

$$J_i = -C_i \frac{D_{Ti}}{RT} \frac{d\mu_i}{dz} \tag{26}$$

C_i and μ_i are the local concentration and chemical potential of component i. Since the chemical potential μ_i is related to the activity a_i by

$$\mu_i = \mu_i^0 + RT \ln a_i \tag{27}$$

Eq. 26 can be rewritten as:



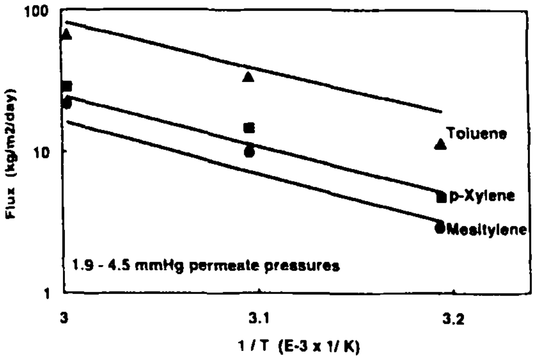
6. ETBE partial fluxes during pervaporation of ETBE/EtOH mixtures through a polyurethaneimide film at 30°C. The cure represents the data obtained by integration of the coupled "thermodynamic" Fick's laws.[174]

$$J_i = D_{Ti} C_i \frac{d \ln a_i}{dz} = D_{Ti} \frac{\partial \ln a_i}{\partial \ln C_i} \frac{dC_i}{dz} \tag{28}$$

Comparison of Eq. 26 with 28 gives the relation between Fick's diffusivity and thermodynamic diffusivity.

$$D_i = D_{Ti} \frac{\partial \ln a_i}{\partial \ln C_i} \tag{29}$$

Mulder and Smolders[7] and Zhu et al.[9] used Eq. 28 with concentration-dependent diffusivities to predict pervaporation fluxes. Typically the activities in the polymer phase may be determined by using a suitable thermodynamic model for the polymer-permeant system. Activities depend on the local concentrations in the polymer and the interaction parameters. The direct consequence of this model is that the fluxes



7. Experimental and calculated fluxes of toluene, p-xylene and mesitylene. Membrane: polyethylene; permeate pressure 1.9-4.5 mm Hg. [—, calculated; ▲,■,●, experimental] [149]

are now coupled not only through the concentration dependent diffusion coefficients but also through coupling of the driving forces of the permeant.

Very recently Jonquieres et al.[174] used the transport Eq. 28 together with the six-parameter concentration-dependent diffusivity expressions, Eq. 22, in order to model pervaporative transport of a mixture of ethyl tertiary butyl ether and ethanol through a polyurethanimide membrane. The predicted and experimental flux values agreed quite well (Figure 6) particularly in view of the polarity of one of the components as well as of the membrane.

Doong et al. [149] used a slightly different form of Eq. 28 for modeling pervaporation of a multicomponent mixture of toluene, p-xylene and mesitylene using a polyethylene film. Assuming isotropic membrane swelling and using their thermodynamic model (section 3.3.4) for activities of the solutes, and their hybrid model for diffusivities of the permeant, they computed the flux and selectivity values of the components at three different temperatures. As Figure 7 and Table IV show, their model predicts the flux and selectivity data well.

TABLE IV. Comparison of experimental pervaporation selectivities with model predications for the separation of three-component mixtures using a polyethylene membrane [149]

Temperature (°C)	Permeate pressure (mm Hg)	Toluene/mesitylene selectivity		p-Xylene/mesitylene selectivity	
		Model	Experiment	Model	Experiment
40	1.9	3.22	2.08	1.76	1.79
	12.3	4.11	3.89	2.06	2.33
50	3.3	2.94	1.78	1.69	1.59
	12.3	3.26	3.19	1.81	1.87
60	4.5	2.71	1.62	1.65	1.44
	12.3	2.82	2.62	1.70	1.71

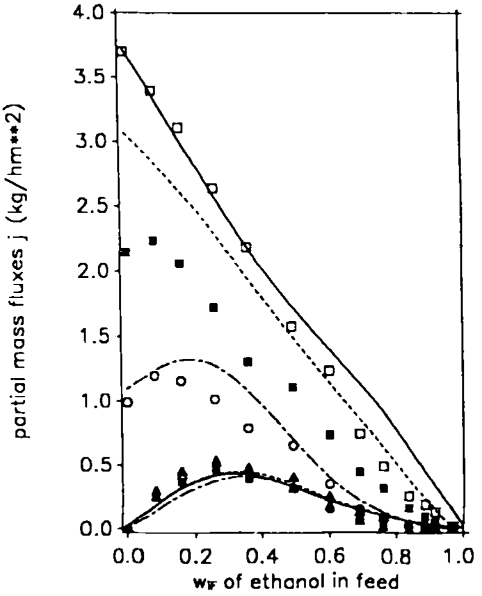
It is sometimes more convenient to use the "self-diffusion coefficient" D^*_{im} to describe the diffusive flux for multicomponent system.[133] For diffusion of component i in a mixture m, the diffusive flux can be expressed by the Darken, Prager, and Crank equation:

$$J_i = -C_i \frac{D^*_{im}}{RT} \frac{d\mu_i}{dz} \tag{30}$$

Diffusive transport can also be described by the Maxwell-Stefan equation originally established to describe multicomponent diffusion in low density gases.[178]

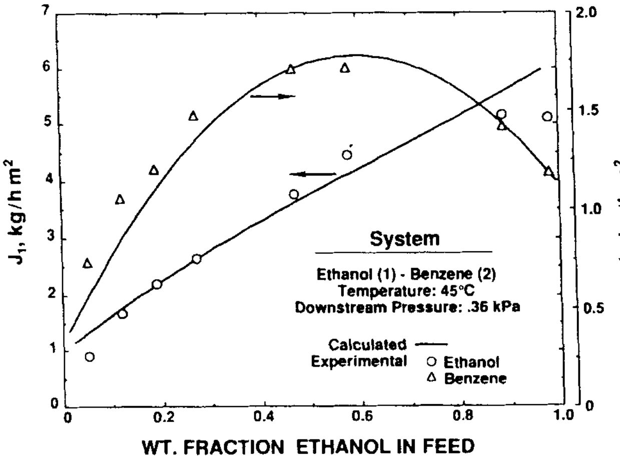
$$\frac{1}{RT} \frac{d\mu_i}{dz} = \sum_{j=1}^{n} x_j \frac{v_j - v_i}{D^o_{ji}} \tag{31}$$

where x_j is the mole fraction of component j (j= 1,2,3,..., n), v_j is the local velocity. The reciprocal of D_{ji}^0 has the meaning of a friction coefficient representing the



8. Partial fluxes for the system water/ethanol/PVA at 333 K. Experiments (□) water, (Δ) ethanol, Pp=20 mbar, (■) water, (▲) ethanol, Pp=100 mbr, (O) water, (●) ethanol, Pp=200mbar. Calculation: coupled diffusion, including effect of support layer, experimental partial flux data (—) Pp=20, (- — -) Pp=200 mbar. [147]

frictional effect exerted by component j on component i. Assuming that the friction force is independent of concentration and composition, Bitter[175] developed a modified Maxwell-Stefan equation using the coefficients of self-diffusion to describe pervaporation of n-C_7/i-C_8 mixtures through polyethylene membranes. The self-diffusion coefficients of component i in the mixture was calculated by Eq. 24. Ennecking et al.[145] also derived a modified Stefan-Maxwell equation to model the mass transfer of benzene/cyclohexane mixtures through a polyurethane membrane. Most recently, a generalized Maxwell-Stefan model was developed by Heintz and Stephan,[146, 147] and was applied to the pervaporation of six aqueous/organic mixtures through a poly(vinyl alcohol)(PVA)/poly(acrylonitrile)(PAN) composite membrane



$\beta_1 = (3.36 \pm 0.6) \times 10^{-4}\ m^3/kg$

$D_{10} = (4.92 \pm 0.57) \times 10^{-9}\ m^2/h$ $\alpha_1 = 0.047 \pm 0.007\ m^3/kg$

$D_{20} = (6.45 \pm 0.8) \times 10^{-8}\ m^2/h$ $\alpha_2 = 0.005 \pm 0.001\ m^3/kg$

9. Experimental and calculated flux values—, ethanol (O) benzene (Δ) system.[93]

consisting of a permselective dense PVA layer on a porous PAN backing. These authors also considered the diffusional resistance offered by the backing which was assumed to have pore bundles of given pore-size distribution. Model prediction agreed very well with the experimental data for these highly non-ideal mixture/membrane systems (Figure 8) while other models failed to predict fluxes and selectivities in these PVA/PAN membranes.

Whatever be the choice of driving forces and the diffusion equations, the solution-diffusion model involves several parameters, including plasticization parameters, that have to be determined by nonlinear fitting of experimental data. Once the model parameters are known, permeant fluxes can be calculated for a given feed concentration, downstream pressure, membrane thickness and temperature.

One of the usual drawbacks of the work reported on solution-diffusion model is that the thickness of the "dry membrane" has been used as the length of the diffusion path on one extreme, or that of the uniformly swollen membrane in equilibrium with the feed on the other (see, for example, Doong et al.[149]). The swelling gradient across the membrane ought to be included in the modeling exercise. Dutta and Sikdar[93] introduced a fractional swelling function β (C_i, C_j) such that

$$l_s = l_d(1+\beta) \tag{32}$$

where l_s is the membrane thickness under equilibrium swelling at sorbed liquid concentrations of C_1 and C_2, and l_d is the dry membrane thickness. The flux equations then reduce to

$$J_i = -\frac{D_i(C_i, C_j)}{1+\beta(C_i, C_j)}\frac{dC_i}{dx} \tag{33}$$

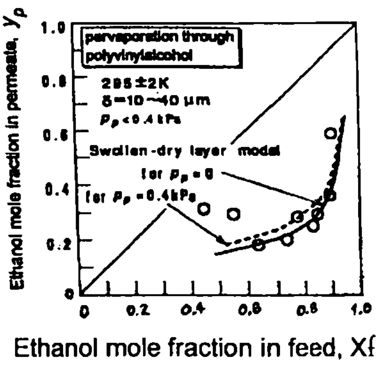
$$J_j = -\frac{D_j(C_i, C_j)}{1+\beta(C_i, C_j)}\frac{dC_j}{dx} \qquad 0 \leq x \leq l_d \tag{34}$$

The functions $\beta(C_i, C_j)$ can be determined from experimental swelling data taken over the concentration ranges of components. This model successfully interpreted the pervaporation data of ethanol-benzene mixtures through perfluorosulfonated ion-exchange membranes (Figure 9).

A few other approaches of pervaporation modeling based on solution-diffusion mechanisms have been reported in the literature. Wijmans and Baker[179] visualized the pervaporation process to occur as the following sequence which is thermodynamically equivalent to the usual solution-diffusion scheme: (i) evaporation of the feed liquid to a saturated vapor, (ii) selective permeation of the vapor through the membrane driven by the pressure difference between the saturated vapor and the downstream pressure. The model could predict the permeation flux of ethanol from an aqueous solution using PVA membrane. Other models based on pore-flow mechanisms have also been studied.[180, 181]

An intermediate approach has recently been reported by Ito et al.[182] which they called the "swollen-dry-layer model". During pervaporation, a part of the membrane near the downstream side remains virtually dry particularly if the downstream pressure is low. Their model assumes the membrane consists of two zones: (i) a "liquid-swollen zone" through which the permeant are driven by a hydrostatic pressure difference, and (ii) a "dry zone" through which vapor permeation of the components occur. They further assumed that the liquid-swollen zone remains in sorption equilibrium with the feed and the rate of permeation of liquid, with no enrichment, through this region can be calculated using a hydraulic permeability. "Equilibrium vaporization" occurs at the interface between the zones followed by vapor permeation of the components through the "dry zone" where enrichment of one (or more) of the components takes place. Thus the dry zone determines both flux and selectivity of separation. Ito et al. experimentally observed the existence of the boundary between the swollen and the dry zones, which largely depends on the feed composition, by putting a tracer in the feed that would stain the swollen zone. The application of their model to dehydration of aqueous ethanol by using PVA membrane is shown in Figure 10. Vapor permeabilities of the individual components were used to calculate the flux and separation factor values.

A conceptually similar visualization of the solute transport process through the membrane has been done by Tyagi and Matsura[183] and Tyagi et al.[184] They considered the membrane to consist of two regions — in one region the local concentrations of the solutes are considered to be in equilibrium with a hypothetical liquid phase, while the solutes in the other region are in equilibrium with an imaginary vapor phase. A change of phase of the imaginary liquid occurs at the boundary between the regions. They assumed pressure-driven transport all through the membrane although liquid and vapor transport parameters were used to express the fluxes. Further, they assumed coupling of fluxes in the liquid transport region of the membrane. The predicted solute concentration profiles in the membrane were in approximate agreement with experimental concentration profiles measured by the stack-of-membranes technique.



10. Comparison between swollen-dry layer model and pervaporation experiments for hydrophilic membranes.[182]

From an engineering point of view, a transport model should be easy to use, but should adequately take into account all the steps involved in the actual transport process mentioned in Section 3.2. Most of the pervaporation models discussed so far concentrate primarily on the phenomena of sorption of the solutes at the feed side followed by diffusional transport through the swollen membrane. This approach provides an insight into the sorption and transport processes and also helps in membrane selection. For the design and performance analysis of a pervaporation module, however, a resistance-in-series approach is more convenient. The resistance-in-series model, first introduced for membranes in connection with gas separation by Henis and Tripodi,[185] has been applied to the pervaporation process (see, for example, Gudernatsch, et al.[186] Huang and Feng[187]). Recently Liu et al.[188] developed a comprehensive resistance-in-series model that included all the steps of the process except the one involving transport of the vapor from the transmembrane side of a composite membrane to the condensing surface. The resistance offered by this step, however, is generally regarded as small.[51] Liu et al.[188] accommodated the feed-side mass transfer resistance or concentration polarization through a phenomenological mass transfer coefficient. The effect of concentration dependence of diffusivities on the flux was taken into account through an enhancement factor that was calculated from the functional dependence of diffusivities on component concentrations. For removal of a component A from a dilute solution in solvent B such as waste water, Liu et al. came up with the following simplified equations for the fluxes of the solute and the solvent.

$$J_A = \frac{1}{R_A}\left(C_{A,L} - \frac{P}{H_A}\frac{J_A}{J_A + J_B}\right) \tag{35}$$

$$J_B = \frac{1}{R_B}\left(1 - \frac{P}{p_B^0}\frac{J_B}{J_A + J_B}\right) \tag{36}$$

$$R_A = \frac{1}{k_L} + \frac{\delta_M p_A^0}{L_A H_A} + \frac{1}{k_{A,V} H_A} \tag{37}$$

$$R_B = \frac{\delta_M}{L_B} + \frac{1}{p_B^0 k_{B,V}} \tag{38}$$

Here J_A and J_B are the solute and solvent fluxes respectively, and R_A and R_B are the corresponding lumped transport resistances. The other terms are: $C_{A,L}$=solute concentration in the bulk of the feed; k_L= feed-side mass transfer coefficient; $k_{A,v}$, $k_{B,V}$ = effective mass transfer coefficients of A and B for transport through the support layer; P_A^0, P_B^0 = saturation vapor pressures of A and B at the operating temperature; H_A = Henry's law constant for the solute: L_A, L_B = permeability of A and B in the permselective layer of a composite membrane; and, δ_M = thickness of the permselective layer. The influence of concentration dependence of diffusivities on the flux are lumped into the permeabilities L_A and L_B. The resistance offered by the porous support layer is estimated by assuming the vapor transport to occur by a combination of pore diffusion and Knudsen diffusion. Although no comparison with experimental data was provided, a parametric study of flux and selectivity for removal of VOC's from waste water was presented. Transport resistance offered by the support layer of the GFT membrane has recently been analyzed by Bode and Hoempler.[189]

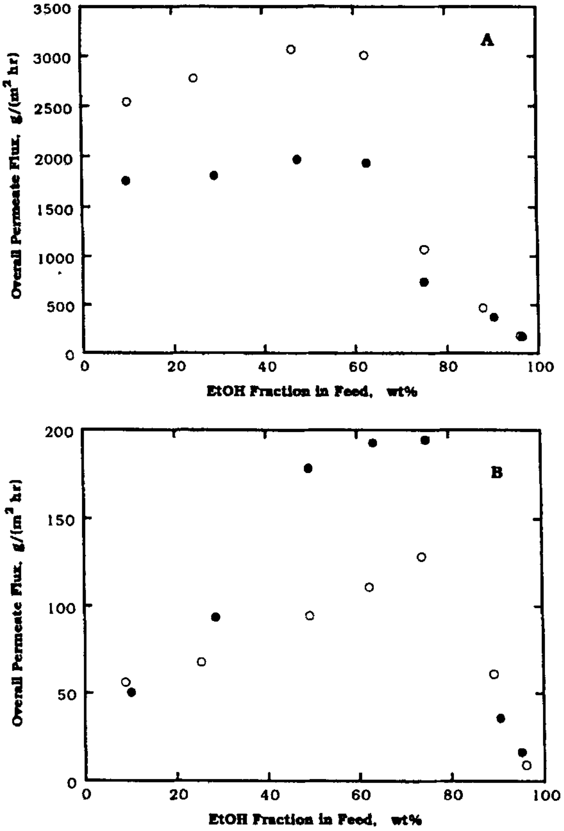
Considerable effort has gone into modeling the thermodynamics of sorption and the rate of solute transport in pervaporation. The resistance-in-series model may provide a phenomenological description of the process, which is satisfactory so long as the degree of swelling of the membrane remains too little to induce coupling of fluxes. For highly swollen membranes, however, we need a rigorous transport model which, besides being interpretive, can predict the flux and the separation factor with minimal experimental data. Although there has been very good progress, the presence of adjustable parameters severely restricts the use of the available models. Techniques to estimate transport parameters from fundamental properties of the membrane and the solutes need further refinements to be applicable to highly non-ideal and multicomponent systems. This is essential to the success of any predictive model.

4. Process Variables

The process factors that influence pervaporation flux and selectivities are: (i) feed composition, (ii) downstream pressure, (iii) temperature, (iv) continuous-phase mass transfer resistances (on both upstream and downstream sides), and (v) membrane conditioning. It is essential to understand the effects of these factors so as to select proper operating conditions for the separation of a particular mixture.

4.1 Feed Composition

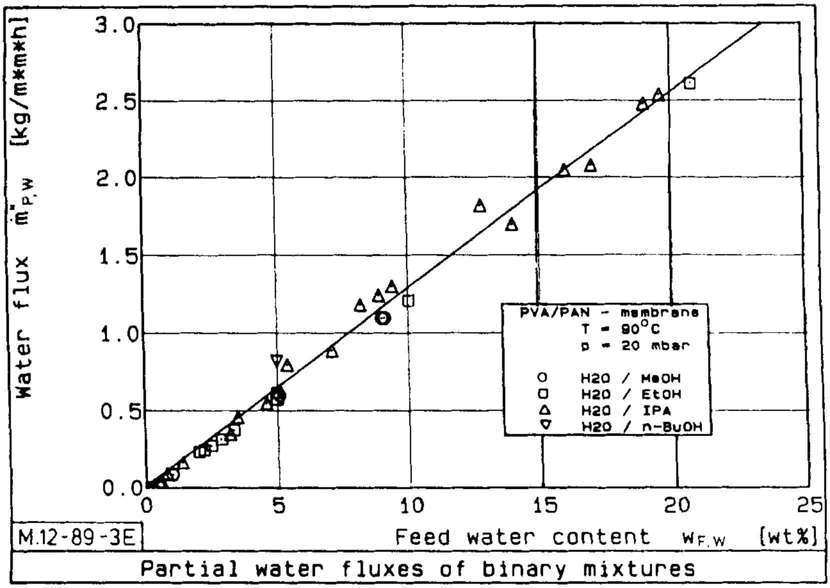
The feed composition is the single most important factor in determining pervaporation flux and selectivity. It affects liquid sorption and membrane swelling. In a two-component feed mixture, for example, one of the components interacts more strongly with the membrane than the other. As the concentration of this component increases the membrane swells more and flux increases. Diffusivities of both components increase with membrane swelling, and pervaporation selectivity decreases. For a given membrane and liquid mixture, the total pervaporation flux increases monotonically with the concentration of the more permeating component in the feed, while selectivity suffers a gradual fall. This effect has been observed by Acharya et al.[87] [for separating benzene-cyclohexane mixtures using PPOBrP/CA membrane], Shimidzu and Okushita[190] [for separating cyclohexane-cyclohexanone-cyclohexanol using poly-N-vinylpyrrolidone membrane], Okamoto et al.[56] [for separating water-ethanol mixtures by PDMS block copolymer membrane], Gonclaves et al.[11] [for separating water-ethanol mixtures by silicone rubber membrane], Yoshikawa et al.[25] [for separating water ethanol mixtures using amide-substituted polystyrene], Drioli et al.[33] and Joyce et al.[59] [separation of pyridine from an aqueous solution], Park et al.[191] [separation of alcohol-toluene mixtures using poly(acrylic acid)-poly(vinyl alcohol) blend membrane], Ihm and Ihm[192] [separation of ethanol-water using sulfonated polystyrene membrane], Park et al.[96] [separation of MTBE-methanol mixtures using PAA-PAN blend membrane], and Marine et al.[193] [separation of water-ethanol mixtures using the hydrophilic GFT membrane]. Itoh et al.[24] [water-ethanol separation using cross-linked PMA], Huang and Jarvis[194] [water-ethanol separation through cellophane and polyvinyl alcohol membranes], Huang and Lin[195] [separation of binary organics by polyethylene], observed a flux increase followed by a decrease as the concentration of the more permeating component in the feed increased. Radovanovic et al.[196] in their work on permselective separation of ethanol from an aqueous dilute solution using a hydrophobic membrane (PDMS) reported nonlinear dependence of both alcohol and water fluxes on the respective activity coefficients in the feed solution. This is suggestive of strong interactions among the components and the membrane material giving rise to coupling effects. Radovanovic et al. interpreted this observation by assuming nearly immobile clusters of water in silicone which break down in the presence of alcohol to form a mobile water-ethanol dimer that significantly contributed to the water flux. Chen et al.[29] reported a flux maximum in the separation of water-ethanol mixtures by using a polystyrene sulfonate ion-exchange film on a porous alumina support. They observed the maximum within the concentration range of 50-70 wt% ethanol depending on the degree of sulfonation of the polymer (Figure 11). The phenomenon was suggested to



11. Plots of the overall permeate flux vs. the ethanol fraction in the feed solution.

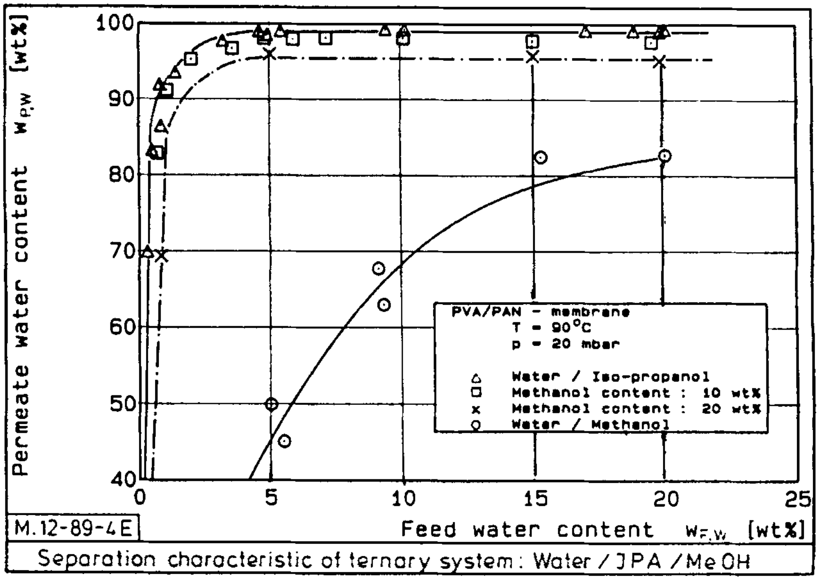
Top: 27.5 mol% sulfonate, Bottom: 10.5 mol% sulfonate. (O) PSS-Na, (●) PSS-Mg. [29]

arise out of the partitioning of water and alcohol between the ionic sites and the hydrophobic junctions of the polymer. They also reported a substantial rise in selectivity at the cost of flux when Na-form of the ionomer was used, an observation made by others for ionomer membranes (e.g., Dutta and Sikdar[93]). Huang and Wei[197], in their work on dehydration of ethanol using solvent-cast as well as latex membranes of poly(acrylonitrile-co-butyl acrylate), reported enhancement of both water and alcohol fluxes as the alcohol concentration in the feed solution increased



12. Permeate water flux of aqueous binary mixtures of different alcohols.[201]

although alcohol is the slower permeating species. They attempted to explain these phenomena by hypothesizing "fixed carrier" transport of the species, the functional groups of the copolymer acting as the fixed carriers. Simultaneous increase of flux and selectivity was also reported by Yoshikawa et al.[198] in the separation of aqueous alcohol with cross-linking of the polybutadiene polymer matrix. Park et al.[191] in their study on separation of methanol and ethanol from toluene using poly(acrylic acid)-poly (vinyl alcohol) blend membranes observed an exponential increase of alcohol flux with concentration which is indicative of a high degree of swelling. Ruckenstein and Sun[199] reported an unusual behavior exhibited by poly(vinyl acetal) membranes separating aqueous ethanol and acetic acid. While the membrane sorbs large volumes of these organics, and swell very little in water, it preferentially sorbs water from aqueous alcohol or aqueous acetic acid, making the membrane more permselective to water. This behavior is related to the swelling characteristics of the membrane.



13. Influence of methanol content on the separation characteristic of the ternary system water-isopropanol-methanol.[201]

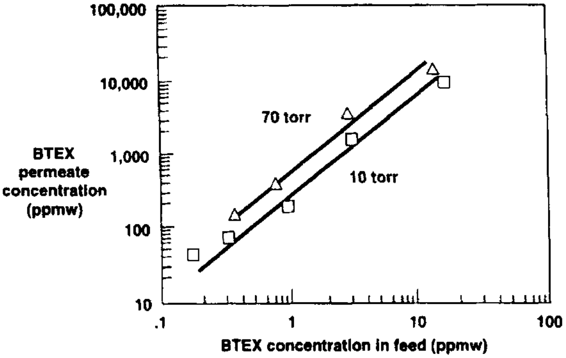
Permeation increase followed by a decrease and the corresponding variation in separation factor, may be the result of an inversion in preferential sorption, which occurs with some polymer-solvent systems (Zinvy and Pouchy;[200] Pouchy and Zinvy[123]). For pervaporation of dilute aqueous organic solution, in a concentration range of practical interest, a linear relationship between flux and feed concentration was observed and selectivity remained independent of feed concentration.[51] These results imply that sorption of organic compounds into membranes from dilute aqueous solution follows a Henry's law of sorption, and diffusivities in the membranes are essentially constant.[51] Swelling of an elastomer membrane in a dilute aqueous solution of an apolar organic, like a hydrocarbon or a chlorinated hydrocarbon, remains quite small, and as a result the flux and sorption remain linear in concentration.

The relationship between flux and feed composition is more complex when more than two components are present in the feed. Data on pervaporation of multicomponent systems are much less abundant in the literature, though real-life separation problems are mostly multicomponent. Rautenbach et al.[201] studied the effect of adding a second organic compound (methanol or monoethylene glycol monomethyl ether, MMME) on the dehydration of ethanol, iso-propanol, n-butanol, and diethylene glycol monobutyl ether (DMBE) using a PVA-PAN composite membrane. The former two organics are less rejected by the membrane than the latter four. For all the binaries the water flux remained linear in water content in the feed (Figure 12). For the dehydration of isopropanol containing a maximum of 20% water, they observed that addition of methanol up to 20% did not have an appreciable effect on the separation characteristics, and the ternary feed might be considered as pseudobinary. Above 20% methanol the behavior deviates gradually from the binary pattern (Figure 13). Multicomponent effects have been reported by several other workers.[201-203] For example, in the study of pervaporation of trichloroethane-chloroform-water mixture through silicalite-filled PDMS membranes, Goethaert et al.[203] found that the flux of trichloroethane was lower in the ternary mixture than in the binary mixture presumably because of obstruction of trichloroethane diffusion through zeolite by small amount of chloroform present in the zeolite. For removing VOC's from water using PEBA membrane, however, the coupling effects for trace organic transfer through the membrane were not observed when the downstream pressure was very low.[51] Both organic and water permeabilities for one VOC-water, two VOC-water and three VOC-water mixtures were found to be comparable with each other. Again this was because of small swelling of the membrane and less interaction among the solute VOC's. A simple transport equation based on binary feed mixtures described the multicomponent pervaporation results quite well.[51]

4.2 Permeate Pressure

Permeate pressure (or vacuum) provides the driving force for permeation. In general, the driving force will decrease, resulting in a lower flux, as downstream pressure increases. However, several exceptions exist, which will be discussed in the following sections. Downstream pressure greatly affects the process operating cost because the cost of maintaining vacuum is substantial. It also determines component concentrations in the product stream, and affects the membrane selectivity.

An operating pervaporation membrane has a swelling gradient in it. For many practical situations the upstream surface may be assumed to remain at swelling equilibrium with the feed solution (except where significant diffusional resistance exists at the feed side) whereas the cross-membrane surface, with its low solute concentration under the prevailing vacuum, is swelled only slightly. Because of this the permeate solute diffusivity in the membrane near the permeate side remains lower than that near the feed side. There appears to be a threshold value of the downstream pressure below which the permeate face of the membrane remains virtually dry, as a result of which both flux and selectivity level off with further decrease in permeate pressure.[12] Above this permeate pressure value, both flux and selectivity decline with increasing permeate pressure (i.e. decreasing vacuum) because of increased permeate concentration in the downstream compartment. This threshold pressure may be the optimum operating downstream pressure in a commercial unit. Invariant membrane flux and selectivity within a certain pressure range was observed for the pervaporation of benzene and n-heptane mixture through an NBR membrane.[103] The results were attributed to the high degree of swelling of the membrane at feed side. The existing concentration profile did not change significantly as permeate pressure increased. As a result, the driving force for transport remained nearly constant. The effect of permeate pressure was incorporated in the solution-diffusion models of Greenlaw et al.[161, 162] and Nguyen.[43] Except in the case of a highly swollen membrane, permeate pressure, in effect, changes the boundary condition at the cross-membrane surface. An increased permeate pressure, and consequently higher permeant concentrations in the permeate compartment, influences the solute concentration profiles in the membrane because of the changed



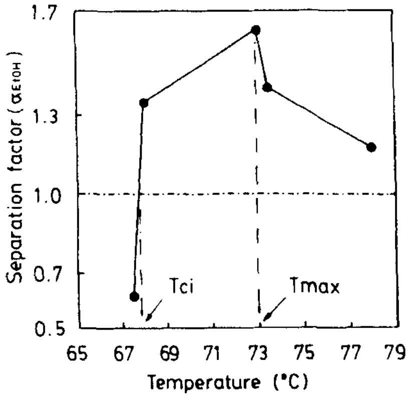
14. BTEX permeate concentration as a function of BTEX concentration in the feed for two different permeate pressures. Data obtained with a spiral-wound module containing a composite polydimethylsiloxane membrane, for a feed solution of BTEX in water at 40 °C. [204]

driving force and its associated effect on diffusivities. A quantitative estimate can be obtained using the solution-diffusion model.

As permeate pressure increases, membrane selectivity can either increase,[51, 64, 149] decrease[39, 64] or remain constant.[162] Positive effects of downstream pressure on selectivity have been reported by Ji et al.[51] for removal of 1, 1, 1-trichloroethane, methylene chloride and toluene from water. A ratio of overall organic permeability to water permeability, β^{perm}, was defined to indicate the positive ($\beta^{perm}<1$) or negative ($\beta^{perm}<1$) effect of permeate pressure on selectivity. This ratio is a function of organic and water intrinsic vapor permeabilities, liquid boundary layer mass transfer coefficient, Henry's law constant and membrane thickness. Recently, Wijmans et al.[204] also presented experimental data in support of the positive effect of permeate pressure on selectivity in the pervaporative separation of BTEX (benzene-toluene-ethyl benzene-xylene) from water using a spiral wound membrane module (Figure 14).

4.3. Temperature

Pervaporation flux increases with temperature but the selectivity usually decreases. An Arrhenius-type of temperature dependence of flux has been reported by most of the workers in the field (e.g. Madsuda et al.,[205] Acharya et al.,[87] Cabasso et al.,[18] Okamoto et al.,[56] Rautenbach and Albrecht,[206] Cen and Lichtenthaler,[64] Lamer and Voilley[65]). Reported activation energy values lie in the range 3-12 kcal/gmol. Increased sorption and diffusivity at higher temperatures is responsible for higher permeation flux. The effect of temperature on selectivity, however, does not follow such a simple relation probably because of complex temperature dependence of the polymer-solvent interaction parameters which determine sorption characteristics of solutes in solution. Since the diffusivities of both components increase with temperature, the selectivity is not expected to change much. Kucherski and Stelmaszek,[71] Rautenbach et al.[17, 207] and Chen and Lichtenthaler[64] found only little effect of temperature on selectivity while some other workers (e.g., Huang and Jarvis[194]) observed some decline of selectivity. Qunhui et al.[208] reported extensive experimental data on the temperature effect of separation of mixtures of alcohol and water over a wide range of feed concentration using a chitosan membrane. They observed a dependence of activation energies of both the species on the feed concentration but the activation energy of ethanol transport was always found to be greater than that of water. The sorption selectivity and separation factor both decreased with temperature. The higher activation energy of ethanol transport was attributed to increased plasticization of the membrane at higher temperatures. Madsuda et al.[205] reported a selectivity maximum with temperature. An interesting phenomenon of temperature dependence was reported by Lai et al.[209] who, in their work on the separation of aqueous ethanol using a polysiloxaneimide membrane, observed that the membrane allowed preferential permeation of water below a certain temperature. Above this temperature ethanol permeated preferentially and the separation factor passes through a maximum. This behavior is shown in Figure 15.



15. Effect of feed temperature on the separation factor for ethanol using Polysiloxaneimide membrane.[209]

4.4. Interface Mass Transfer Resistance

A great majority of the reported investigations indicate that diffusional resistance of the membrane essentially controls the permeation flux, and interfacial equilibrium prevails on both upstream and downstream sides. However, that interfacial mass transfer resistance not only does exist but can even control the overall transport process in the case of enrichment of a very dilute solution was first demonstrated by Psaume et at.[42] In their work on the removal of traces of trichloroethylene (TCE) from water using silicone tubings, they observed that the diffusional resistance for transport through the membrane was negligible compared to the feed-side mass transfer resistance over a Reynolds number of 1 to 60. They calculated the mass transfer flux of TCE using the Leveque correlation for mass transfer coefficient for laminar flow through a tube. The calculated fluxes very closely matched the experimental values. Psaume et al.'s work was the start of a series of studies on the importance of feed-side mass transfer resistance. Lipski and

Cote[46] reported a study on the removal of TCE from waste water using silicone tubings with axial and transverse flow of the feed. They also performed simulation studies to predict the performance of membrane modules of different configurations. Strong feed-side mass transfer resistance in aroma compounds recovery from aqueous solutions using silicone tubings was reported by Karlson and Tragardh.[210] These and other studies in this direction used the resistance- in-series model to correlate and interpret pervaporation data.[49, 51, 210, 211, 212, 213] An extended form of this model applicable to a composite membrane has been described before [Eq. 34 through 37]. In the case of an unsupported dense membrane, or if the support layer does not offer any appreciable resistance, [$1 / (k_{A,V} H_A)$ is small], and a plot of $\{C_{AL} - (P/H_A)[J_A/(J_A + J_B)]\}/J_A$ against the membrane thickness δ_M, yields both mass transfer coefficient, k_L, and the membrane permeability, L_A.[49, 51, 211] Although most of the studies in this direction were concerned with the removal of sparingly soluble volatile organics from water, Rautenbach and Helmus[214] presented computed results to show that interfacial resistance may play a significant role even in the process of enrichment of aqueous ethanol using PVA membrane.

While the above approach is very useful in estimating the relative contributions of the transport resistances offered by the membrane and by the boundary layer under a given hydrodynamic condition in a laboratory pervaporation cell, the liquid-side mass transfer coefficient should be known a priori in order to estimate the flux, for example while designing a pervaporation unit. For a well-defined flow like laminar flow through a tubular membrane, it is rather simple to calculate the mass transfer coefficient by solving the corresponding Graetz problem.[49] For other situations, a suitable mass transfer correlation can be used. In a spiral wound module, one of the common membrane separation devices, it is possible to substantially reduce the feed-side resistance by incorporating spacers to increase the turbulence. Hickey and Gooding[215] performed a detailed experimental study in this direction and found that incorporating an adequate number of spacers in the flow channel of a spiral wound module, the mass transfer coefficient could be increased by 1.5 to 4 times.

Several theoretical analyses of the importance of feed-side mass transfer resistance in the pervaporation of volatile organics have been reported.[204, 216, 217] Michaels[217] started with Eq.13, replaced, as an approximation, the molar average velocity of the components by that of water only, and developed an expression for the "solute enrichment ratio". Charts were provided to give an estimate of the importance of the boundary layer resistance compared to that of the membrane, and also described the limiting situations when the feed-side resistance virtually controls the process.

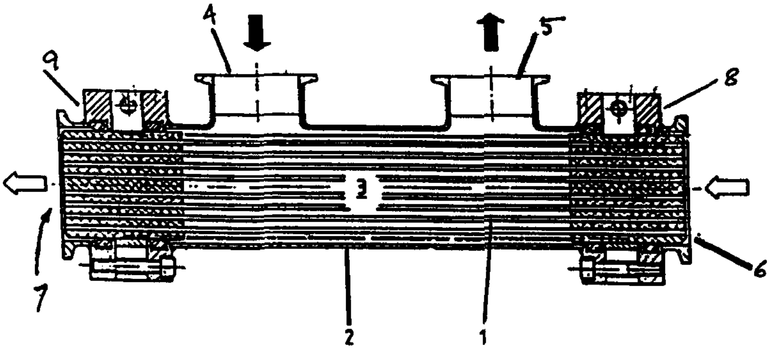
Although the importance of feed-side mass transfer resistance in controlling the membrane flux and selectivity have been extensively studied, few studies have addressed the importance of permeate side vapor phase mass transfer resistance. A diffusion-convection model was used by Ji et al.[51] to describe mass transport in the vapor phase. They found that permeate-side vapor phase mass transfer resistance cannot be ignored as downstream pressure increased and diffusion became significant for the mass transfer in vapor phase. If the convective flow from the membrane-vapor interface into the bulk of the permeate dominated the mass transfer in the vapor phase, as occurred at low permeate pressure, the concentration at the membrane-vapor interface would be equal to that of the condensed permeate. In this case, the vapor phase mass transfer resistance is negligible. This analysis agreed well with their experimental data for several solute-water systems. Bo and Nielsen[218] assumed that diffusion was the only process for mass transport in vapor phase. A mathematical model was developed by these authors to analyze the pervaporation data of tetrahydrofuran-water-cuprophane system collected by Neel et al.[12] They found that the difference between the interface and bulk concentration in vapor phase increased with increasing downstream pressure. Nguyen[13] reported an average vapor phase mass transfer coefficient of 2×10^{-5} m/s for tetrahydrofuran-water-cuprophane system. The diffusion-convection model was also used by Beaumelle and Marin[219] to describe the partial pressure gradient in vapor phase. The model was tested using pilot plant pervaporation data of both a pure component (water) and binary mixtures (water-ethanol) through PDMS membranes.

4.5 Membrane Pretreatment/Conditioning

Film conditioning or pretreatment has been attempted by several researchers to improve the permeation characteristics of a pervaporation membrane. Heat treatment of polyvinylidene fluoride membrane was found to enhance the selectivity of p-xylene in the separation of isomeric xylenes.[220] More efforts, however, went into studying the effects of solvent pretreatment. Since the degree of swelling of a particular membrane is the single most important factor in determining the permeation flux, pre-swelling using the feed mixture or a solvent of suitable composition increases the flux considerably although at reduced selectivity. An elaborate study of film conditioning by soaking in a solvent followed by annealing was reported by Michaels et al.[221] for the separation of isomeric xylenes through polyethylene films. They argued that a rearrangement of amorphous and crystalline regions of the film was responsible for higher permeability of the conditioned films. Rautenbach and Albrecht[206] in their study on the separation of benzene-cyclohexane mixtures using polyethylene films observed that films pretreated with benzene offered lower flux but higher selectivity while reverse was true when pretreatment was done with cyclohexanes. Tealdo et al.[23] published data on the effect of membrane pre-swelling on the flux and selectivity for the separation of water-ethanol mixtures using styrene-grafted and sulfonated PTFE films.

Unconditioned membranes were found to offer smaller flux during the initial periods but eventually performed as good as pre-swelled membranes. Nagy et al.[10] undertook a detailed study on the separation of alcohol-water mixtures using conditioned cellulose hydrate membranes. Pre-swelling was done by keeping the membrane in a refluxing mixture of alcohol and water for a period of 1 to 20 days. Solvent uptake was as high as 1 kg/kg dry membrane. The pretreated membrane was found to offer significantly enhanced flux but at reduced selectivity. It was suggested that pretreatment affects the crystal structure and degree of crystallinity of the polymer. However, the long-term effect of pre-swelling, if any, has not been decisively established. Acharya et al.[87] reported the role of conditioning of a polymer alloy membrane (composed of cellulose acetate and a polyphoryl ester derivative of polydimethyl phenylene oxide) on pervaporation of benzene-cyclohexane mixtures. They suggested that irreversible swelling of the membrane in solutions of high benzene concentration was the cause of high fluxes. Marin et al.[193] reported a pilot plant study of the effect of membrane conditioning on the separation of aqueous ethanol using the GFT membrane. They observed that more than fifty hours of conditioning involving contact of the membrane with the feed with vacuum applied on the downstream side gives high flux and selectivity. They also observed that keeping the membrane in contact with an ethanol solution of 85-93% concentration for more than five days with atmospheric pressure at the permeate side greatly deteriorated the membrane performance.

Literature data show that conditioning or pre-swelling of a membrane sometimes increases the flux and reduces selectivity but prolonged experiments are required to establish its longterm effect. Studies of possible morphological changes are also necessary. This has been done with some gas-separation membranes (e.g. Heany and Pellegrino[222]) but conclusive evidence is lacking for pervaporation.

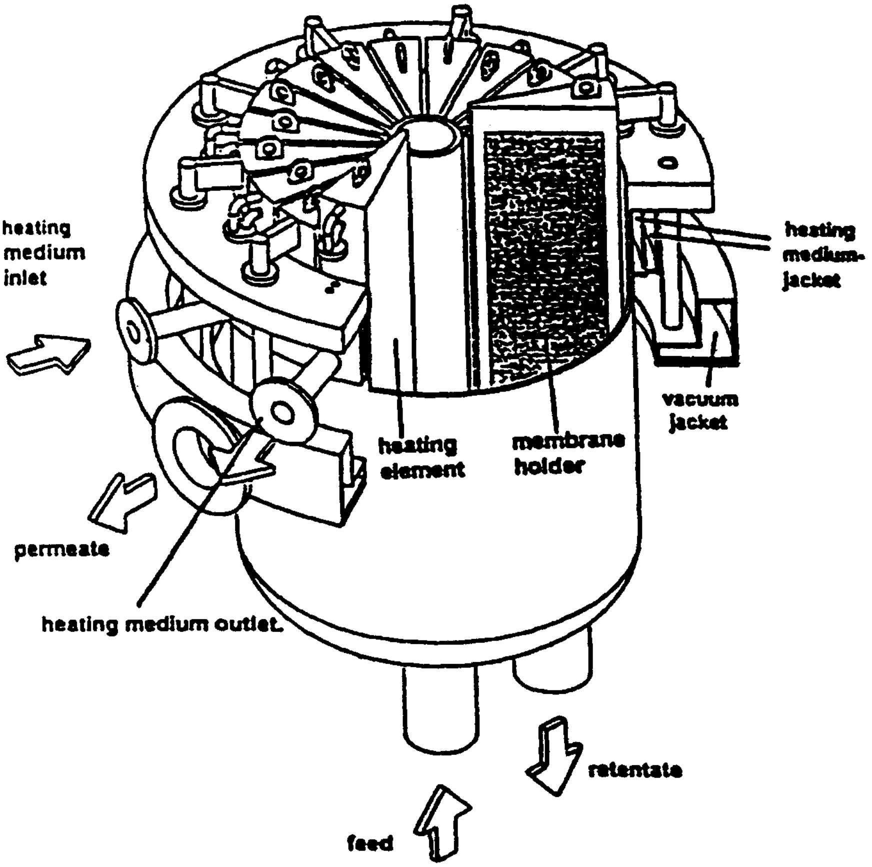


16. SEMPAS capillary module [1. Capillaries, 2. Housing, 3. Insert of capillary bundle, 4,5. Shell-side nozzles, 6,7. Potted ends of the insert, 8,9. End flanges.] [224]

5. Commercial Modules and Design of a Pervaporation Plant

5.1 Module Design

Most of the operating pervaporation units use modules of plate-and-frame construction with a rugged porous support for the membrane. The feed flows over the membrane and the product is drawn from the other side. A number of modules in series is preferred to a single one of large area. This is because large defect-free membranes are difficult to make consistently, it is harder to maintain constant temperature over a large membrane area, and it is easy to replace a defective module and restore operation. The disadvantages of these plate and frame modules include high capital cost, labor intensive assembly, and leakage problems due to the large amount of gaskets used in the system[4]. Total membrane area requirement is governed by the membrane type and thickness, operating temperature and downstream pressure. In these modules continuous phase mass transfer resistance is



17. KREBS SWISS pervaporation module.[225]

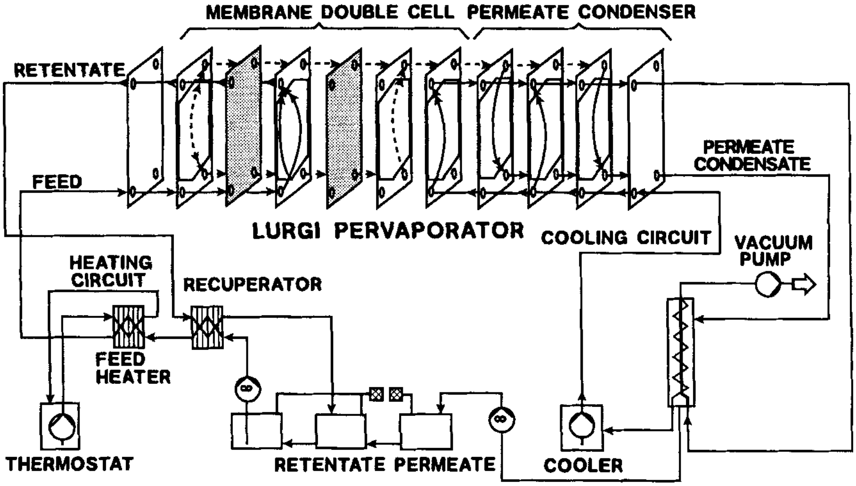
usually much smaller than the diffusional resistance of the membrane, except for removal of VOC's from dilute aqueous solutions.

Spiral wound modules, which have been widely used for pressure-driven membrane separation processes such as reverse osmosis, ultra- and microfiltration, are now being adapted for pervaporation applications. Like the plate-and-frame module, the spiral configuration also uses a flat membrane. Sealing at the edges is done by an adhesive rather than by a gasket. This may, however, pose a problem when the feed is an organic mixture. Another disadvantage of the spiral module is the pressure drop on the permeate side caused by the spacers thereby reducing the effective vacuum. Texaco[223] has marketed a spiral wound module for dehydration of organics.

Another class of module used in pervaporation is the hollow fiber or capillary fiber module. Figure 16 shows a novel hollow fiber module design. The construction is similar to that of a heat exchanger.[224] A bundle of hollow fibers potted at the ends using a suitable adhesives is fitted in a housing or shell. For a larger scale installation, a number of the modules can be arranged in the series-parallel mode depending upon process requirements. Recently Merz and Danziger[225] described the construction of a new type of pervaporation module (Figure 17) that consists of a pressure vessel containing an assembly of alternate membrane holders and heating elements oriented radially. The feed enters axially and then flows radially through a narrow slit formed by the membrane holder and the heating element, and leaves at the bottom of the vessel. The membrane holders and the heating elements are connected to jackets for vacuum or the heating fluid. The novelty of the constuction is that it generates less pressure drop on the permeate side. It also provides accessibility to all internals making it possible to inspect, test and replace the components. Vapor product from a module is withdrawn through a header to a vacuum condenser cooled by a suitable refrigerant flowing through tubes or coils which should ensure a very low pressure of the condensate but avoid icing of the condenser. An integrated heat exchanger network is used to recover the heat from hot liquid product to preheat the feed. Feed is further heated to the desired temperature using low pressure steam. Preheating the feed is an effective means of supplying the energy requirement of the latent heat of vaporization.

5.2. Process Design and Economic Considerations

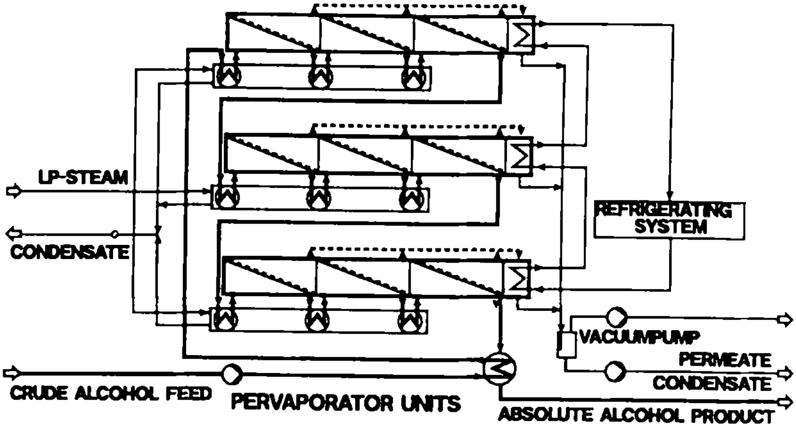
The core of a commercial pervaporation plant consists of the following basic units: (a) the pervaporation modules; (b) a heat exchanger network for heating the



18. LUGI pervaporator pilot plant.[3]

feed and cooling the liquid product; and (c) vacuum condensers for permeate product. Figures 18 and 19 show the layouts of the important components of a pervaporation pilot plant and a commercial plant, designed and built by Lurgi for ethanol purification.[3]

The important design variables for pervaporation process are (a) membrane area, (b) feed temperature, and (c) downstream pressure. For a particular membrane the area required to achieve a specified degree of separation depends strongly on the choice of feed temperature and permeate pressure. If the sorption and diffusion coefficient data are available the solution-diffusion model can be used to compute the membrane area. For this purpose it is necessary to solve the coupled mass and energy balance equations for the system. Pressure drop calculations for both feed and permeate flow are done using the Poiseuille equation, because the flow in a pervaporation module generally remains in the laminar regime. Some aspects of pervaporation process design were discussed by Rautenbach and Albrecht.[226] The equipment and operating cost corresponding to assumed feed temperature drop and



19. Pervaporation plant for dehydration of ethanol. [3]

downstream pressure can be calculated and the optimal design can be arrived at. A temperature drop of 3-10 K is usually allowed[207] and the membrane area of the modules in series are calculated with the provision of interstage heating of the feed. Temperature drop in the transverse direction should also be considered since it would change the permeation flux and selectivity. This "temperature polarization" has been reported by Rautenbach and Albrecht.[206, 227] The temperature differences between bulk flow and membrane surface of up to 4.5 °C were observed in their experiments using high flux asymmetric membranes. However, for a reliable design it is preferable to use pilot scale data and to use scale-up techniques, particularly if more than one solute are involved. The comments of Rautenbach et al.[201] in connection with the separation of multicomponent aqueous alcohols are notable in this connection: "Presently a safe design of the pervaporation process has to be based on experiments with the real system since nothing is reported in the literature on the possibilities and limitations of a prediction based on experiments with the individual binary aqueous organic solutions". The picture has not changed much since then.

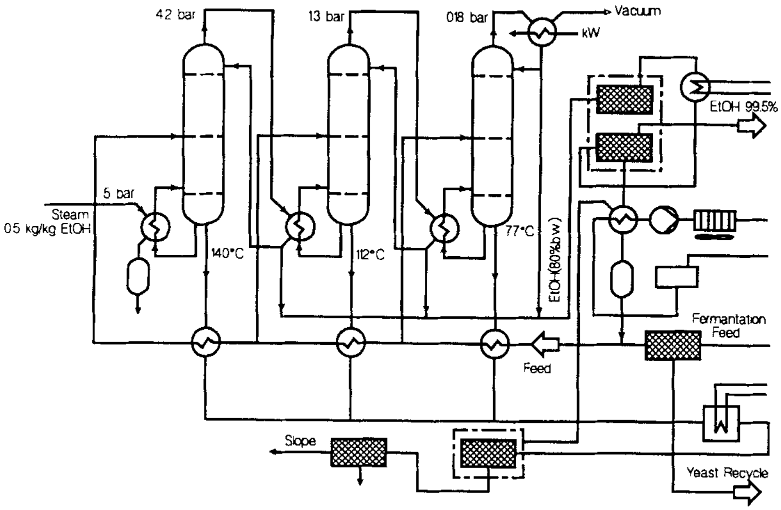
Most often the pervaporation process is very sensitive to the downstream pressure, since permeation fluxes are directly affected by this process variable.[51] The pressure drop on the permeate side becomes critical in the pervaporation module design.[226-229] The calculation carried out by Rautenbach and Albrecht[211] showed that a marked decrease of selectivity and flux could occur due to friction loss on the permeate side for hollow fiber module with permeate flow in the tube side. The Hagen-Poiseuille equation was used to calculate pressure drop in the capillary tube. Since the pressure loss is inversely proportional to the pressure level, larger fibers should be used if the system were operated at low downstream pressure. The selectivity loss due to the downstream pressure drop was also reported by Boddeker et al.[73] in the pervaporation of aqueous phenol on the pilot plant scale. Gooding and Teague[228] developed a series of equations based on differential mass and momentum balances to simulate the permeate side flow for both hollow fiber and spiral wound module. Hickey and Gooding[215, 229] evaluated the friction loss and mass transfer characteristics for several spacers in spiral wound modules, and a pressure drop and mass transfer correlation was developed. Estimation of permeate buildup inside the fibers (when a hollow fiber module is operated in the shell-feed mode) and its effect on the performance of a module has been reported by Feng and Huang.[230]

The process economics of pervaporation has been studied by several authors.[45, 46, 128, 231] The cost of a pervaporation system is sensitive to the permeation flux, separation factor, the removal or concentration fraction and the feed concentration. Costs decreased with the increase of either the permeation flux or separation factor.[45] For example, pervaporation must generally have a separation factor for VOC/water of at least 300 and a permeation flux of 10-30 Kg/m^2-day in order to be economically competitive with carbon adsorption or air stripping.[231] Pervaporation is applicable to the waste stream containing moderate or high concentration of VOC's, since the driving force for transmembrane transport is proportional to the feed concentration.[128] It has been shown by Blume et al.[45] that the cost for removal of the last 9% of the VOC's is equal to that of the first 90%. Optimization of multicomponent pervaporation processes for the removal of volatile organic compounds from water was carried out by Ji et al.[232] Hollow fiber module was used in this calculation. Their model included the effects of multicomponent feed mixtures, liquid boundary layer mass transfer resistance, and downstream pressure on module performance and process economics. It was found that the treatment cost was relatively insensitive to the downstream pressure in the low pressure range, and the contribution of capital and operating costs to the overall treatment cost strongly depended upon the feed flow hydrodynamics (laminar or turbulent flow). Similar calculations were performed by Hickey and Gooding[233] for spiral wound membrane modules.

In studying the application potential of pervaporation processes, Rautenbach and Albrecht[227] found that a unit consisting of multi-stages cannot compete with conventional separation process such as extractive distillation for breaking azeotropes. However, hybrid processes combining extractive distillation and pervaporation would be very competitive, especially for the manufacture of high-purity products. Integration of pervaporation with conventional separation or other membrane processes could become a fast track to commercialization of pervaporation.[234] Hybrid pervaporation systems have been studied both for chemical production[235, 236] and for wastewater treatment.[17, 77, 231, 237, 238] In hybrid pervaporation processes reported by Fleming[234] and Mecki and Lichtenthaler[77] for VOC removal, the bulk of the VOC was removed by pervaporation, whereas the final purification was done by processes such as adsorption or stripping. The hybrid process of pervaporation combined with activated carbon adsorption was found to operate in a more cost effective way than activated carbon adsorption alone. A pervaporation-reverse osmosis hybrid process was developed by Schofield et al.[231] in which each single component process can operate at its optimum concentration range.

5.3. Status of Commercialization

Pervaporation has been commercially exploited for dehydrating organics, especially ethanol, isopropanol and ethylene glycol. In mid-1970's GFT



20. Integrated distillation pervaporation plant for ethanol production. [240]

commercialized an economical pervaporation process to produce high purity ethanol from 5-7% ethanol in fermentation broths. Two plants were built in Brazil and Philippines respectively.[239, 240] This was followed by installation of several other integrated distillation-pervaporation plants (Figure 20) in Europe and Asia. Capacities range from 1000 to 50,000 liters per day ethanol recovered with a product purity of 99.85%. The world's largest pervaporation plant is operating in Bethenville, France, to produce 150,000 liters per day of ethanol using 2,400 m^2 membrane area. GFT uses an asymmetric composite membrane consisting of three layers — a support of non-woven polyester on which a polyacrylonitrile or polysulfone ultrafiltration membrane is cast. On the top there is an ultrathin (0.1 micron) layer of cross-linked polyvinyl alcohol (PVA). While the PVA layer is responsible for the ultimate separation, the two bottom layers provide the mechanical strength, and chemical and thermal stability. About seventy commercial plants for alcohol dehydration are now in operation worldwide.

Other commercial plants in operation are for alcohol reduction in beer and wine using polydimethyl siloxane (PDMS)-type membranes[241, 242] and for dehydration of hydrocarbons, chlorohydrocarbons and other solvents using hydrophilic PVA composite membranes. In fact, dehydration of a variety of solvents is done by pervaporation in many commercial installations. Some time ago four solvent dehydration plants were in operation in Japan.[243] Texaco manufactured pervaporation units in U.S.A. for solvent dehydration, but is reported out of this business now. Membrane Technology Research supplies commercial units for removal of VOC's from waste water.

6. Recent Trends in Pervaporation Research

Application-oriented research in pervaporation started with the separation of a mixture of hydrocarbons.[2] Since then many investigations were carried out for more than two decades for the separation of apolar-apolar and apolar-polar organic mixtures involving mainly hydrocarbons and alcohols (see Table III). Commercial applications, however, remained remote because of insufficient flux and selectivity offered by the membranes available at that time. From the late seventies the thrust of pervaporation research significantly shifted to separation of aqueous organics, particularly dehydrating alcohols, that led to the remarkable commercial success of this technique.

Separation of aqueous alcohols and other organics using hydrophobic membranes remains a thrust area for pervaporation research. Increased efforts are, however, being put to using organophillic membranes to concentrate ethanol and other organics from dilute solutions. In particular, concentration of ethanol from dilute aqueous solution by pervaporation has been extensively studied.[244, 245, 246] However, widespread applications of pervaporation to ethanol concentration are limited by low selectivity of currently available organophilic membranes. PDMS membrane is the choice for most of these applications. Selectivities of PDMS membrane for ethanol/water mixture are low (less than 10). It has been found that both the selectivity and flux of PDMS membranes can be enhanced by addition of a hydrophobic filler such as silicalite into the polymeric matrix.[55, 62] Zeolite-filled membranes provide an opportunity of improving the separation properties of pervaporation membranes.[247] However, fabrication of such a membrane with an ultra-thin separation layer for commercial applications remains a challenging problem. A variety of new polymeric materials, both hydrophilic and organophilic (see, for example, Yamasaki et al.,[248] Qunhui et al.,[208] Feng and Huang;[249] Roizard et al.[250]) are being prepared and tested for this process with varying degrees of success. Polyelectrolyte complex membranes made by reacting polycations with polyanions[251, 252] are highly hydrophilic and have considerable potential for dehydration of organics. Inorganic membranes, which have hitherto been used for filtration and gas separation applications, are also being explored for pervaporative separation of aqueous solutions. Recently Liu et al.[84] prepared zeolite membranes supported on microporous stainless steel tubes and nanoporous alumina tube, and tested these for the separation of methanol, ethanol, and acetone from aqueous solutions with impressive fluxes and selectivities. Because of the inherent advantages of inorganic membranes such as mechanical strength and stability, their potential needs to be explored more thoroughly. Facilitation of the rate of a reversible reaction by selectively removing one of the products through a membrane reactor wall which also catalyzes the reaction is also an important area of research.[253-255] David et al.[253] used a blend of two polymers - one acting as the catalyst, while the other is permselective - for the reaction-separation process. Recently Zhu et al.[256] used a pervaporation membrane reactor consisting of a film of polyetherimide formed on a porous tubular alumina support to study the efficiency of esterification of acetic acid with ethanol. The continuous removal of water through the permselective membrane wall of the reactor increases the product yield substantially above the calculated value for a conventional plug-flow reactor.

Pervaporation is also an effective technology for temperature-sensitive bioseparation used in food and fermentation industries, such as recovery of alcohols and aromatic compounds from dilute aqueous solution[257]. Fermentation is typically a batch process, usually producing a very dilute product. Distillation towers are currently used to separate alcohols produced from fermentation. However, the distillation process is an energy intensive system which needs fuel to operate its reboilers. The second problem associated with the fermentation process is the product inhibition in which the microbial activity is inhibited with increasing product formation. The products impose severe damage to the cell membrane function.[258] Among various technologies evaluated for eliminating product inhibition by continuous removal of fermentation products, fermentation coupled with pervaporation appears to be the most efficient process for ethanol fermentation.[259] Numerous examples[260-262] showed that ethanol productivity increased due to the alleviation of ethanol inhibition and the complete retention of cell population by pervaporation. Similarly, removal of toxic metabolites helps in maintaining steady productivity in cell culture. Sikdar and Sawant[263] demonstrated that ammonia, a common metabolite, can be effectively removed from a culture medium by pervaporation using ion-exchange membranes.

Pervaporation as a technique is also being evaluated and developed for removing volatile organic compounds (VOC's) from industrial wastewaters.[264] In situations where treating the wastewaters before discharge, by methods such as steam stripping, adsorption, or bioremediation, is expensive, pervaporation may offer an attractive alternative. By using organophilic membranes, VOC's can be concentrated by orders of magnitude at permeate side compared to feed and recovered by condensation. The VOC concentrate can either be disposed of by combustion, or be recycled for reuse.[45, 46, 265] Experimental and theoretical work on the removal of VOC's from dilute aqueous solutions have focused on three areas. The first deals with the selection of organophilic membranes for different VOC contaminants and the study of the relations between membrane materials and their selectivities and permeabilities with different VOC systems.[16, 33, 38, 51, 69] Effects of multicomponent waste solutions on membrane performance were also investigated.[51, 52, 203] The second area is the study of mass transfer of organic solutes through membranes, i.e., sorption and diffusion processes within membranes[39, 40, 47, 266], as well as organic transport in the liquid and vapor phases.[42, 49-51, 78, 211, 216, 217, 267] The third is system design and optimization to determine the best module configuration and operating conditions for minimum treatment cost.[45, 46, 232, 233] In contrast to using organophilic membranes, hydrophilic membranes have also been exploited for permselective transport of water followed by catalytic oxidation of any residual organic contaminant to produce ultrapure water.[268]

The use of pervaporation for recovery of aroma compounds has been demonstrated in a number of studies.[269] Thermal evaporation and distillation processes, currently used in the food and cosmetics industries for aroma compound recovery, often cause deterioration of quality, thus lowering the market value of aroma compounds. Studies on recovery of both low-boiling and high-boiling aroma compounds by pervaporation have been conducted with various membrane materials including PDMS,[65] zeolite-filled PDMS,[65] polypropylene,[257] PEBA,[269] and PDMS-polycarbonate.[270] Enrichment factors of 5 to 11 for C_2-C_6 alcohols, over 100 for esters and 40-65 for aldehydes (hexanal and trans-2-hexenal) were obtained by Bengtsson et al.[271] Both PDMS and zeolite-filled PDMS membranes exhibited high selectivity (with enrichment factors of 160 and 372, respectively) for separation of 1-octen-3-ol from aqueous solutions.[65]

The least developed area for pervaporation process is the one in which the first research on pervaporation occurred - i.e., organic/organic separation. Pervaporation has been used for the separation of azeotropic mixtures of aromatic and aliphatic hydrocarbons and of close boiling liquid. Examples of such applications include isomeric separations (e.g., p-xylene/m-xylene),[86] paraffin/olefin separations,[104] paraffin/aromatic separation,[87-89, 103] branched hydrocarbon/n-paraffin separations, polar organics from their azeotropic mixtures (e.g., ethanol/benzene, methanol/MTBE),[93, 97, 256] separation of chlorinated hydrocarbons[98] and chlorinated hydrocarbons/hydrocarbons, and purification of dilute streams (e.g., isopropanol removal from heptanelhexane). Aminabhavi et al.[272] recently reviewed the work performed in this area. There are at least two factors which hinder the further development of pervaporation for commercial organic separations. One is the lack of membranes which exhibit both high flux and selectivity. Most membranes developed so far are either high-flux or high-selectivity but not both. The performance of these membranes decreased with time due to membrane swelling. The other problem is the lack of membrane modules able to withstand long-term exposure to organic compounds at normal or elevated temperatures. A commercial pervaporation plant for the methanol/MTBE separation using a cellulose acetate membrane has been developed by Air Products.[105] These membranes worked well at methanol concentration up to 6%. However, above this concentration, membrane selectivity was lost due to membrane plasticization. Operating temperature was limited to less than 50°C since the membrane was not stable in the methanol/MTBE mixtures at temperatures above 50°C.

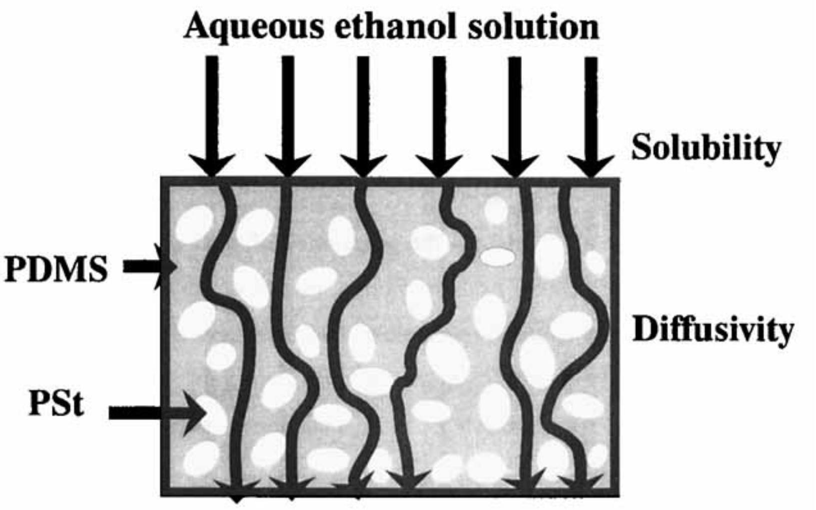
Much activity is evident in developing novel polymeric materials that would offer better flux and selectivity. Attempts to develop and test new homopolymers, novel block and graft copolymers, and polymer blends with improved properties have attracted serious attention. For example, PDMS is the foremost organophilic material for a pervaporation membrane. But its film-forming properties are not good, although the scope of achieving better flux and selectivity exists. A number of attempts have been made recently to synthesize block and graft polymers containing siloxane chains for performances better than that of PDMS. These include a poly(1-phenyl-1-propyne)/PDMS graft copolymer membrane,[273] a graft copolymer of polysulfone/PDMS,[274] and a segmental copolymer of polyimide/PDMS with varying silicone contents in the chain.[209] These membranes exhibited satisfactory separation factors and good organic fluxes. Preparation and use of polyimide/PDMS block copolymer has also been reported by Schauer et al.[275] for separation of aqueous alcohols. Okushita et al.[116] grafted nylon-6 with polyoxyethylene to prepare a membrane for the technically important separation of mixtures of cyclohexane/cyclohexanone/cyclohexanol. Jonquieres et al.[276, 277] synthesized a series of polyurethaneimide block copolymers containing soft segments or blocks of α, ω-diamino polyoxyethylene, polyethylene glycol or polycaprolactonediol precursors in which the soft block molecular weight was made to vary. With increase in the soft segment lengths (and, therefore, the weight fraction) there was a linear to exponential rise in the fluxes for the separation of mixtures of ethanol and ethyl tertiarybutyl ether - but the weight fraction of ethanol (and consequently the separation factor) decreased. The activation energy of ethanol transport, however, was considerably larger for a copolymer with shorter soft segments. But the permeate concentration did not suffer any significant fall. This study is indicative of the potential of block copolymers in customizing pervaporation membranes.

Park et al.[191] prepared solution-cast membranes from a homogeneous blend of poly(acrylic acid) and poly(vinyl alcohol) for the separation of polar-apolar organic mixtures (alcohols and toluene). However, chosen polymers are often found to be incompatible to form homogeneous blends.[278] Formation of interpenetrating polymer networks (IPN) provides a technique for blending incompatible polymers. Recently IPN membranes have been used for pervaporation. Liang and Ruckenstein[279] prepared an IPN membrane of polyvinyl alcohol/polyacrylamide for separation of ethanol-water mixtures. An organophilic IPN membrane containing polydimethylsiloxane and polystyrene was prepared by Miyata et al.[280] for the same separation. A schematic illustration of the mechanism of enhancement of ethanol selectivity for this organophilic membrane is given in Figure 21. Use of nonhomogeneous blends containing a bulk polymer phase having a micro-dispersed second polymer phase in it has also been reported by Sun and Ruckenstein.[122]

Asymmetric membranes with integral dense skins, which have so far been used in reverse osmosis, do have a great potential for application in pervaporation. The chief advantage of this type of membrane is that no separate porous backing is required for casting the membrane. The membrane material itself forms the porous support of the integral dense skin. In two recent interesting studies Jian and Pintauro[281] and Jian et al.[282] reported the preparation of such membranes having a dense layer thickness of about 0.3 micron from a solution of polyvinylidene fluoride. They used these membranes for the separation of benzene and styrene from aqueous solutions and reported remarkably good flux and moderately good selectivity. Further exploration of the potential of such membranes is expected to produce encouraging results.

7. Concluding Remarks

Despite great potential of pervaporation processes, industrial applications of pervaporation have been limited to purification of ethanol and a few other alcohols and solvents. Developing innovative membranes which provide high flux and selectivity is the greatest challenge to widespread commercialization of pervaporation. A better understanding of polymer-solvent interactions in multi-component mixtures, which is hitherto primarily based on the Flory-Huggins theory, will be essential if we are to successfully design pervaporation membranes suitable for specific applications. In recent years compatible polymers have been blended, and polymers have been grafted with suitable functional groups, in order to obtain desirable separation properties from several commercial membranes. Inorganic membranes (such as zeolite membranes) and organic/inorganic composite membranes have been tested for pervaporation applications. More emphasis needs to be placed on developing membranes with thermal stability so that larger fluxes at higher temperatures can be attained. Membranes with improved resistance to organic solvents would be critical in the development of pervaporation processes for organic/organic separations.



21. Tentative illustration of the relationship between the microphase-separated structures of the PDMS/PSt IPN membranes and the permselectivity for an aqueous ethanol solution.[280]

More extensive theoretical and experimental work is needed on species diffusion in swollen polymers in the presence of temperature and swelling gradients. The results of these proposed studies will be helpful in designing commercial-scale units from laboratory-scale test data. Theoretical development in pervaporation modeling has progressed to the stage that only single-component solubility and diffusivity data are required for the prediction of multicomponent pervaporation results. These single component data are determined by vapor sorption or single component permeation experiments. However, these models still involve several parameters, related to the concentration-dependent diffusivity or sorption equilibrium at the fluid/membrane interfaces which have to be determined by fitting the model to single component sorption or permeation data. In this matter, uncertainty in diffusion and solubility parameters are unavoidable. For instance, different sets of parameters can fit a given set of experimental data equally well.[146, 171] Also it is difficult to provide physical interpretation of the fitted parameters. Therefore, a completely predictive model, in which all model parameters are calculated from pure component thermophysical properties, without any knowledge of permeation or sorption data would be very useful. Mass transfer resistance on the permeate side of the membrane may play an important role when leakage of air into a module because of imperfect sealing is appreciable. This topic has yet to receive attention of the researchers.

Lastly, process and module developments will critically determine rapid commercialization of pervaporation processes. Optimization of process and module designs will reduce both capital and operating costs. Hybrids designs of pervaporation with conventional separation technologies will also accelerate commercialization of pervaporation processes.

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