Pervaporation

Theory, Practice, and Applications
in the Chemical and Allied Industries

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8.1 INTRODUCTION

The contributions of separation to human society cannot be underestimated. Majority of chemicals that are an essential part of our life are synthetics manufactured by different techniques. These range from foods, pharmaceuticals, and colorful dyes for our clothes to detergents for washing and cleaning. It is an established fact that much of these activities involved in the manufacture of the synthetics are causing damage to the delicate balance in the ecosystem. Developments in green technologies are not just academic curiosities but are increasingly finding commercial applications. Widespread use of natural resources has led to depletion of nonrenewable energy sources. There is an ever-increasing awareness about optimum utilization of the nonrenewable sources (NRS). One major cause of consumption of the NRS in the chemical process industries (CPI) is the use of fossil fuels as the source of heat in various processes. Separation processes are an integral part of the CPI. Among the various separation processes used in the CPI, the major consumer of fuels is distillation. It is impossible to build a chemical plant without using distillation at some point in the process. Even isolation of natural products such as essential oils, spices, and phytochemicals cannot be accomplished without distillation. Distillation as commonly employed uses a high-grade heat in the reboiler and rejects the same as very low-grade heat in the condenser. With the awareness about efficient utilization of these fuels, the CPI is looking at alternatives to this highly energy-intensive operation. Thus, membrane separations that either do not involve a phase change or use low-grade heat for the phase change are becoming increasingly important alternative to distillation. Several newer, promising approaches have been made in the recent past. Membrane-based separation techniques include microfiltration (MF), ultrafiltration, nanofiltration, reverse osmosis (RO), pervaporation (PV), and vapor permeation (VP). PV based on differential permeation through a dense membrane followed by evaporation is the subject of this chapter.

P.A. Kobar first used the term pervaporation in 1917 to denote a phenomenon observed in laboratory. In the course of some experiments on dialysis, his assistant, C.W. Eberlein, pointed out the fact that a liquid in a collodion bag suspended in air evaporated, although the bag was tightly closed. These investigators alluded it to evaporation through a small aperture at the top of the bag. Further experiments and especially the rate of evaporation soon led them to the conclusion that the loss occurred through the membrane. This phenomenon was termed pervaporation (PV) by Kobar in an article published in the Journal of American Chemical Society in 1917. In 1952, Schwob in his doctoral thesis employed the PV process for dehydration of alcohol using a regenerated cellulose (RC) film. Between 1958 and 1962, Binning et al. carried out a series of investigations using hydrophobic membranes such as polyethylene for the separation of hydrocarbon mixtures. Meanwhile, Neel et al. had also started systematic PV studies. Simultaneously, Tusel and Ballweg were working on dehydration using PV. Besides these studies, investigations by Sander and Soukup and Asada on pervaporative dehydration established PV as a safe, energy-efficient process for the separation of homogeneous liquid mixtures.

PV as a separation process has potential applications in almost all categories. These include (1) industrially important dehydration applications such as dehydration of alcohols, ketones, chlorinated hydrocarbons, and other organics, (2) removal of organics from water, and (3) separation of organic–organic mixtures. Although the first category has seen widespread application, the other two have not been as commercially successful. Currently, PV is best identified with dehydration of ethanol, isopropyl alcohol, and ethylene glycol. Due to its favorable economics, efficiency, and simplicity, PV can be easily integrated with distillation. In the mid-1970s, GFT first commercialized an economical process for producing anhydrous ethanol at high purities that rival azeotropic distillation. Subsequently, continuing into the early 1980s, other integrated distillation/PV plants were built in Europe and Asia. Currently, a number of commercial PV plants exist for recovery of solvents, removal of organics from wastewaters, dealcoholization of wines and liquors, and many more for ethanol dehydration. A 150,000 L/day ethanol dehydration plant in Betheniville, France, was started in early 1988 and became the world’s largest PV facility. The groups of Mulder, Wessling, Rautenbach, Huang, Cabasso, and Pangarkar have carried out considerable work at respective universities.

PV has the following advantages:

1. Much lower capital and operating cost. The separation could be made more economical by combining distillation and PV processes. Thus, a part of the total separation employs distillation where it is economical. PV replaces the subsequent separation where distillation becomes expensive. The overall operating cost of such a hybrid process is much lower than that of distillation alone.
2. Azeotropes can be readily broken by using an appropriate membrane.
3. No additive is needed.
4. Easy operation and space saving.
5. Reduced energy demand; low-grade heat replaces high-grade heat, and a vacuum pump is required in the initial stages.
6. Freedom from environmental pollution caused by the entrainers.
7. Possibility of multipurpose application and easy scale-up.
8. Membrane properties can be varied and adjusted to suit different applications.
9. Closed-loop operations with only a small volume of recycled permeate.

Selective separation of liquids by PV is a result of selective sorption and diffusion of a component through the membrane. PV process differs from other membrane processes in the fact that there is a phase change of the permeating molecules on the downstream face of the membrane. PV mechanism has been described by Binning et al.\textsuperscript{3} using the solution diffusion mechanism. According to this model, selective sorption of the component of a liquid mixture takes place at the upstream face of the membrane followed by diffusion through the membrane and desorption on the permeate side.

Based on the aforementioned mechanism PV can be divided into three distinct steps:

1. Sorption: At the membrane–liquid interface, the membrane sorbs the components according to their relative affinity.
2. Diffusion: The sorbed components diffuse across the membrane under a chemical potential gradient.
3. Evaporation: Permeating species are evaporated at the downstream surface of the film.

Selectivity and productivity depend on sorption and diffusion. Sorption is dictated by thermodynamic properties, namely, the solubility parameter of the solute(s)/membrane system. On the other hand, the size, shape, and availability of the inter-/intramolecular free space of the polymer largely govern the diffusion coefficient. For an ideal membrane, both the sorption and diffusion processes should favor the chosen solute. The overall selectivity decreases if one step becomes unfavorable for a given solute.\textsuperscript{28}

Desorption on the downstream side of the membrane is generally considered to be rapid and nonselective. The high gas phase diffusivities at this step offers the least resistance in the overall transport process. As a separation process, PV relies on the difference in membrane permeabilities, which are dependent on the thermodynamics activities of the components to be separated.

This chapter deals with the following:

1. Basic aspects of PV and related theory to familiarize the reader with the selection of the membrane material for a given application.
2. Membrane modules used industrially and their specific areas of applications.

A comprehensive survey of the literature on PV for all the three categories is finally presented in order to update the reader with the latest developments in this field.

8.2 TRANSPORT THROUGH MEMBRANES

The mode of transport through a membrane may be passive, active, or facilitated. In passive transport, the membrane acts as a barrier, and permeation of the components is determined by their diffusivity and concentration gradient in the membrane. In facilitated transport along with the chemical potential gradient, mass transport is coupled to specific carrier components in the membrane. In active transport, driving force for transport is achieved by a chemical reaction in the membrane phase.

8.2.1 TRANSPORT IN PERVERAPORATION

In PV, the transport of the solutes occurs under a chemical potential gradient. This gradient is maintained by applying a vacuum at the downstream face of the membrane in the classical PV mode. This vacuum creates an activity gradient across the membrane. Alternatively, an inert sweep gas on the downstream face of the membrane can also be used to create an activity gradient. The transport process is purely physical since no chemical reaction with either a carrier or membrane material occurs. The permeate is condensed using suitable heat exchange system. When a sweep gas is used to create the driving force, the presence of noncondensable components requires much lower temperatures due to the relatively low dew point of the mixture. This fact must be considered while designing the condenser and coolant circuit as well calculating the operating cost. Overall, the vacuum mode is more popular since no extra cost associated with the sweep gas and its recirculation is involved. Different models have described passive transport through the membrane in PV. Mulder\textsuperscript{29} has discussed this subject in details. The following discussion is therefore limited to only two models:

8.2.1.1 Preferential Sorption–Capillary Flow Model

This model was proposed by Sourirajan and Shiyao.\textsuperscript{30} It depicts the membrane as a porous barrier. The model is based on a combination of preferential sorption of the rapidly permeating solute followed by flow through the capillaries and finally evaporation at the downstream face of the membrane. The extent of separation is governed by the effective molecular sizes of the permeants, the pore size, and its distribution besides the interactions between the membrane polymer and the solutes, which result in preferential sorption. According to the preferential sorption–capillary flow (PSCF) model, flow through the cylindrical pores of the membranes is rate determining. Liquid–vapor transition occurs at the pore outlet in the downstream side, and phase equilibrium between liquid and vapor is established. A straight cylindrical pore is assumed at the surface layer of the membrane, and cylindrical coordinates $(r, z)$ are set in the pore. Diffusion forces...
working on components A and B (permeants), the viscous force, and the pressure force are those that have to be balanced at the steady state of the liquid movement in the pore leading to the following equation:

$$\frac{\delta^2 U}{\delta r^2} + \frac{1}{r} \frac{\delta U}{\delta r} + \frac{1}{\eta} \frac{\partial (p_2 - p_1)}{\partial r} = 0 \quad (8.1)$$

To obtain concentration of A in the permeate, diffusive force is considered to work only on A, friction force between A and B and A and pore wall. This leads to the following differential equation:

$$-RT \frac{d \ln a_A(r,z)}{dr} = r,$$

$$- (c_{AB} + c_{AM}) U(r) C_A(r,z) / C_A(r,z) + \xi_{AB} U(r) C_{AB}(r,z) / C_{AB}(r,z) = 0 \quad (8.2)$$

Equations 8.1 and 8.2 can be solved with appropriate boundary conditions and interfacial interaction force constants, generated from liquid chromatography experiments.

8.2.1.1 Limitations of This Model
The pore flow mechanism has a number of limitations. The assumption of so-called cylindrical pores in PV membranes and effect of their size and distribution in the membrane on separation performance of the membrane is not always tenable. The concept of pore size and distribution in PV membrane is not likely to be important inasmuch as membranes made by ordinary solution casting/solvent evaporation process have been found to yield reproducible performance. According to the PSCF model, differences in pore size and distribution would significantly affect the membrane performance. Similarly, PSCF model cannot explain the simple inverse relation of flux and membrane thickness, membrane swelling, and trade-off relationship between flux and selectivity. According to this model, asymmetric membrane made by phase inversion technique would be the most ideal PV membrane. However, this membrane has been found to give better performance than the prevailing PV membranes made by ordinary solution casting method.39

8.2.2 Solution Diffusion Model
Solution diffusion model is the most widely used to describe permeation in dense membranes, as is the case for PV.38,39 It consists of three distinct steps outlined in Section 8.1: sorption, diffusion, and desorption/evaporation.

The first two steps, that is, sorption and diffusion, are dominant contributors to separation of the mixture by PV. Desorption of the permeant vapor in the permeate side under low vacuum is very fast and unlike pore flow mechanism does not offer significant resistance to the transport of the solute.

8.2.2 Sorption in the Membrane
8.2.2.1 Sorption Selectivity and Membrane Polymer
Relative sorption of the permeants in the membrane depends on the interactions between the solutes and the membrane polymer. Solubility or miscibility of a component with the membrane polymer depends on their relative solubility parameter values. For good mutual solubility of two components, their free energy of mixing $\Delta G_m$ should be negative.

$\Delta G_m$ is defined as

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (8.3)$$

Enthalpy of mixing, $\Delta H_m$, has been related to the solubility parameter ($\delta$) by

$$\Delta H_m = n_1 n_2 V \left[ (\delta_1 - \delta_2)^2 \right] \quad (8.4)$$

Equation 8.3 is based on the Scatchard–Hildebrand Regular solution theory that considers interaction due only to dispersion forces. This was extended to include hydrogen bonding and polar forces through a 3D solubility parameter by Hansen.38 In this form, Equation 8.3 becomes

$$\Delta H_m = n_1 n_2 V \left[ (\Delta \delta_1)^2 + (\Delta \delta_2)^2 + (\Delta \delta_3)^2 \right] \quad (8.5)$$

From Equations 8.3 and 8.4, it is clear that $\Delta G_m$ is negative when the difference between $\delta_1$ (solvent) and $\delta_2$ (polymer), that is, $\Delta \delta$, for all the three forces of interactions is vanishingly small. It implies that the membrane polymer and the desired component to be separated should have similar properties.

Thus, $\delta_{1s} \approx \delta_{1p}$. This results in preferential sorption of solute S in polymer P. The extent of sorption can also be evaluated in terms of activity of solvent in membrane using Flory–Huggins technique or UNIFAC method.34–37 The mutual interaction of solvent in feed and membrane is obtained in terms of interaction parameter, $\chi$, using Flory–Huggins thermodynamics.36 For polar–polar solvents, clustering of solvents takes place in membrane, and hence, Flory–Huggins theory cannot be applied for determining interaction parameter. For these polar solvents, engaged species-induced clustering (ENSIC) model is used to estimate solvent–solvent and solvent–membrane interaction parameter.38,39

8.2.2.2 Sorption and Nature of Membrane Polymer
8.2.2.2.1 Ideal Case
If sorption process is ideal, the concentration of a component \(i\), \(C_{mi}\), in the membrane is linearly proportional to the concentration of this component in the feed mixture, \(C_{bi}\).

From Henry’s law for dilute solutions,

$$C_{mi} = k C_{bi} \quad (8.6)$$

“k” denotes the sorption coefficient for the solute in the polymer. This relationship holds good for sorption of a component from dilute solutions and when specific interactions between
the solute and polymer are absent. However, in most of the cases, membrane phase concentration of a component is not a linear function of its bulk concentration. Further, it is also influenced by the presence of the other components.

8.2.2.2 Sorption Isotherms

Rogers\cite{40} described four different types of sorption isotherms. For very dilute solutions (type I), Henry’s law holds (Equation 8.6).

For polymeric membranes filled with absorptive fillers, sorption in the filler is governed by Langmuir adsorption isotherm while for the polymer matrix Henry’s law holds. This sorption isotherm is designated as type-II isotherm or dual mode sorption. This is a combination of Henry’s type (bulk polymer) and Langmuir type (filler/microvoids).

For polymers with high degree of crystallinity, stiff and inflexible chains, and strong cohesive force, type-III sorption isotherm is observed. In this case, solute–solute interactions are stronger than solute–polymer interactions resulting in clustering of solute molecules.

One form of type-IV sorption isotherm is a combination of type-II sorption at low concentration and type-III sorption at high concentrations.

Netke et al.\cite{41} have studied the permeation of acetic acid–water mixtures in silicalite-filled PDMS. Total solute concentration in the polymer in type-II isotherm is

$$C_T = C_M + C_Z$$  \hspace{1cm} (8.7)

$C_M$ is given by

$$C_M = H_M C_b$$  \hspace{1cm} (8.8)

And $C_Z$ is given by

$$C_Z = \frac{C_Z^* k_Z C_M}{1 + k_Z C_M}$$  \hspace{1cm} (8.9)

Figure 8.1 shows the sorption isotherm of Netke et al.\cite{41} for acetic acid–water–PDMS containing 20% silicalite SA-5 (UOP). Evidently, this system belongs to type II.

8.2.2.2.3 Sorption of Single Component in Amorphous Polymers

Sorption of a pure component $i$ in an amorphous polymer can be described by the Flory–Huggins\cite{42} equation:

$$\Delta \mu = RT \ln(1 - \Phi_p) + \Phi_p \left( 1 - \frac{1}{n_i} \right) + \chi_{ip} \Phi_p^2 = 0$$  \hspace{1cm} (8.10)

where

- $n_i$ is the ratio of molar volume of polymer to solute $i$.
- $\Phi_p$ is the volume fraction of the polymer.

The membrane phase concentration of $i$, that is $1 - \Phi_p$, may be calculated from this equation provided interaction parameter $\chi_{ip}$ is known.

8.2.2.2.4 Sorption of Binary Liquid in Amorphous Polymer

For the simplest case, interaction parameters are concentration independent\cite{43}:

$$\ln \left( \frac{\Phi_1}{\Phi_2} \right) - \ln \left( \frac{V_1}{V_2} \right) = \left( 1 - \frac{1}{n_1} \right) \ln \left( \frac{\Phi_1}{V_1} \right)$$

$$- \chi_{12} [V_1 - V_2 + (\Phi_2 + \Phi_1)] - \Phi_3 (\chi_{13} - \chi_{23})$$  \hspace{1cm} (8.11)

8.2.2.2.5 Sorption of Pure Component in Cross-Linked Polymer

Cross-links retard swelling and thus decrease concentration of the permeants in the polymer matrix. Effect of cross-linking on the sorption of low-molecular-weight...
components in polymers can be obtained by Flory–Huggins thermodynamics:

\[
\ln(1 - \Phi_p) + \Phi_p \left(1 - \frac{1}{n_i}\right) + \chi \phi_p^2 + \frac{V \rho_p}{M_c} \left(\phi_p^{1/3} - \frac{\Phi_p}{2}\right) = 0
\]

(8.12)

where

- \(M_c\) is the molecular weight between two cross-links
- \(\rho_p\) is the polymer density

### 8.2.2.2.6 Sorption of Pure Liquid in Semicrystalline Polymer

The crystallites are impermeable to penetrants leading to a hindered diffusion (tortuosity effect). For a semicrystalline polymer, sorption of pure liquid is given by:

\[
\ln(1 - \Phi_p) + \Phi_p \left(1 - \frac{1}{n_i}\right) + \chi \phi_p^2 + \frac{V \rho_p}{M_c} \left(\Delta H_i / R \left(1 / T - 1 / T_m\right) - (3/2)\chi \phi_p^2\right) = 0
\]

(8.13)

A low value of \(\chi\) indicates greater affinity between the solute and the polymer. It is relatively easy to estimate single-component \(\chi\) from sorption experiments with pure solvent. For a binary mixture, similar sorption data yield the values of \(\chi\). These can be used to ascertain the relative sorption of the two components by a given polymer.

### 8.2.3 DIFFUSION

Diffusion is also important in determining the separation characteristics of a membrane. The component with higher diffusivity diffuses faster and thereby gets enriched in the permeate. The diffusion coefficient of a permeant through a polymer is a strong function of its size and shape. In a homologous series, molecules with lower molecular weight move faster. When molecular weight and chemical nature are the same, molecules with smaller cross section diffuse faster. However, sorption has a strong bearing on diffusion. High sorption always results in higher rates of diffusion as explained in the following:

1. An increase in concentration of the permeant in the polymer causes (1) polymer swelling and (2) promotes the free rotation of the polymer segments about the chain axis and (3) lower activation barrier for diffusion.
2. In PV, the amorphous region alone is responsible for sorption/permeation. Sorption causes increase in free volume and facilitates diffusion.
3. At high sorbed concentrations, a major part of the polymer matrix contains permeants in liquid state. Diffusion of the incoming permeant through this liquid zone of the solid polymer is faster than through the dry solid polymer.

#### 8.2.3.1 Single-Component Diffusion

The diffusion coefficient is a strong function of concentration. Long expressed it as an exponential function of concentration:

\[
D_i = D_{i0} e^{A_i C_i}
\]

(8.14)

where \(A_i\) is the plasticization coefficient accounting for interaction of the permeant, \(i\), and polymer. It represents the magnitude of the effect of solute concentration on its mobility in the membrane.

Greenlaw et al. proposed another relationship between diffusivity and concentration:

\[
D_i = D_{i0} \left(1 + A_i C_i^n\right)
\]

A simplified form of Equation 8.15

\[
D_i = k C_i
\]

(8.16)

fitted the data of Rogers et al. up to a vapor phase activity of 0.5 for diffusion of hexane in polyethylene membranes. Rautenbach and Albrecht suggested a modified form of Greenlaw and coworker’s equation with \(n\) equal to unity:

\[
D_i = D_{i0} \left(1 + A_i C_i\right)
\]

(8.17)

#### 8.2.3.2 Multicomponent Diffusion

Diffusion in multicomponent system is difficult to analyze. Transport of one component is affected by the presence of the other component due to mutual interaction resulting in coupling of fluxes. Thus, single-component diffusion equation is not applicable in multicomponent system. Greenlaw et al. proposed a simple relationship in which the diffusion coefficients for components “i” and “j” are given by:

\[
D_i = k_{i0} (C_i + B_i C_j)
\]

\[
D_j = k_{j0} (C_j + B_j C_i)
\]

Shelden and Thompson used the following equations while modeling PV of toluene/ethanol mixture with polyethylene membrane and water/ethanol with both homogeneous and asymmetric PVA membranes:

\[
D_i = D_{i0} + k_{i0} (C_i + B_i C_j)^k
\]

\[
D_j = D_{j0} + k_{j0} (C_j + B_j C_i)^k
\]

Brun et al. described binary transport using an exponential diffusion model that is dependent on individual component concentrations:

\[
D_i = D_{i0} \exp(A_i C_i + A_j C_j)
\]

\[
D_j = D_{j0} \exp(A_j C_j + A_i C_i)
\]
A positive or negative value of $A_i$ or $A_j$ indicates a positive or negative effect of the presence of component, $i$, on the transport of component, $j$. Sferrazza et al.\textsuperscript{30} analyzed the behavior of binary systems using an approach similar to that of Brun et al.\textsuperscript{49} They used a similar model to describe diffusion:

\[
D_i = D_o \exp[(A_i (C_i + B_j C_j))] \quad (8.24)
\]
\[
D_j = D_o \exp[(A_i (C_i + B_j C_j))] \quad (8.25)
\]

Magnitudes of the interaction coefficients give an indication of the extent of coupling in diffusion.

### 8.2.4 Transport Equation Through Membranes

Solute permeation through the membrane can be described by Fick's first law:

\[
J_i = -D_i \frac{dC_i}{dx} \quad (8.26)
\]

As mentioned earlier, the diffusion coefficient is a function of membrane phase concentration of the permeants. Hence, the aforementioned equation yields

\[
J_i = -D_{in}/f(C_i) \frac{dC_i}{dx} \quad (8.27)
\]

Here, $D_{in}$ is the diffusion coefficient of “$i$” at infinite dilution. Integrating over the membrane thickness $L$ leads to

\[
J_L = -D_{in} \int_{C_{ni}}^{C_{pi}} f(C_i) C_i dC_i \quad (8.28)
\]

For dilute solutions, $f(C_i)$ is given by Henry’s law (Equation 8.26). For higher concentration of “$i$”, $C_{ni}$ can be obtained from experimental sorption data. Membrane phase concentration on the permeate side of “$i$,” that is $C_{pi}$, may be neglected since the low downstream pressure ensures low activity of the component. Using relevant $f(C_i)$ models discussed earlier, Equation 8.28 can be integrated to yield $J_i/J_j$ and $D_i/D_j$.

### 8.2.5 Concentration Polarization and Permeation

In an ideal case, in the absence of any concentration polarization (CP), the concentration of the permeants should not change from bulk-feed phase to the membrane–feed interface. However, due to finite mass transfer effects, there could be a decrease in concentration of the permeants over the diffusion film. In the case of ultrafiltration, microfiltration, or reverse osmosis, the retained solute on the membrane surface may cake out (when its concentration exceeds its solubility product) adding to the overall resistance. Further, with increasing accumulation, a diffusive backflow from membrane phase to bulk liquid develops. These phenomena result in a decrease in flux with time. In the case of PV, CP is not a serious factor due to the relatively low diffusion coefficients in the dense membrane phase. Further, unlike UF, RO, or MF, none of the permeants are retained on the membrane surface since all are capable of permeating across the membrane. However, CP becomes significant, when the membrane is very thin and highly selective to one of the permeants present in very low concentration (e.g., removal of traces of volatile organic compound [VOC] from aqueous solutions). In this event, the permeation rate through the membrane can greatly exceed the rate of mass transfer across the diffusion film resulting in CP for the specific permeant. A commercially important example is that of dehydration of compressed natural gas. The membranes used are highly hydrophilic and afford relatively high water permeation rates as compared to the rate of mass transfer.\textsuperscript{51} In industrial application, a thin PV membrane on a porous UF support is generally employed. Diffusion across the boundary layer and permeation are steps in series. The overall mass transfer coefficient is given by the following:\textsuperscript{29,52}

\[
\frac{1}{K_{ov}} = \frac{1}{k_L} \frac{L}{DS} \quad (8.29)
\]

The product $DS$ is the intrinsic permeability obtained from experimentally determined values of $D$ and $S$ or through experiments at very high levels of turbulence such that the boundary layer resistance is eliminated ($k_L \gg DS/L$) and $K_{ov} = L/DS$. A number of correlations are available in the literature for reliable estimates of $k_L$ for various module geometries.\textsuperscript{29,52}

Proper hydraulic management on the feed side generally eliminates CP. However, for very dilute solutions where the driving force for the fluid–membrane mass transfer process is relatively very low, CP cannot be avoided. In addition to CP, temperature polarization (TP) may also affect the overall flux. This is due to the fact that the enthalpy of vaporization of the solute in the permeate compartment is supplied by the hot feed. The hot fluid transfers sensible heat to the membrane (by convection) which in turn supplies it by conduction to the permeate side of the membrane. This is also a case of resistances in series, and an equation similar to (8.29) can be written. When the supply of sensible heat from the bulk feed to the membrane is much less as compared to the heat required to vaporize the solute in the permeate compartment, TP develops. Thus, there is a drop in temperature from the bulk feed to the membrane surface. Mulder\textsuperscript{29} has given detailed description of both CP and TP and methods of tackling them. In particular, the loss of sensible heat by the feed stream must be compensated. This is generally achieved by employing interstage heat exchangers.
In the PV mode, the feed side is in contact with a liquid, which tends to sorb in the polymer and swell it. At the permeate side face of the membrane, the solutes are vaporized. Thus, the membrane exhibits different structures from the feed to the permeate side. The former is wet and swollen and hence yields high diffusion rates. The downstream part being relatively dry affords much lower diffusion coefficients than the swollen feed side. Therefore, the assumption of a constant diffusion coefficient across the membrane in Equation 8.28 may not be tenable.

8.2.6 Selectivity in Pervaporation

The overall selectivity in PV $\alpha_s$ is a combination of (1) sorption and (2) diffusion selectivities. Sorption selectivity $\alpha_s$ is defined as the ratio of the sorption coefficient of solutes A and B in a binary mixture:

$$\alpha_s = \frac{S_A}{S_B} \quad (8.30)$$

Diffusion selectivity, $\alpha_D$, is similarly defined as follows:

$$\alpha_D = \frac{D_A}{D_B} \quad (8.31)$$

The overall selectivity, $\alpha_o$, is given by

$$\alpha_o = \alpha_s \times \alpha_D \quad (8.32)$$

Another parameter used to define the efficacy of a membrane is the separation factor, $\beta$:

$$\beta = \frac{C_p}{C_i} \quad (8.33)$$

where $C_p$ and $C_i$ are the concentrations of the selectively permeating solute, i, in the permeate and feed, respectively. In general, for PV, $\alpha_o$ is the dominating contributor to $\alpha_o$, and most membranes are designed to achieve high values of $\alpha_o$. However, in some cases, although $\alpha_o$ is favorable, $\alpha_D$ is not and in such cases $\alpha_s$ is poor. The pervaporation separation index (PSI) indicates the overall productivity of PV membrane:

$$\text{PSI} = J_i \times \beta \quad (8.34)$$

8.3 Membrane Fabrication Methods and Membrane Modules

8.3.1 Introduction

The membrane is the heart of any membrane-based separation processes. Initial breakthrough in membrane technology came from the phase inversion technique developed by Loeb and Sourirajan. This technique became the first commercial RO membrane. A second breakthrough in membrane development occurred in the early 1970s. This was in the form of thin-film composite (TFC) membrane made by interfacial polymerization technique pioneered by Cadotte et al. This is now widely used for preparing defect-free membranes only a fraction of a micron in thickness from a variety of polymeric materials particularly for RO. The development of composite membranes, in 1980s by Bruschke, allowed the transformation of PV process from laboratory to industrial scale. GFT in Germany reported the first commercial use of membranes in PV. This section covers the various methods used for producing PV membranes and corresponding modules.

8.3.2 Ideal Membrane for Pervaporation

An ideal PV membrane consists of an ultrathin defect-free nonporous skin supported by a porous support. The selectivity of the membrane is derived from this skin layer. However, the porous support also plays an important role in the overall performance of the membrane as discussed later. Ideal PV membrane should possess the following characteristics:

1. The top layer/skin should be as thin as possible and without any defects.
2. It should exhibit high sorption and diffusion selectivities for the desired solute when contacted with a mixture containing it.
3. It should not excessively swell in order to retain its selectivity and structural integrity.
4. It should possess good mechanical strength besides chemical and thermal stability.
5. It should offer high fluxes without compromising selectivity.

Productivity of a PV membrane can be described by the PSI defined by Equation 8.34. A higher value of PSI indicates superior overall productivity.

In view of the various advantages of PV, there is considerable research interest in developing suitable membranes for different applications. The efforts in this direction are not limited to the academic sector. Some major industrial contributors are Sulzer ChemTech; Membrane Technology and Research (MTR), United States; Mitsui Engineering; Ube (Japan); Rhone Poulenc; Dow Corning; Memprio; Atochem; Kodak; Exxon; General Electric; Fluorofilm; etc. Different factors that have a major impact on membrane morphology are listed as follows:

1. Choice of polymer
2. Viscosity of casting solution
3. Curing temperature
4. Glass transition temperature ($T_g$) of the polymer

Among these, the choice of the polymer is the most important since it decides the sorption selectivity for the solute...
of interest. The techniques for preparing PV membranes can be broadly classified into three types:

1. Phase inversion
2. Coating of the permselective polymer skin on a UF support
3. Other types

The phase inversion technique is not very popular for making PV membranes. On the other hand, UF membranes prepared by the phase inversion technique are invariably used as the porous support to prepare composite PV membrane by the solution coating process. This is the most widely used process for producing PV membranes. The major advantage of composite membrane is that a very thin layer of the permselective polymer can be coated on the UF support. However, the two polymers should form strong bond to prevent peeling of the skin layer from the support membrane. Different methods of preparing permselective coating are discussed briefly in the following.

### 8.3.3 SYNTHESIS OF MEMBRANE TOP LAYER

These are usually prepared by casting from polymer solution followed by solvent evaporation. It results in formation of a dense membrane. Membrane may be (1) homogeneous, (2) blend, (3) mixed matrix, (4) polyelectrolyte, or (5) polymer–ceramic composite depending on the type of polymer and other additives used for making the membrane.

#### 8.3.3.1 Homogeneous Membrane

These membranes are prepared by solution casting of homo or copolymers. Polyvinyl alcohol (PVA), cellulose acetate (CA), sodium carboxymethyl cellulose (CMC), sodium alginate, polyacrylonitrile (PAN), chitosan, polysulfone, polyether sulfone, copolymers such as those of acrylonitrile (AN) with acrylic acid, hydroxyethyl methacrylate (HEMA), etc., yield hydrophilic skins. Polydimethyl siloxane (PDMS), NR, styrene-butadiene rubber (SBR), polyurethane (PU), ethylene propylene diene monomer (EPDM) rubber, etc., are some of the polymers used for obtaining organophilic skins. The copolymers are made from their respective monomers by free radical or condensation polymerization reaction using suitable initiator (for free radical) or catalyst (for condensation polymerization). These homogeneous dense skin membranes should be defect-free as seen in scanning electron microscopy (SEM). Other characteristics of the permselective polymer are determined by standard techniques like Fourier transform infrared spectroscopy (FTIR), for functional groups, x-ray diffraction (XRD) (for crystalline/amorphous nature, i.e., for PVA, CA), differential scanning calorimetry (DSC) or differential thermal analysis (DTA) (for glass transition and softening temperature), TGA (for thermal decomposition), and UV–visible spectroscopy for absorption spectra of certain polymers like PVA, CMC, and PAN.

#### 8.3.3.2 Blend Membrane

These are prepared by blending some of the aforementioned polymers. Membranes made from blend of different polymers are more versatile since properties of the constituent polymers can be varied by varying the proportion of the constituents. Because of strong polymer–polymer interaction, such blends can be tailored to meet specific selectivity requirements. However, permeability of a blend membrane depends on the degree of molecular interaction between the constituent polymer. Membranes made from thermodynamically incompatible polymers exhibit poor interfacial adhesion properties and unstable phase morphology. Such incompatibilities result in inferior selectivity. To reduce phase separation in incompatible blends, either physical or chemical compatibilizers are used. Thermodynamic compatibility is excellent when the constituent polymers have similar solubility parameter values. Solution blending of two or more polymers is an efficient method when a common solvent is available. Interpenetrating network (IPN) polymers are a blend characterized by strong physical and chemical interaction that results in mutual interpenetration of the constituent polymers and their cross-linking. If one of the polymers of an IPN is cross-linked, it is called semi-IPN. In a full IPN, both polymers are cross-linked. Blend membranes exhibit heterogeneous morphology, containing continuous and dispersed phase depending on blend composition. As the blend compatibility decrease, the morphology becomes coarser. In high-quality blends, absorption bands of constituent polymers are also shifted in FTIR and UV–visible spectroscopy. Similarly, Tg and Tm also display overlap. These features suggest that blends can be characterized by methods similar to those for homogeneous membrane.

#### 8.3.3.3 Mixed Matrix Membrane

There is a trade-off of permeability and selectivity for most of the polymer membranes made from homopolymers, copolymers, or polymer blends. Permeability increases at the cost of selectivity. This permeability–selectivity trade-off is eliminated in most of the mixed matrix membranes (MMMs). MMMs are made by incorporation of adsorptive filler into a continuous polymer matrix. These filled membranes maintain high selectivity due to combined effects of molecular sieving action, selective adsorption, and difference in diffusion rates. In MMM, the fillers not only display high sorption of the desired component but also provide superior mechanical properties due to polymer–filler reinforcement. MMM, also called organic–inorganic hybrid membrane, consists of two phases: filler as the dispersed phase and the polymer as the continuous phase. Any homopolymer, copolymer, IPN, or blend polymers may be used as polymer part, and there are various micro-/nanosize inorganic/organic fillers such as zeolites, nonporous silica, titanium dioxide, activated carbon, carbon molecular sieve, phosphomolybdic heteropolyacid, and graphite. For preparing MMM, the filler is dispersed in the polymer solution and then mixed mechanically. To prevent agglomeration of filler, sonication is also required for certain fillers. The filler can also be mixed with monomer solution prior to polymerization.

#### 8.3.3.4 Polyelectrolyte Complex Membrane

Polyelectrolytes are polymer-containing cationic or anionic functional groups. Cationic class includes polyacrylic acid
and its copolymers, sodium CMC, sodium alginate, polyvinyl sulfate, and cellulose sulfate. Typical anionic polyelectrolytes are polyvinylamine, chitosan, polyethyleneimine, polyvinyl pyridine (2 and 4 vinyl), etc. Polyelectrolyte complex membrane (PECM) is prepared by combining two oppositely charged polyelectrolytes. However, homogeneous casting solution cannot be prepared by mixing two polyelectrolyte solutions of opposite charges. Because of strong ionic complexation reaction, mixing of polyelectrolyte solutions results in precipitation of polyelectrolyte complexes. PECM is formed by electrostatic interaction of oppositely charged polyelectrolytes in bulk or at interface. Thus, PECM is prepared in interface or bulk by three methods, that is, (1) interfacial complexation, (2) acid mixing, and (3) solution processable method. Interfacial complexation is carried out by two-ply casting or layer-by-layer assembly method. In two-ply casting, solution of one polyelectrolyte is first cast on to the plate or supporting membrane and dried for certain time. Another oppositely charged polyelectrolyte solution is cast on this dried membrane (first ply), and this second ply is then dried. Bonding of the two layers occurs by ionic complexation at the interface. For layer-by-layer assembly, low concentration polyelectrolyte dipping solution is used. In acid mixing method, the degree of ionic complexation is reduced by adding acid like dilute hydrochloric acid to a week anionic polyelectrolyte like polyacrylic acid, sodium alginate, or CMC. The ionization of these week polyelectrolyte is further reduced by the presence of the acid due to common ion effect. It is then mixed with cationic polyelectrolyte like chitosan solution to produce a homogeneous casting solution that allows facile casting. In this case, the precipitate of polyelectrolyte complex is not formed because of weak ionic complexation reaction. Solution processable poly electrolyte complex (PEC) method is similar to acid mixing method, but it produces processable precipitate of PECs instead of homogeneous casting solution, and this solid PECs can be easily dispersed in sodium hydroxide solution since the protected carboxylic functional groups are converted to its sodium salt. PECMs prepared by the aforementioned three methods are stable and highly hydrophilic and show limited swelling in aqueous solution. Thus, PECMs are very effective for perivaporative dehydration.

8.3.3.5 Polymer–Ceramic Composite Membranes

Inorganic membranes can tolerate harsh conditions like high temperature, low or high pH, or concentrated corrosive chemicals. However, most of the inorganic membranes show poor selectivity. On the other hand, polymer membrane shows high selectivity but poor tolerance to harsh conditions. In a polymer–ceramic composite membrane, high selectivity of polymer is combined with high mechanical strength and chemical resistance of relevant ceramic material. Polymer–ceramic composite membrane is prepared by (1) asymmetric incorporation of ceramic powder material in polymer membrane, (2) coating of polymer membrane on porous ceramic membrane, and (3) chemical grafting of polymer material on ceramic support. The synthesis of membrane by incorporation of ceramic particles in polymer matrix is similar to MMM. The coating of polymer on ceramic support membrane may be achieved by solution casting, coating, or dip coating followed by cross-linking, for example, dip coating of ceramic support in a solution of PDMS and its cross-linker tetraethyl orthosilicate in n-heptane followed by cross-linking. Ceramic-supported polymer (CSP) membrane is prepared by graft copolymerization of a monomer on ceramic porous support. Ceramic support like γ alumina is first chemically modified to generate vinyl silane on its surface. Surface silylation is carried out by treating the inorganic membrane with vinyl trimethoxy silane solution. This alumina silyl bond is then subjected to graft polymerization with monomer like vinyl acetate or its comonomers. By graft copolymerization, the monomer polymerizes, and polymer chain is terminally anchored (grafted) on the ceramic support, for example, grafting of vinyl acetate or poly(vinyl acetate-co-vinyl pyrrolidone) on alumina ceramic support. Since this polymer is not cross-linked, it shows greater mobility than polymer–ceramic membrane produced by coating and cross-linking. In spite of mobility, this polymer is stable even in solvents in which its native polymer is completely soluble. This stability is afforded by grafting of the polymer with ceramic support.

8.3.4 Fabrication of Membrane for Industrial Applications

For laboratory research, various types of membranes mentioned earlier are used without any support in PV cells. For large-scale applications, where the membrane sizes are larger, the reinforcement of this top skin layer by an appropriate support is required to maintain dimensional stability. These types of membranes consisting of a skin layer (permselective layer) supported by a suitable support are called composite membranes. Ceramic-supported membranes already have a support, and hence, no additional support is required.

8.3.4.1 Importance of the Support Layer

The support beneath the skin has a strong influence on the performance of the permselective skin layer. Heinzelmann has given the consequences of the various types of support defects leading to change in permeation properties of the composite membranes. Trifunovic and Tragardh studied the role of the support layer of a composite membrane in PV. Although mass transport of permeates through the active, dense layer is the rate-determining step, the support layer can also be a contributor to the overall mass transport resistance, especially in the case of components that can condense/vaporize due to small variations in the pressure. The support layer used for PV membranes is usually an asymmetric UF membrane made from PAN, polysulfone, polyethersulfone, etc., by phase inversion method with molecular weight cutoff of 15–20 K. There is a variation in the pore diameter across the thickness of such an asymmetric membrane. Next to the dense layer, the pore diameter in the support is relatively very small. The pores widen as the solute diffuses across the support. At the permeate side face,
the support has the largest pores. The support thickness and pore morphology should be such that excessive pressure drop is avoided. A simple model for the porous support is that of a bundle of straight cylindrical capillaries. The type of flow in a pore depends upon the relative size of the pore and the mean free path of the molecules involved. When the mean free path is much smaller than the pore diameter, viscous flow prevails. In such a case, the support layer is not a serious impediment to mass transport. However, if the pores are smaller than the mean free path, Knudsen diffusion, which has a much lower rate, can cause significant reduction in the overall mass transport. In these pores, the local vapor pressure can exceed the critical condensation pressure causing capillary condensation. Rautenbach and Albrecht\textsuperscript{47} indicated that in such a case a part of the pore length contains the solute(s) in liquid form and the remaining part only contributes to the evaporation process. Thus, in case of capillary condensation, there is a reduction in membrane selectivity due to the decrease in the driving force for PV. The Kelvin equation can be used to predict the critical (partial) vapor pressure at which condensation occurs in the pore:

\[
P_v^C = P_v^0 \exp \left( -\frac{4\alpha P V_i}{d_{pore} RT} \right)
\]  

(8.35)

Trifunovic and Tragardh\textsuperscript{66} in their study of PV of homologous series alcohols and esters using poly(octyl methyl siloxane) (POMS) membranes with different supports derived the following general conclusions:

1. Larger molecules with lower Knudsen diffusion coefficients suffer higher loss in selectivity.
2. Solutes with low vapor pressures (easily condensable) suffer greater loss in selectivity due to pressure build-up in the Knudsen capillaries.
3. The internal capillary surface also affects the composite membrane performance. For alcohols with hydrophilic OH groups, it is desirable to have a hydrophobic capillary surface.
4. To avoid the detrimental effects mentioned earlier, the Knudsen capillaries should be as short as possible.

8.3.4.2 Techniques for Fabrication of Composite Membranes

The following methods can be adopted to prepare composite membranes used for PV.

8.3.4.2.1 Direct Coating

Heinzellmann\textsuperscript{65} and Briston\textsuperscript{66} have given details of these methods. The main problem with direct coating is that incompatibility of the porous support with polymer solution can result in formation of pinholes in the membranes. However, this problem can be overcome by ensuring sufficient wetting of the support by the polymer solution. Parameters that can be varied in optimizing the process for a defect-free membrane are

1. Pretreatment of the support prior to coating
2. Optimization of composition, viscosity, and surface tension of the polymer solution

Choice of appropriate coating method along with drying/curing conditions can yield a stable-defect-free membrane.

8.3.4.2.2 Interfacial Polymerization

Interfacial polymerization provides another method for depositing a thin layer upon a porous support.\textsuperscript{54,56} In this case, polymerization occurs between the two reactive monomers at the interface of the two immiscible solvents. Heat treatment is often applied to complete the interfacial polymerization. The advantage of this technique is that the reaction is inhibited by passage of a limited supply of reactants through the already formed polymer layer, resulting in an extremely thin film of thickness in the range of 1–2 nm. Such membranes are therefore referred to as TFCs. TFCs of various poly(amides) are very popular in RO applications.

8.3.4.2.3 Radiation-Induced Formation of Composite Membranes

1. Radiation-induced grafting
2. Radiation-cured composite membrane
3. Plasma chemical processes

Radiation-initiated grafting of polymer films, radiation-initiated curing of thin-film coating on porous supports, and coating of porous substrate by plasma polymerization are alternative methods for preparing nonporous flat-sheet PV membranes. Specific sorption capability for distinct solutes is achieved by introducing different functional groups onto the polymer backbone of supporting substrate.\textsuperscript{69–71} These groups are selected such that they exhibit specific interactions with the solute.

8.3.4.2.4 Transfer Coating

Details of transfer coating or lamination of permselective skin on a porous support are available in the literature.\textsuperscript{56,58} The advantage of this method is that a predefined skin layer thickness can be achieved. Secondly, the problem of insufficient wetting of support by coating solution/incompatibility of the support with solvent can be overcome.

8.3.5 Pervaporation Modules

PV modules have been basically adapted from the designs already used in other applications like RO, NF, and UF. The major difference, however, is that in the latter case, the applications involve predominantly aqueous solutions. Therefore, the glues, gaskets, etc., to be used do not require any special consideration except that they should yield a strong bonding. In the case of PV, one of the two sides of the module (feed/permeate) is in contact with an organic solvent.
This solvent may attack the glue/gasket used. Therefore, selection of the glue/gasket material needs special attention. In the case of dehydration of organics, the feed side is in contact with a predominantly organic medium, whereas for removal of trace organics from water, the permeate side has to bear the attack of the organic solvent. Finally, in the case of organic–organic separations, both the feed and permeate sides have to be suitably designed considering the presence of organics that may have high solvent power. Thus, besides the strength of the bond, solvent resistance of the glue is also important. In view of this, initially, the plate and frame module was much more popular than the spiral wound module.

Another consideration that is important in PV is the prevention of excessive pressure drop on the permeate side. Too high a pressure drop reduces the flux (also see Section 8.3.4.1). Therefore, to avoid excessive pressure drop, generally, the permeate side is kept open and in close proximity of the condenser/heat transfer surface.

The economic advantage of PV lies in the fact that particularly for the two extreme applications—dehydration of organics and removal of organics from water—the focus is on the trace quantity. In the case of dehydration of organics, a highly water selective membrane is used. On the other hand, for removal of organic from water, an organophilic membrane is used. In both these cases, the solute to be removed is a minor/trace quantity. With this approach, the duty of the module (total amount to be removed) is greatly reduced. However, since the solute is present in much smaller quantities in the feed side, CP can be a serious drawback. To overcome this, the design of the feed side needs some attention. The feed side should allow rapid mass transfer from bulk liquid to the membrane surface so as to achieve the intrinsic membrane flux. This is achieved by operating at sufficiently high Reynolds number on the feed side. This condition implies a higher power input because of high flow rates on the feed side.

A number of module designs are possible. These are based on the two types of membrane configuration: (1) flat sheet such as plate and frame and spiral wound and (2) tubular such as tubular, capillary, and hollow fiber.

8.3.6 SELECTION OF THE MEMBRANE MODULE

The choice and arrangement of the membrane module in a system is based on economic considerations with the correct engineering parameters being employed to achieve this. Some aspects to be considered are

1. Nature of the separation problem
2. Ease of cleaning
3. Ease of maintenance
4. Compactness of the system
5. Membrane replacement

The module is selected depending upon the nature of application and operating conditions.

8.3.7 SOME PROBLEMS IN INDUSTRIAL USE OF PERVAPORIZATION

The major large-scale applications of PV have been for dehydration of ethyl and isopropyl alcohols. In both these cases, severe fouling of the membranes was observed. In the case of ethyl alcohol, the fouling was attributed to the rust particles from the mild steel (MS) fermenters used. In the case of i-propanol, the applications were for its recovery from a mixture containing water and dissolved salts from the washing operations. In this application, the membranes developed severe blisters and became useless. These blisters can be traced to the crystallization of the salt in the membrane. Some ingress of the salt cannot be avoided due to the high water sorption in the membrane. The membrane removes water. The water is volatile and is evaporated at the downstream face. The salt, however, cannot do so and is hence trapped in the membrane. As the water is removed, the salt introduced into the top layer with water crystallizes out of the alcohol rich phase. This is probably the most likely reason for the formation of blisters. Observation of the blisters under a microscope showed the presence of solid particles confirming the aforementioned postulate. This problem can be overcome by resorting to VP rather than PV. Thus, the alcohol stream is boiled to supply a vapor to the membrane module. VP obviously has a higher energy requirement than PV since the liquid needs to be vaporized. Careful design of the reboiler and provision of a mist eliminator prevents any carryover of the salt. Thus, a mixture of water and alcohol vapors totally devoid of the salts is supplied to the membrane module. This arrangement has been found to be quite effective in ensuring a longer membrane life.

8.4 APPLICATIONS OF PERVAPORIZATION

As discussed in Section 8.1, PV has applications in all types of separations involving aqueous/organic phases. These are

1. Dehydration of organics
2. Removal of organics from aqueous phase
3. Organic–organic separations

The discussion in Section 8.2 on theory of PV indicates that the membrane polymer to be selected for a given separation should have high sorption affinity for the solute to be removed preferentially. For the first two categories, it is relatively easy to choose a polymer. Thus, the following types of polymers are suitable as membrane materials for these two cases: category (1), hydrophilic polymers with large contributions due to hydrogen bonding and polar forces to the overall solubility parameter, and category (2), hydrophobic (organophilic) polymers with major contributions from dispersion forces. These applications are discussed separately in the following:

8.4.1 DEHYDRATION OF ORGANICS

Most of the commercialization of PV technology occurred in this category for dehydration of ethanol and i-propanol.
For ethanol, a hybrid system comprising distillation to remove bulk of the water (enrichment of ethanol from 8 to ~85 wt%) followed by a PV module to reach 99.8 wt% ethanol has been popular. This hybrid system combines the strengths of distillation and PV in their respective areas. In this case, generally, a small amount of water (<10 wt%) is required to be removed by PV. It is evidently far more economical to focus on removal of this small water quantity rather than trying to remove the organic. With this logic, the membrane polymer selection becomes very easy. Thus, hydrophilic polymers that selectively sorb water are used. PVA is a very popular polymer for dehydration of organics. The hydroxyl group in PVA imparts high hydrophilicity since the OH group has a dominant effect in deciding the properties rather than the relatively small CH₂=CH alkyl group. However, the high hydrophilicity, which is the strong point in favor of PVA, is also its weak point. The thin top selective layer made of PVA that is in continuous contact with water-rich solution gradually dissolves, and hence, the membrane loses its permselectivity. To enhance the active life of such a PVA membrane, the polymer is cross-linked by a suitable compound having a functional group that can react with the OH group of PVA. Suitable cross-linkers are carboxylic acids/anhydrides, dialdehydes, etc. Maleic anhydride (Figure 8.2a) is reportedly used in the first PVA membrane commercialized by GFT (now Sulzer Chemtech). Glutaraldehyde is also used as cross-linker (Figure 8.2b). Cross-linking connects two polymer chains and hinders the dissolution of individual chains that are now bound to other chains. The advantage of extended life gained by the cross-linking is, however, offset by the reduced mobility/flexibility of the chains due to the same cross-links. This reduced flexibility of the polymer chains results in a reduction in the diffusion coefficient of the solute, and hence, the flux decreases (Equation 8.26).

In view of this, the cross-linking is moderate. The usual range is about 4%–8% of the total functional groups being cross-linked. This is a case of the classical trade-off between (1) low depreciation due to extended life and (2) lower productivity due to lower flux. Another serious problem of PVA membrane is its extensive swelling in feed mixtures containing

![Poly vinyl alcohol](image1.png)

**Maleic anhydride**

![Poly vinyl alcohol](image2.png)

**Glutaraldehyde**

![Cross-linking of poly(vinyl alcohol) with maleic anhydride. (b) Cross-linking of poly(vinyl alcohol) with glutaraldehyde membrane.](image3.png)
large amount of water that results in loss of water selectivity. To reduce extensive swelling of PVA for diluted feed, it has been physically modified by incorporating hydrophilic adsorptive fillers and chemically modified by using different type of cross-linker and in situ polymerization of different monomers in its matrix to form IPN-type membrane. Accordingly, Singh et al. 72 modified PVA by in situ polymerization of HEMA in its matrix followed by cross-linking with glutaraldehyde to produce semi-IPN type of membrane. Kuila et al. 73 copolymerized acrylic acid and acrylamide in PVA matrix followed by cross-linking the copolymer with N,N-Methylenesacrylamide (MBA) and PVA with glutaraldehyde to form full-IPN-type membrane. Das et al. 73 investigated various types of cross-linkers and fillers for PVA and optimized the amount of cross-linker and adsorptive filler for filled PVA membranes used for pervaporative dehydration of isopropyl alcohol (IPA).

In many cases, the organic to be dehydrated (for instance, acetic acid) attacks the ether linkage in the PVA membrane. Indeed, the PVA membrane has very limited life in the presence of most acids. Ray et al. 14 used the concept of copolymer membranes to dehydrate acetic acid over the entire range of concentration from 0% to 100%. These investigators prepared copolymers of AN with different hydrophilic monomers like HEMA, acrylic acid, methacrylic acid, and itaconic acid. These copolymers have carbon—carbon bonds, which unlike the ether linkage in the cross-linked PVA membrane are stable to attack by carboxylic acids. The AN part is not sufficiently hydrophilic but imparts mechanical strength while the other monomers improve the hydrophilicity. The overall result is an efficient and stable membrane. Variation of the ratio of AN to (the other) monomer allows freedom of adjusting the hydrophilicity of the membrane to achieve a certain selectivity and flux. The high ratio of the more hydrophilic comonomer to AN increases water sorption and hence flux but results in a concomitant loss in selectivity. Ray et al. 14 showed that this concept of copolymer membrane yields a low-cost alternative to the more expensive hydrophilic polymers like Nafton® and poly(ethylene). Apart from PVA, copolymer, or IPN, blend of hydrophilic polymers like blend of PVA with CMC, hydroxyethyl cellulose (HEC), sodium alginate, chitosan, etc., has been reported for PV-based solvent dehydration. 58,75 Different properties of constituent polymers are combined in a blend polymer membrane. Kalyani et al. 24 blended sodium alginate with HEC in water and cross-linked the blend ionically with phosphoric acid. This membrane showed selectivity as high as 3237 for dehydration of azeotropic tertiary butanol water (88 wt% butanol) mixture. However, performance of a blend membrane strongly depends on relative compatibility of the constituent polymers. A compatibilizer forms bridges between the two constituent polymers through its functional groups improving blend compatibility and performance. Guzman et al. 58 used polycarbonate-grafted HEMA as compatibilizer for blending of polycarbonate and HEMA polymer. They found superior dehydration of methanol with polycarbonate–HEMA blend containing compatibilizer. Another interesting hydrophilic membrane is inorganic–organic hybrid or MMM. These membranes maintain high selectivity even for feed mixtures containing large amount of water. MMMs with in situ incorporation of nanoparticles during polymerization have been reported. Samanta et al. 61 synthesized MMM by in situ incorporation of nanosize bentonite filler during copolymerization of AN and butyl acrylate by emulsion polymerization. The resulting filled membrane yielded high flux and selectivity for dehydration of acetic acid. Because of the presence of nanosize inorganic filler, this membrane maintained high selectivity. Some of the industrial applications of PV based on hydrophilic membranes are given in the following.

8.4.1.1 Chemical Reaction Coupled with Pervaporation

An important application of hydrophilic membranes is in esterification reactions that are generally equilibrium limited. High conversions (low acid numbers) are achieved by removal of the water formed in the reaction. Distillation has been a popular method for water removal. However, distillation is energy intensive. Further, it cannot be applied for heat-sensitive chemicals or biocatalyst. These difficulties of distillation can be overcome by a PV reactor. The coupling of a chemical reaction and a separation process for in situ separation of the reaction products using hydrophilic membrane in a membrane reactor (MR) is becoming significant in industrial processes because it is efficient and less energy intensive. An MR consists of a membrane module and catalyst system. The membrane selectively permeates the product or by-product of the reaction, while the catalyst system promotes the desired direction. Bruschke 59 has described the first continuous industrial plant combining PV with an esterification reaction employing a cascade of reactors and PV units. A simple mathematical model was described for calculating the optimum membrane area per unit mass of the reaction mixture. The kinetics of the esterification reaction required for use in this model are either available in the existing literature or can be obtained using standard techniques.

8.4.1.2 Dehydration of Glycerine

Another very promising application of PV is for dehydrating glycerin. Glycerin is mainly produced as a by-product in the fat-splitting process or biodiesel manufacture. The scale of operation is quite large (several hundred tonnes per day). In fat splitting, glycerin is produced as a weak (–10–15 wt%) aqueous solution. Conventionally, it is converted to anhydrous glycerin using distillation. The low decomposition tempera-ture of glycerin necessitates distillation under high vacuum. Despite high vacuum distillation, some degradation of glycerin cannot be prevented. PV can be an ideal low energy alternative to distillation. 12,75 It has been shown 57 that PV can yield selectivities 1000 times higher than the corresponding distillation selectivity at temperatures as low as 70°C.

8.4.1.3 Dehydration of Mineral Acids, Peroxides, and Aggressive Solvents by Pervaporation

A number of polymeric membranes have been reported for dehydration of organic compounds like carboxylic acids, but it is difficult to find a suitable membrane for dehydration
of (1) mineral acids such as nitric acid and sulfuric acid, (2) aggressive solvents like dimethyl formamide (DMF) and N-methyl pyrrolidone (NMP), and (3) peroxides such as hydrogen peroxide. Most conventional polymers are not resistant to these chemicals. Some recent efforts in this direction are discussed as follows.

8.4.1.3.1 Dehydration of Nitric Acid and Sulfuric Acid by Pervaporation

Nitric acid forms an azeotrope at 68 wt% acid in water. Sulfuric acid is used as an entrainer to break this azeotrope. However, material of construction for this aggressive system is a problem. Further, the additional separation step of sulfuric acid–water mixture greatly increases the operating cost of this very energy-intensive separation. PV is an alternative low energy separation process if suitable polymer is available. For dehydration of corrosive acids, ionomer type of polymer has been reported.76,77 Ionomers are a class of polymer containing functional carboxylic or sulfonic groups in its hydrocarbon backbone. Nafion is such an ionomer originally developed by DuPont for chlor-alkali process. It consists of a polytetrafluoroethylene (PTFE) backbone and regularly spaced perfluorovinyl ether pendant side chains that are terminated by sulfonic ionic groups. This Nafion membrane was reported for dehydration of nitric acid by PV.76 Mechanical integrity and chemical resistance of Nafion membrane is excellent. It also gives high ionic flux but selectivity of the membrane is not satisfactory.76,77 Therefore, in one modification, the sulfonic functional group of Nafion was replaced with carboxylic group.77 This modification gives lower flux but higher selectivity. A multilayer membrane consisting of these two types of Nafion fortified with PTFE was found to give good flux and selectivity of water from nitric acid–water mixtures. Concentration of sulfuric acid is also problematic. Conventionally, it is concentrated by evaporation of water. Thus, dehydration of sulfuric acid has been tried by PV using Nafion-112 and Nafion-117 membranes. These membranes yielded high flux of 0.1–8 kg/m² h and high water selectivity of 10,000 for 40–80 wt% acid in feed.77

8.4.1.3.2 Dehydration of Hydrogen Peroxide by Pervaporation

Hydrogen peroxide is produced by catalytic hydrogenation and auto-oxidation of a suitable organic molecule. It is then concentrated to 70% purity by distillation. Membrane-based separation allows small scale on site production of peroxide solution of desired concentration without expensive solvent extraction and distillation.79,80 However, hydrogen peroxide is a very strong oxidizing agent that attacks most conventional polymeric dehydration membranes. Nafion-type fluoropolymer is useful80 for dehydration of peroxides. Tetrafluoroethylene (TFE)-based copolymers, that is, perfluoro dimethylidioxide (PDD)—TFE copolymer membranes (CMS-3 and CMS-7), were reported82 for dehydration of hydrogen peroxide. For a hydrogen peroxide concentration of 43 wt% in water, CMS-3 and CMS-7 membrane yielded flux of 61.5 and 96 g/m² h at water selectivity of 12 and 9.2, respectively.

8.4.1.3.3 Dehydration of Dimethyl Formamide and N-Methyl Pyrrolidone

DMF is a powerful polar solvent that dissolves most polymers. DMF is used as solvent or extractant for which high purity (<0.03 wt% water) is required. Pervaporative dehydration of DMF was reported with ceramic81 and polymer membranes.82 Copolymer of acrylamide and HEMA with different degree of cross-linking yielded good flux (24 g/m² h) and high water selectivity (464) for dehydration of 99.5 wt% DMF.82 Inorganic membranes are mechanically stable and have good chemical resistance. However, the Si–O–Si bond of silica-based inorganic membrane is vulnerable to hydrolytic decomposition.82 Thus, in recent years, inorganic–organic hybrid membranes have been developed where Si–O–Si bond has been replaced with Si–hydrocarbon–Si bridge structure that can resist water. HybSi is such an organic–inorganic hybrid membrane made from precursor of bis(triethoxysilyl)methane (BTESM), 1,2-bis(triethoxysilyl) ethane (BTESE), and methyltriethoxysilane (MTES). This membrane was found to dehydrate highly NMP at an elevated temperature of 190°C.83

Table 8.1 lists various hydrophilic polymers used for dehydration applications. Table 8.2 gives a comprehensive coverage of the available literature on dehydration of organics. It is evident from Table 8.2 that this application is the most widely investigated class of PV. Further, as mentioned in Section 8.1, this category has seen the most significant commercial utilization among the three categories listed earlier. In addition, in another potential large-scale applications, such as esterification, selective removal of water in an equilibrium-limited reaction can yield practically 100% conversion. However, in most esterification reactions, a mineral acid is used as a catalyst, and the conventional PVA-based membranes are easily attacked by the acid catalyst leading to short lives. The polymer membranes proposed can be used in these applications since C–C bond is not prone to attack by conventional acid catalyst used in esterification reactions. Alternatively,

<table>
<thead>
<tr>
<th>TABLE 8.1 Hydrophilic Polymers Available for Selective Water Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(vinyl alcohol)</td>
</tr>
<tr>
<td>Copolymer of acrylic acid, acrylamide, vinyl pyrrolidone, itaconic acid, methacrylic acid, etc., with AN</td>
</tr>
<tr>
<td>Chitosan</td>
</tr>
<tr>
<td>Sodium CMC, CA (various degrees of hydrolysis)</td>
</tr>
<tr>
<td>Other cellulose derivatives/forms</td>
</tr>
<tr>
<td>Sodium alginate</td>
</tr>
<tr>
<td>Various poly(amide)s (different substituents)</td>
</tr>
<tr>
<td>Various poly(amide)s (different substituents)</td>
</tr>
<tr>
<td>Nafion</td>
</tr>
<tr>
<td>Blend of the aforementioned polymers</td>
</tr>
</tbody>
</table>

* All of the aforementioned polymers except the copolymers need cross-linkers to make them water resistant.
### TABLE 8.2
Dehydration of Organics

<table>
<thead>
<tr>
<th>System</th>
<th>Membrane Used</th>
<th>Remark</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent dehydration</td>
<td>Hydrophilic membranes</td>
<td>A review article with 155 references describing various hydrophilic polymer and inorganic membranes for alcohols, acetic acid, THF, and acetone.</td>
<td>[84]</td>
</tr>
<tr>
<td>Ethanol–water</td>
<td>Quaternized poly(vinyl alcohol) (q-PVA) cross-linked with glutaraldehyde</td>
<td>85 wt% alcohol at 50°C. Water permselectivity of 75.</td>
<td>[85]</td>
</tr>
<tr>
<td>Ethanol–water</td>
<td>Microbial exopolysaccharide (EPS) membrane</td>
<td>95 wt% alcohol at 30°C. Water selectivity of 3,000.</td>
<td>[86]</td>
</tr>
<tr>
<td>Ethanol–water/IPA–water/1-butanol–water/tert-butanol–water</td>
<td>Copoly(4,4'-diphenyleneoxide/1,5-napthalene-2,2-bis (3,4-dicarboxyl phenyl) hexa fluoro propane diimide) 6FDA-ODA-NDA/Ultrem® 1010 dual-layer hollow-fiber membrane</td>
<td>85 wt% C2–C4 alcohols are concentrated to more than 99.7 wt%; flux, 464, 465, 391, and 389 g/m² h, and selectivity, 200, 2,516, 2,518, and 5,600.</td>
<td>[87]</td>
</tr>
<tr>
<td>Methanol–water/ethane–water/IPA–water/2-butanol–water</td>
<td>Polyamide–polyimide dual layer Hollow-fiber membrane</td>
<td>C1–C4 alcohols at 75°C for 2 h. Flux, 1,033, 659, 765, and 744 g/m² h, and selectivity, 471, 50, 1,944, and 1,801.</td>
<td>[88]</td>
</tr>
<tr>
<td>Dehydration of IPA</td>
<td>Hybrid PV–distillation processes intensification Hybrid process economics.</td>
<td></td>
<td>[89]</td>
</tr>
<tr>
<td>1-Methoxy propanol–water</td>
<td>AN-based copolymer membrane</td>
<td>The copolymer properties, in particular, solubility parameter, component group contribution, and interaction parameter values, are used to explain perm-behavior (selectivity and flux). Copolymers of AN showed good selectivity with reasonable flux.</td>
<td>[90]</td>
</tr>
<tr>
<td>Acetic acid–water</td>
<td>Sulfonated polybenzimidazole (SPBI) membrane</td>
<td>Flux of 207 g/m² h and a separation factor of 5,461 for dehydration of a 50/50 wt% acetic acid–water feed solution at 60°C.</td>
<td>[91]</td>
</tr>
<tr>
<td>Acetic acid–water</td>
<td>Poly(acrylonitrile-methyl acrylate) Polymer</td>
<td>At 30°C for 0.95 wt% water in feed, thickness normalized flux, and water selectivity were 1,710 g µm² h and 409, respectively.</td>
<td>[92]</td>
</tr>
<tr>
<td>Acetone–water</td>
<td>Poly(diallyldimethyl ammonium chloride)/poly (sodium styrene sulfonate) and poly(ethylenimine)/polyacrylic acid filled with aluminum and zirconium oxide</td>
<td>95 wt% acetone at 50°C. Flux, 700 g/m² h; selectivity, 1,881.</td>
<td>[93]</td>
</tr>
<tr>
<td>Dehydration of acetic acid, alcohols, and acetone by PV</td>
<td>AN–maleic anhydride copolymer membrane</td>
<td>The membrane exhibits reasonable performance with respect to both separation factor and permeance (11.0 and 279.4 g/m² h/bar, respectively, at 92 wt% feed cone, of water) for acetone dehydration.</td>
<td>[94]</td>
</tr>
<tr>
<td>THF–water</td>
<td>Poly(acrylamide-hydroxyethylmethacrylate)</td>
<td>Flux, 570 g/m² h; selectivity, 216. At 50°C for 0.5 wt% water in feed. Flux, 158 g/m² h; selectivity, 39.</td>
<td>[95]</td>
</tr>
<tr>
<td>Dioxane–water</td>
<td>Polyvinyl alcohol filled with aluminosilicate filler</td>
<td>For 10 wt% water in feed.</td>
<td>[96]</td>
</tr>
<tr>
<td>Ethylene glycol–water</td>
<td>Full IPN membrane of PVA and copolymer of acrylic acid and acrylamide. PVA cross-linked with glutaraldehyde, copolymer with MBA</td>
<td>At 30°C, for 97.1 wt% EG in the feed mixture, the full IPN with 5:1 polymer ratio showed total flux of 37.5 g/m² h and selectivity of 2,655.</td>
<td>[73]</td>
</tr>
<tr>
<td>Acetonitrile–water</td>
<td>PVA–iron oxide nanocomposite</td>
<td>10.7 wt% water at 35°C. 700 g µm² h flux and 711. Selectivity for 10% FeO loading.</td>
<td>[97]</td>
</tr>
<tr>
<td>Ethyl acetate–water</td>
<td>PVA cross-linked with maleic anhydride and tartaric acid coated on PAN hollow fiber</td>
<td>For 98 wt% ethyl acetate, flux is 34 g/m² h and selectivity is 7,270 at 40°C.</td>
<td>[98]</td>
</tr>
<tr>
<td>Pyridine–water</td>
<td>Poly(acrylonitrile-co-monoacryloxyethyl phosphate) (PANPH) membrane</td>
<td>59 wt% aqueous pyridine was concentrated to 97 wt% with flux of 132 g/m² h at 75°C.</td>
<td>[99]</td>
</tr>
</tbody>
</table>

(Continued)
TABLE 8.2 (Continued)

Dehydration of Organics

<table>
<thead>
<tr>
<th>System</th>
<th>Membrane Used</th>
<th>Remark</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caprolactam–water</td>
<td>Nano-TiO$_2$ into RC membrane</td>
<td>RC–TiO$_2$ inorganic–polymer hybrid membrane containing 5 wt% TiO$_2$ exhibited the good PV performance with a flux of 1,787.3 g/m$^2$ h and separation factor of 55,091.7 at 328 K for 50 wt% caprolactam.</td>
<td>[100]</td>
</tr>
<tr>
<td>NMP–water</td>
<td>Heat-treated PAN hollow-fiber membrane</td>
<td>30 wt% aqueous NMP was concentrated &gt;99 wt% with 1,500 g/m$^2$ h flux at 70°C.</td>
<td>[101]</td>
</tr>
<tr>
<td>Phenol–water</td>
<td>PVA–PAA cross-linked</td>
<td>B = 3,500 for aqueous phenol solution.</td>
<td>[102]</td>
</tr>
<tr>
<td>Esterification reaction of IPA and acetic acid</td>
<td>Commercial polymeric membrane PERVAP® 2201</td>
<td>Preferential water permeation from the quaternary mixture involved in the esterification of acetic acid with isopropanol has been observed.</td>
<td>[103]</td>
</tr>
<tr>
<td>Esterification of long-chain (C$_{18}$) oleic acid with methanol</td>
<td>Polyethersulfone–PVA composite membrane</td>
<td>Using PVA composite membrane, 99.9% conversion of methyl ester having acid value of 0.2 could be obtained using 0.3 wt% sulfuric acid at 65°C.</td>
<td>[104]</td>
</tr>
</tbody>
</table>

if PVA-based membrane is to be used, then the conventional acid catalysts that attack these membranes may be replaced by more benign forms such as strongly acidic ion exchange (H$^+$ form) catalysts.

8.4.2 Removal of Organics from Aqueous Phase

This class deals with removal of trace organics from a predominantly aqueous body. In most of the cases, these trace organics are volatile (VOCs). VOCs are generated from different sources like industries, agricultural sectors, and municipal waste. Industry-related VOCs of major concerns are petroleum-based solvents such as benzene, toluene, ethylbenzene, and xylene (BTEX) and chlorinated solvents. If the aqueous stream is very dilute, pollution control is the principal economic driving force. In this case, the objective of PV is to remove this trace amount of VOCs from the wastewaters, allowing the water to be discharged to the sewer and concentrating the VOCs in a small-volume stream that can be sent to a hazardous treatment unit like incineration. Without a treatment system such as PV, the entire waste stream is required to be transported to the final treatment site incurring considerable transport and treatment cost. Similar to most membrane processes, the cost of PV increases linearly with system capacity, whereas the cost of processes such as stream stripping is proportional to 0.6–0.7 power of the capacity.$^{105}$ This makes PV competitive for small- to medium-sized stream for removal of highly volatile VOCs.$^{104,105}$ Several VOCs have solubilities in water sufficient to reckon both in terms of potential economic loss and pollution. The solubilities are too low to be dealt with by distillation since distillation is expensive. PV is an ideal alternative in this case. In stark contrast to distillation wherein the selectivities are in single digits, PV can yield several orders of magnitude higher selectivities$^{106,18,21}$ resulting in very high recovery of the dissolved organics at much lower cost.

8.4.2.1 Membrane for Organic Removal

Most of the membranes used for removal or recovery of trace organics are made from organophilic cross-linked elastomers (rubber). Elastomers are amorphous in nature, that is, their polymer chains are not closely packed and have large free volume. Further, $T_g$ of rubber is much below room temperature. Hence, the polymer chains of rubber are very flexible. Thus, most elastomeric membranes yield high flux at the cost of selectivity.$^{107}$ Dagaonkar et al.$^{28}$ studied cross-linked PDMS for piperazine/water separation. This membrane showed sorption selectivity for piperazine. However, during PV operation, the membrane was found to show preferential water permeation. This was ascribed to much smaller size of water molecule than most of the organic molecule that causes preferential diffusion selectivity for water. Netke et al.$^{41}$ developed a comprehensive dual mode model for permeation in membranes containing adsorptive fillers. The model proposed can predict the effects of various parameters like absorbability of the solute and loading of the filler. The proposed model also correctly describes the asymptotic behavior of such membranes. Singha et al. filled SBR and NR$^{107,108}$ with nano-size N330 carbon black filler. These filled membranes were efficiently vulcanized with sulfur and accelerator. Efficient vulcanization means cross-linking of rubber with sulfur and accelerator where the mass ratio of accelerator (cross-linking catalyst, e.g., zinc dithiocarbamate) and sulfur is greater than unity. These filled membranes preferentially permeated low concentration of pyridine from water. Thus, elastomeric membranes can be used for removal of organics
provided these membranes are filled with organophilic adsorptive filler. However, the presence of filler reduces flux of these membranes. Nonelastomeric organophilic membranes have also been explored for organic removal. These include polyvinylidene fluoride (PVDF), copolymer of 2 and 4 vinyl pyridine with styrene or AN, PU, and polyvinyl chloride (PVC). Most of these nonrubber polymers are hard and brittle and have $T_g$ above room temperatures. In contrast to rubber, these polymers contain very little void space (0.2%–10%). Thus, diffusion coefficients and flux through these glassy polymers are much lower than rubber membranes. Indeed, the transport of organics through these polymers is non-Fickian case-II transport as evidenced by diffusional Deborah number close to unity for this nonrubber amorphous or semicrystalline polymers. The criterion for selection of these polymers as membrane material is based on solubility parameter of the organic and the polymer. Since the organic is present in trace amount in water, it does not attack a copolymer or blend of two polymers where one polymer is soluble in that organic but the other polymer is not. In this case, the organic-resistant polymer provides mechanical strength and stability of the membrane while organic-soluble polymer lends organic permeability. Ray et al. blended polystyrene and PVC and used this blend membrane for selective removal of tetrahydrofuran (THF) from water. This membrane showed high selectivity but low flux (8.5 g/m² h) for removal of 0.44 wt% THF from water at 30°C.

Thus, both elastomeric and nonelastomeric polymers are used as PV membrane for selective removal/recovery of organics from water. The polymers used for this class of application are listed in Table 8.3. Although some of the polymers listed in Table 8.3 are readily available and less expensive, the standard for hydrophobic membranes has been set by poly(dimethyl siloxane) a silicone rubber membrane popularly abbreviated as PDMS. This is a room temperature vulcanization (RTV)–type rubber. It is generally made from a two-pot mixture consisting of the silicone rubber and a cross-linker. POMS is a similar silicone rubber. POMS is more hydrophobic than PDMS but is expensive. Most investigators have used PDMS although some have also used other elastomers, that is, NR, SBR, N-butyl rubber (NBR), and EPDM. These elastomeric membranes filled with organophilic fillers appear to be the optimum membrane polymer in terms of flux, selectivity, and durability. Table 8.4 gives a summary of the literature investigations on removal/recovery of organics from aqueous solutions.

### 8.4.2.2 Membrane Module and Configuration

PV offers an extremely promising technology for treating effluents containing dissolved organics. This is apparent from Figure 8.3. A hydrophobic membrane module is used to recover (almost) completely the dissolved organics from the effluent. Three types of membrane module, that is, plate and frame, hollow-fiber, and spiral wound modules, are used for this purpose. Apart from these three modules, several new configurations have been attempted in recent years. Vane and coworkers used plate and frame module in vibrating mode (vibrational shear-enhanced process [VSEP]). In this modified configuration, the entire stack of membrane plates vibrates rotationally about the axis of the stack at a frequency of ~60 Hz. This modification results in 10-fold increase of overall mass transfer coefficient for TCE, perchloroethylene (PCE), and TCA. A coiled hollow-fiber module was found to show twofold increase of chloroform flux and around threefold increase of separation factor in comparison to a straight hollow-fiber module.

#### 8.4.2.2.1 Phase Splitting

The selectivities of a typical organophilic membrane are such that the permeate is enriched well above the solubility limit of the organic. At these concentrations, phase splitting occurs. In the liquid–liquid separator (Figure 8.3), two separate layers, (1) organic rich with traces of dissolved water and (2) water rich but saturated with the organics, are obtained. The second small stream containing water saturated with the organics is returned to the feed side of the membrane module. Figure 8.3 shows a closed-loop operation with only the untreated (mainly aqueous) stream going to the effluent treatment plant. An idea of importance of the process shown in Figure 8.3 can be obtained from the following example. Although benzene has a low solubility (~1000 ppm) in water, each mole of benzene requires 7.5 mol of oxygen for complete conversion to $CO_2$ and $H_2O$. Removal of more than 90% of the benzene is possible by employing the process in Figure 8.3. This implies a significant decrease in the chemical oxygen demand (COD)/significantly lower load on the effluent treatment plant. At the same time, the recovered organic is an added value to the organization. Some of the major applications related to selective organic removal from water are given as follows.

<table>
<thead>
<tr>
<th>TABLE 8.3</th>
<th>Hydrophobic/Organophilic Polymers Available for Selective Removal of Organics from Aqueous Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(dimethyl siloxane) (PDMS)</td>
<td></td>
</tr>
<tr>
<td>POMS</td>
<td></td>
</tr>
<tr>
<td>EPDM rubber</td>
<td></td>
</tr>
<tr>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>SBR</td>
<td></td>
</tr>
<tr>
<td>NBR</td>
<td></td>
</tr>
<tr>
<td>Nitrile rubber</td>
<td></td>
</tr>
<tr>
<td>Poly(ether block amides) (PEBA)</td>
<td></td>
</tr>
<tr>
<td>Elastomeric poly(urethanes)</td>
<td></td>
</tr>
<tr>
<td>PVDF</td>
<td></td>
</tr>
<tr>
<td>Polyvinyl acetate</td>
<td></td>
</tr>
<tr>
<td>PVC</td>
<td></td>
</tr>
<tr>
<td>Styrene copolymer</td>
<td></td>
</tr>
<tr>
<td>Polyetherimine (PI)</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 8.4
Removal of Organics from Aqueous Solutions

<table>
<thead>
<tr>
<th>System</th>
<th>Membrane Used</th>
<th>Remark</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recovery of phenol from wastewater streams arising from a phenolic</td>
<td>70 wt% PDMS with 30 wt% SiO₂</td>
<td>Application of membrane aromatic recovery system (MARS). The average</td>
<td>[161]</td>
</tr>
<tr>
<td>resin production plant</td>
<td></td>
<td>phenol recovery was 84%.</td>
<td></td>
</tr>
<tr>
<td>Recovery of phenol and chlorophenol from water</td>
<td>Polyurethane urea (PUU) membrane</td>
<td>The porous PU membranes performed separation of phenol and chlorophenols</td>
<td>[162]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>with separation factors ranging from about 570 to 1,760 at total</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>permeate fluxes of 7,700–14,100 g/m² h over feed concentrations of</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,000–4,000 ppm (0.1%–0.4%, w/v) at 30°C.</td>
<td></td>
</tr>
<tr>
<td>Removal of methyl ethyl ketone from water</td>
<td>PDMS and PEBA</td>
<td>For 10 wt% MEK–water solution at 40°C and 3 mmHg pressure. PDMS—flux,</td>
<td>[163]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60 g/m² h; selectivity, 100. PEBA—flux, 120 g/m² h; selectivity, 13.5</td>
<td></td>
</tr>
<tr>
<td>Removal of pyridine from water</td>
<td>Filled SBR (5 wt% N330 carbon black filler)</td>
<td>For 0.5 wt% feed, pyridine concentration flux is 88.4 g/m² h and</td>
<td>[107]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pyridine selectivity is 28.77 at 40°C.</td>
<td></td>
</tr>
<tr>
<td>Removal of pyridine from water</td>
<td>Filled NR (5 wt% N330 carbon black filler)</td>
<td>For 0.5 wt% feed, pyridine concentration flux is 84.4 g/m² h and</td>
<td>[108]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pyridine selectivity is 27.4 at 40°C.</td>
<td></td>
</tr>
<tr>
<td>Removal of pyridine from water</td>
<td>PEBA</td>
<td>For 7 wt% feed, pyridine concentration flux is 69 g/m² h and</td>
<td>[164]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pyridine selectivity is 14.5 at 70°C.</td>
<td></td>
</tr>
<tr>
<td>Removal of isopropyl acetate from water</td>
<td>ZSM-5 filled PUU membranes</td>
<td>The best separation factor and total flux reached 288.72 and</td>
<td>[165]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>53.21 g/m² h, respectively, at 60°C when the feed concentration of</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>IPAC is 0.39 wt%.</td>
<td></td>
</tr>
<tr>
<td>Toluene–water mixtures</td>
<td>Ethylene–chlorotrifluoroethylene copolymer (ECTFE)</td>
<td>At 25°C, for 170 ppm. Toluene in water. Flux = 193 g/m² h. Enrichment</td>
<td>[166]</td>
</tr>
<tr>
<td></td>
<td>Membrane</td>
<td>factor = 894.</td>
<td></td>
</tr>
<tr>
<td>Chlorinated volatile organics–water</td>
<td>PUU–poly(methyl methacrylate) (PMMA) IPN membrane</td>
<td>For 0.1% feed, at 30°C. Flux 200 g/m² h. Selectivity = 7,842.</td>
<td>[102]</td>
</tr>
<tr>
<td>Removal of mixture of organic acid</td>
<td>Membranes having amino group containing polymer</td>
<td>High α and flux for organic acids reported.</td>
<td>[171]</td>
</tr>
<tr>
<td></td>
<td>surface coating</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Removal of DMF from water</td>
<td>N-Vinyl pyrrolidone grafted sodium alginate</td>
<td>Flux = 960–2,050 g/m² h separation factors of 5.6–15.4.</td>
<td>[168]</td>
</tr>
<tr>
<td></td>
<td>membrane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Removal of traces of organics from aqueous solutions</td>
<td>PDMS</td>
<td>3D solubility parameter approach shown to be useful in predicting α.</td>
<td>[18]</td>
</tr>
<tr>
<td>Separation of organic solvent from water containing 0.1%–0.2%</td>
<td>Silicone rubber membrane</td>
<td>High α and flux for organics reported.</td>
<td>[169]</td>
</tr>
<tr>
<td>styrene, toluene, chloroform, butyl acetate, diethyl ether</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Separation methods for environmental technologies</td>
<td>High surface area membrane</td>
<td>Review with 32 references.</td>
<td>[170]</td>
</tr>
<tr>
<td>Removal of tetrachloroethylene from surfactant-based soil remediation</td>
<td>Hydrophobic membranes</td>
<td>PCE removal averaged 95.8% during peak surfactant levels and exceeded</td>
<td>[94]</td>
</tr>
<tr>
<td>fluid</td>
<td></td>
<td>99.9% in the absence of surfactant.</td>
<td></td>
</tr>
<tr>
<td>1-Methoxy propanol and water</td>
<td>PDMS and linear low-density poly(ethylene), LLDPE</td>
<td>PDMS gave better results than LLDPE.</td>
<td>[171]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>α for acetic acid as high as 33.</td>
<td></td>
</tr>
<tr>
<td>Separation of acetic acid from dilute aqueous solution</td>
<td>Supported liquid membrane PV (tri alkyl amines as reversible reactants)</td>
<td>This process can be used to remove volatile nonaqueous phase liquids</td>
<td>[172]</td>
</tr>
<tr>
<td></td>
<td>Hydrophobic membrane</td>
<td>from surfactant-based soil washing and soil flushing solutions for</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>recovery of the volatile compounds and reuse of the surfactant.</td>
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<tr>
<td>Separation of VOC from surfactant solution</td>
<td>Hydrophobic membrane</td>
<td>The sorption selectivity of the PSI membranes for chloroform/</td>
<td>[173]</td>
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<tr>
<td></td>
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<td>water solutions was investigated; the silicalite-filled membrane with 120</td>
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<tr>
<td></td>
<td></td>
<td>μm thickness exhibits a high total permeation flux of 280 g/m² h with</td>
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<td></td>
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<td>separation factor of 52.2 for 1.2 wt% of the chloroform/water mixture.</td>
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</table>

(Continued)
### TABLE 8.4 (Continued)

**Removal of Organics from Aqueous Solutions**

<table>
<thead>
<tr>
<th>System</th>
<th>Membrane Used</th>
<th>Remark</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aroma Compound Separation and Pharmaceutical and Flavor-Perfume Industry</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recovery of key components of bilberry aroma</td>
<td>Commercial hollow-fiber PDMS membrane</td>
<td>The analysis of the separation and recovery of some selected aroma compounds belonging to bilberry juice was made by employing a mathematical model.</td>
<td>[174]</td>
</tr>
<tr>
<td>Recovery of aroma from beer</td>
<td>POMS–PEI composite asymmetric membrane</td>
<td>Based on response surface methodology, the optimal operating conditions were 12.4°C for feed temperature, 0.45 m/s for feed velocity, and 1.0 mbar for permeate pressure.</td>
<td>[126]</td>
</tr>
<tr>
<td>Recovery of aroma compounds (1-octen-3-ol, ethyl acetate/butyrate/hexanoate)</td>
<td>Plain PDMS and PDMS filled with silicalite</td>
<td>Influence of different permeates studied. Filled membrane gives better selectivity than plain PDMS but lower flux.</td>
<td>[175]</td>
</tr>
<tr>
<td>Recovery of picolines from aqueous solutions</td>
<td>Elastomeric membranes</td>
<td>α as high as 150 reported.</td>
<td>[17]</td>
</tr>
<tr>
<td>Recovery of aroma compounds</td>
<td>POMS and PDMS</td>
<td>The effects of operating conditions on separation performance were studied. POMS membrane was more permselective to the aroma compound than PDMS. B higher for ETH than for ETB.</td>
<td>[124]</td>
</tr>
<tr>
<td>Recovery of aroma compounds</td>
<td>Organophilic membranes</td>
<td>Review. Comparison of membrane performance for aroma compounds with different functional groups.</td>
<td>[115]</td>
</tr>
<tr>
<td>Recovery of tea aroma compounds (transhexenal, 2-methylpropanol, 3-methylbutanal, phenyl acetaldehyde, benzyl alcohol, linalool, cis-3-hexenol, β-ionone)</td>
<td>POMS and poly(dimethylsiloxane)</td>
<td>Wider range of β (20–1,100) depending upon the functional group. PDMS found to be better than POMS.</td>
<td>[20]</td>
</tr>
<tr>
<td>Scale-up of PV for the recovery of natural aroma compounds in the food industry; part 2: optimization and integration</td>
<td>Hydrophobic membranes</td>
<td>Economic analysis of PV shows high potential for aroma recovery.</td>
<td>[176]</td>
</tr>
<tr>
<td>Recovery of volatile organic flavor compounds (ethyl acetate [EA], ethyl propionate [EP], ethyl butyrate [EB])</td>
<td>Surface-modified tube-type alumina membrane</td>
<td>β for EA, EP, and EB at 40°C were in the range of 66.9–78.9, 106.5–97.3, and 120.5–122.8, respectively. Phase separation in permeate allows facile recovery of the aroma compounds.</td>
<td>[177]</td>
</tr>
<tr>
<td>PV for aroma isolation</td>
<td>Organophilic membrane</td>
<td>Recent developments in this field and the economic implications of the technology for producing natural aroma extracts are studied.</td>
<td>[178]</td>
</tr>
<tr>
<td>Aroma compounds recovery of tropical fruit juice by PV</td>
<td>Composite membranes (flat or hollow fiber)</td>
<td>The water permeability and the overall mass transfer coefficient for each organic solute were determined.</td>
<td>[112]</td>
</tr>
<tr>
<td>Bioproduction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ABE from aqueous solution</td>
<td>Poly(ether block amide) (PEBA2533) membrane</td>
<td>PEBA membrane was used for separation of acetone, butanol, and ethanol from aqueous solution.</td>
<td>[179]</td>
</tr>
<tr>
<td>ABE fermentation coupled with PV</td>
<td>PDMS/ceramic composite membrane</td>
<td>Flux of 670 g/m² h, ABE separation factor of 16.7.</td>
<td>[146]</td>
</tr>
<tr>
<td>Butanol production</td>
<td>PDMS and PEBA</td>
<td>PEBA membrane owned a higher butanol permeation flux of 9.975 g/m² h as opposed to 3.911 g/m² h using a PDMS membrane.</td>
<td>[181]</td>
</tr>
<tr>
<td>Acetone, butanol, ethanol fermentation</td>
<td>SBR, EPDM, PDMS plain and filled with silicalite</td>
<td>Highest α obtained for filled PDMS and lowest for EPDM. SBR yielded highest PSI.</td>
<td>[188]</td>
</tr>
<tr>
<td>Product recovery from biomass fermentation processes</td>
<td>Hydrophobic/hydrophilic membranes for recovery of biofuel and dehydration, respectively</td>
<td>Several issues and research priorities that will impact the ability of PV to be competitive for biofuel recovery from fermentation systems are identified and discussed.</td>
<td>[182]</td>
</tr>
<tr>
<td>Ethanol recovery from fermentation broth by PV</td>
<td>Composite polydimethylsiloxane membrane</td>
<td>Ethanol concentration in fermentation broth decreased to a relatively low level when PV was coupled with fermentation. The more active cells appeared in the fermentation broth, the better the membrane performance was.</td>
<td>[183]</td>
</tr>
</tbody>
</table>
8.4.2.3 Recovery/Concentration of Flavor/Aroma Compounds by Pervaporation

Flavor is a key attribute of foods and beverages. Volatile organic constituents of foods and beverages contribute significantly to the flavor. Aroma/flavor of naturally derived matter is a result of specific compositions of the product derived by processing the feedstock. Modern techniques used for analysis of different kinds of beverages indicate several thousand compounds as contributors to the aroma. These include highly VOCs like esters, alcohols, ketones, and aldehydes. During industrial processing of beverages and foods, such as concentration by steam distillation and multistage vacuum evaporation, losses or chemical modification of these aroma compounds can occur. Besides this, the oxygenated compounds that are major contributors to the aroma/flavor have a higher solubility in water and, therefore, tend to be lost in aqueous stream of the steam distillation condensate. The high-temperature processing can cause degradation/discholoration and undesirable cooked taste results due to thermal effects. This has serious implications on quality of the fragile aroma/flavor components in a commercial composition. Therefore, several investigators have studied aroma recovery and recycle of the recovered components. The objective here is to recover all the valuable components and blend the recovered stream with the steam-distilled portion. The final product in such a case can achieve a near natural composition and consequent natural flavor/aroma.

Owing to the high dilution of the target components in the feed stream, commercial aroma recovery plants are somewhat complex. The current industrial processes for aroma recovery are distillation, partial condensation, or a combination thereof. High vacuum distillation is the preferred method. In partial condensation, the first condenser operates at a higher temperature and produces a liquid stream that is basically water. The remaining aroma-rich vapor is sent to a total condenser with a low operating temperature. In both cases, significant losses occur in the vent gases. Thus, in addition, expensive gas washing and condensation systems are required. Typical concentrations of volatile aroma compounds in the aqueous solutions obtained from steam distillation or exhaust condensate are in parts per million range. Concentration of such highly diluted solutions under mild conditions because of the heat sensitivities of aroma compounds constitutes a major challenge in development of industrial aroma recovery. In view of the aforementioned considerations, PV, which operates under mild conditions and provides high selectivities, is an attractive alternative to the conventional separation processes. Baudot and Marin have presented an excellent review on recovery of aroma compounds by PV. A comparison with recovery by stripping is also made. A recent paper covers the subsequent literature. From the available literature, it is abundantly clear that PV is a far better option than stripping for aroma recovery.

8.4.2.3.1 Evaporator–Pervaporation Hybrid System

Evaporative concentration of volatile aroma compounds results in considerable losses, and, in some cases even total loss, of aroma compounds in the evaporator. It is highly desirable to minimize such losses. This can be accomplished either by recovering the lost aroma from the vent stream or by stripping the aroma from the raw material stream before processing. In both cases, the aroma compounds are separated from a liquid stream (normally aqueous) in such a way that an aroma concentrate is produced, which can then be fed back to the final product. The use of coupled organophilic–hydrophobic membranes for PV recovery of aroma can yield a permeate that is relatively enriched in aroma compounds. The driving force for transport through the membrane is the difference in vapor pressure between the liquid feed solution and the permeate vapor. This vapor pressure difference is maintained by using a vacuum pump. The more permeable component, which is normally the more volatile aroma component, permeates faster than the other components (i.e., water) and is enriched in the permeate.

8.4.2.3.2 Current Status of Research

Membrane separation is a valuable method to concentrate flavor distillates and extracts. Three different membrane processes have been tested and reported in the literature with varying degrees of success. These are RO, osmotic distillation (OD), and PV. Compared to RO, OD, evaporation, and other traditional concentration processes, PV has the following advantages: (1) no thermal damage, (2) minimum loss of flavor compounds, (3) low energy consumption, and...
(4) no additional separation for recovery from vent gas/solvent, etc.\textsuperscript{112,117-119} The recovery of individual aroma relevant to the flavor of grapes or wine has been reported by several authors.\textsuperscript{120,121} Organophilic PV linked to fermentation has been studied for the recovery of individual aroma compounds or inhibiting metabolic products.\textsuperscript{119,121} Voilley et al.\textsuperscript{111,121,123} studied the recovery of volatile aroma compounds (1-octen-3-ol and 2,5-dimethylpyrazine) from model fermentation broths. The water solutions of each aroma compound were sweep gas pervaporated with two different membranes, microporous polypropylene and dense poly(dimethylsiloxane) (PDMS). These studies showed that PDMS membranes were more suitable for the extraction of aroma compounds than polypropylene membranes. Lamer and Voilley\textsuperscript{175} studied the extraction of 1-octen-3-ol, ethyl ethanoate, ethyl butanoate (ETB), and ethyl hexanoate (ETH) with PV through PDMS membranes. In comparison with previous work, their results showed slightly higher fluxes for virgin PDMS membranes than for zeolite-filled ones. Sampranpiboon et al.\textsuperscript{124} employed PV to recover ETB, ETH, and ETB–ETH from their aqueous solutions using POMS and poly(dimethylsiloxane) (PDMS) membranes. In general, the POMS membrane was found to be more permselective to the aroma compounds than the PDMS membrane and was also more efficient for the separation of ETH than ETB. PV of natural apple essence through poly-(dimethylsiloxane) membrane at 22°C and a permeate pressure of 3 mbar was studied by Zhang and Matsuura.\textsuperscript{125} Catarino et al.\textsuperscript{126} studied recovery of aroma from beer using POMS–polyetherimide (PEI) membranes. Kanani et al.\textsuperscript{127} studied POMS and PDMS membranes for recovery of tea aroma. Raut and Pangarkar\textsuperscript{128} studied silicalite-filled PDMS membrane for recovery of aroma constituents of essential oils with respect to their structure and compared respective PV and distillation selectivities. Jiao et al.\textsuperscript{129} discussed recent advances in membrane processes for concentration of various fruit juices while Pereira et al.\textsuperscript{130} discussed recovery of aroma from fruit juice by PV. For concentration of fruit juice and its aroma, a hybrid process is employed. In this hybrid process, an integrated enzyme MR clarifies the raw juice. A RO unit preconcentrates the juice up to 25°Brix. A PV unit recovers and concentrates the aroma mixture. Finally, an evaporator concentrates the fruit juice up to 72°Brix. The total capital investment of this new membrane process is 14% less than the conventional process.\textsuperscript{129} From the available literature, it is abundantly clear that PV is a far better option than stripping for aroma recovery. However, as pointed out by Kanani et al.,\textsuperscript{20} the sensory profile of the PV-recovered aroma mixture can be significantly different because of the different selectivities offered by the membrane for the constituent aroma compounds of the original mixture. In their study on recovery of tea aroma compounds by PV, the following observations were made:

Generally, alcohols showed higher separation factors when present in model multicomponent solutions than in binary systems with water. Aldehydes showed an opposite trend. The actual tea aroma mixture showed a rather different behavior from the model aroma mixture, probably because of the presence of very large numbers of unknown compounds. Overall, the PDMS membrane with vinyl end groups showed higher separation factors and fluxes for most of the aroma compounds. PV is attractive for this application. However, as mentioned earlier, the varying selectivities for the constituent aroma compounds alter the sensory profile, and therefore, the application of PV for the recovery of such mixtures needs careful consideration on a case-by-case basis.

8.4.2.4 Fermentation Coupled with Pervaporation

Acetone–butanol–ethanol (ABE) fermentation is one of the oldest fermentation processes.\textsuperscript{131} During the early part of the twentieth century, this fermentation was commercially viable. By the 1960s, efficient production of ABE by separate processes became highly economical in the oil industry. Thus, the fermentation route based on relatively expensive carbohydrate substrate could not compete with petrochemically produced ABE. This resulted in virtual elimination of industrial ABE fermentation. However, increasing oil prices starting with the Gulf War of early 1970s resulted in a revival of research activities on this fermentation. There is also a clear trend to use inexpensive feedstocks (corn stover and other similar biomaterials) to generate value-added chemicals. ABE fermentation, using anaerobic bacterium \textit{Clostridium acetobutylicum}, became a potential source of feedstock chemicals and liquid fuels.\textsuperscript{132} In these fermentation processes, continuous product removal is necessary to overcome product inhibition and increase substrate conversion.\textsuperscript{133} Inhibition yields a dilute final product that consumes significant energy to reach the desired concentration level.\textsuperscript{4} Success of this route hinges on efficient in situ recovery.\textsuperscript{134} Separation techniques such as gas stripping,\textsuperscript{135} liquid–liquid extraction,\textsuperscript{132,136} adsorption,\textsuperscript{137} ultrafiltration,\textsuperscript{138} RO,\textsuperscript{139} perstraction,\textsuperscript{140} and PV\textsuperscript{141-145} have been applied to ABE fermentation. Considerable work has been carried out to improve the productivity of this fermentation process using membrane-assisted removal/recovery of ABE. Among these processes, PV has attracted far more attention,\textsuperscript{143} because of its high selectivity and ability to separate/partially concentrate in single step without the use of additives.\textsuperscript{146} ABE separation from dilute (<5 wt%) aqueous solutions requires highly selective organophilic membranes.\textsuperscript{134} Since butanol is less volatile than water, the separation of butanol from dilute aqueous solutions by distillation is unfavorable; it is estimated that at a butanol concentration of <5%, the energy consumption required for butanol purification will exceed the energy content of the butanol recovered making the process carbon negative as compared to PV. PV has no harmful effect on the microorganisms in the fermentation broth. Further, PV membranes are unlikely to be plugged/fouled.
8.4.2.4.1 Membranes for ABE Recovery

PV-based in situ recovery of ABE components is attractive because of selective permeation of ABE through the membrane. PDMS (filled and unfilled) is so far the most widely used organophilic membrane material used in recent studies. In addition to the PDMS-based membranes, other rubbery polymer membranes such as POMS rubber, SBR, and EPDM rubber have also been investigated. PDMS–PTFE membranes and supported liquid membrane (triocitlyamine [TOA] in hollow-fiber hydrophobic membrane) have also been reported. Membranes prepared from poly[-1-(trimethylsilyl)-1-propyne], which is a glassy polymer with a large free volume, were also found to be selective to organic compound permeation. Although microporous membranes made from hydrophobic polypropylene and PTFE have been used, they generally do not exhibit selectivities comparable to PV. Poly(ether block amide) (PEBA) is a group of copolymers comprising flexible polyether segments and rigid polyamide segments. Depending on the nature and the relative content of the two segments, certain PEBA polymers have attracted great interest as a promising membrane material.

8.4.2.4.2 Ethanol Production by Integrated Fermentation–Pervaporation

8.4.2.4.2.1 Source Materials

More than 95% of total ethanol is globally prepared by fermentation of biomass using specific microorganisms. Ethanol can be prepared from any biomass-containing sugar. The selection of biomass depends on its availability. High-fructose corn syrup, sugar beet molasses, and wheat or rice straw, paper mill discards, paper portion of municipal waste, nonfood dedicated energy crops, etc.) are also being extensively investigated. Countries that have sizeable agronomic base can greatly benefit from this route. Cellulosic feedstocks require an additional conversion to fermentable sugars. PV can be used beneficially to curtail the overall energy requirement for production of ethanol from these feedstocks. Pangarkar has given details of an integrated process comprising in situ ethanol separation followed by distillation to 95 wt% EtOH. Membrane-based separation by PV can be applied for ethanol production in two ways: (1) One is using organophilic membranes for removing product inhibition in the fermenter while simultaneously increasing the concentration of ethanol feed to the distillation section. This scheme saves substantial amount of high-grade energy source used in the distillation section. (2) And the other is using hydrophilic membranes for dehydration of ethanol near azeotrope point in a hybrid distillation–PV process.

For fermentation, the biokinetics for Baker’s yeast strain Saccharomyces cerevisiae CBS 8066 given by Groot et al. was used. The relevant PV data for flux (J) and separation factor (β) for PDMS on polysulfone support were obtained from Gudernatsch et al. J and β are functions of ethanol concentration that vary along the PV module length. Assuming plug flow, a log mean concentration of ethanol was used as the representative value.

Flux data of Gudernatsch et al. were regressed to yield a correlation between permeate concentration of EtOH, total flux, and log mean concentration of EtOH.

8.4.2.4.2.2 Distillation

The permeate from PDMS PV module is fed to a plate column. Operating (L/D) = 1.5 x (L/D)min obtained from Fenske’s method. Product composition was fixed at 95 wt% EtOH. Gilliland’s equation was used to estimate the number of theoretical plates required and capital cost. An enthalpy balance gave the heat load, reboiler, and condenser capital costs.

The model equations employing biokinetics of Groot et al. and PV data of Gudernatsch et al. were solved using an iterative procedure in a computer program to optimize process parameters for minimum total cost. The hybrid PV + distillation process yields better utilization of the sugar in the feed because of decrease in inhibition. The results indicated that the raw material and membrane fixed cost contribute more than 80% of the direct production cost. Further, the direct production cost of EtOH cost for the hybrid process was found to be 12%–16% lower than the conventional process.

8.4.3 Organic–Organic Separations

In the applications of PV discussed in Sections 8.4.1 and 8.4.2, there are clear and substantial differences in the properties of the solutes to be separated. The major distinguishing features relate to the polarity/hydrogen bonding properties of the solutes. Thus, the selection of the membrane polymer is relatively easy. In the case of organic–organic systems only in the case when one of the solutes contains strong hydrogen bonding (OH) or polar groups while the other is entirely non-polar, the selection of the polymer can be done by the thumb rule of hydrophilicity/hydrophobicity of the polymer. Examples of such systems are methanol–toluene, methanol–benzene, and i-propanol–toluene/benzene. On the other hand, when both the solutes have similar properties, the selection of the membrane polymer requires careful consideration. However, in this case also, small differences in the polarity of the solutes can be exploited to effect relatively good separation. Ray et al. developed several methanol selective copolymer membranes for separating...
methanol from methyl tertiary butyl ether (MTBE) and ethylene glycol. These investigators used the concept of 3D solubility parameter and prepared several copolymers of AN with other hydrophilic monomers like HEMA and vinyl pyrrolidone. By properly tuning the copolymer composition, membranes with relatively high selectivities for methanol were obtained. These membranes have good stability because the hydrophilic group that is bonded to the AN backbone is not easily plasticized by methanol. Similar approach was successfully applied by Ray et al.\textsuperscript{[22]} to effect the much more difficult separation of benzene and cyclohexane. These two compounds have substantially the same properties except that due to the continuous shifting of the double bonds in benzene, there is a small contribution from polar and hydrogen bonding forces to the overall solubility parameter of benzene.

In this case, copolymers of AN with relatively hydrophobic compounds like methyl methacrylate (MMA), vinyl acetate, and styrene were employed for obtaining benzene selective membranes. The choice of the comonomers was dictated by the fact that their homopolymers are soluble in benzene and thus their inclusion in the copolymers would enhance benzene sorption. The extent of the comonomer in the copolymer was varied in order to obtain an optimum composition. All the membranes were found to yield benzene selectivities much higher than those reported earlier. The selectivities depended upon the copolymer type and its composition and varied from 5 to 80. This work clearly proves the utility of the copolymer concept combined with the 3D solubility parameter theory to design suitable membranes for relatively difficult separations. Further, because of the presence of the relatively tough and insoluble AN backbone, these membranes are very stable.

### 8.4.3.1 Sulfur Removal from Petrochemicals

Transportation fuels are a major requirement across the world. Basically, two types of transportation are produced in the refineries: (1) gasoline and (2) diesel. In both cases, environmental regulations are becoming increasingly stringent particularly in terms of the sulfur content of the fuel. These two fuels have distinctly different compositions in terms of the composition, boiling point range, etc. Gasoline is a low-boiling fuel used in small automobiles. Diesel on the other hand is a much higher-boiling fuel. Gasoline contains low-boiling sulfur compounds such as mercaptan and thiophenes. Sulfur species in diesel are relatively high-boiling compounds like alkyl benzothiophenes. Conventionally, in both cases, sulfur is removed by hydrosulfurization (HDS). HDS converts sulfur species into hydrogen sulfide through. The temperature and pressure conditions for HDS depend upon the type of sulfur compounds and their steric hindrance to hydrogenation. Thus, HDS of gasoline with simple mercaptans and thiophenes requires much lower pressures as compared to diesel that has sterically hindered alkyl benzothiophenes. Capital and operating costs of HDS units vary accordingly, that is, lower for gasoline and higher for diesel. However, for both fuels, HDS causes a deterioration of performance in terms of octane/cetane rating since the hydrogenation cannot be restricted to sulfur species alone. The hydrogen balance in a refinery is becoming progressively critical due to increasing hydrogen requirement in hydroprocessing of heavier stocks (bottom of the barrel processing). Therefore, there is a concerted effort to develop benign/cost-effective processes for sulfur removal from fuels. As explained earlier, PV is suitable for selective separation/recovery of low-boiling compounds. Consequently, PV can be applied for sulfur removal in gasoline. It is however, not suitable for the case of diesel due to the relatively low volatility of the sulfur species in it. Adsorption is gaining importance for sulfur removal from diesel.\textsuperscript{[191]}  

Song reported an overview\textsuperscript{[485]} of new approaches to deep desulfurization for ultraclean gasoline, diesel fuel, and jet fuel. Both PV and adsorption are physical processes that do not require severe conditions. Thus, these processes can remove sulfur at insignificant energy and capital costs as compared to HDS. Further, unlike HDS, they do not affect the basic fuel rating. PV has the additional advantage that it does not require regeneration of the membrane, whereas in adsorption, the loaded adsorbent needs to be regenerated.

#### 8.4.3.1.1 Membrane Materials for Desulfurization

The main aim for FCC gasoline desulfurization is to remove thiophenic sulfur compounds. Membranes made from polar polymers with solubility parameter close to thiophenic sulfur are used for desulfurization of gasolines by PV.\textsuperscript{[486]} It is evident that solubility parameter of primary sulfur components of gasolines, that is, thiophenic sulfur components, is 19–21 (J/cm\textsuperscript{3})\textsuperscript{1/2}, while for other hydrocarbons, these values are 14–15 (J/cm\textsuperscript{3})\textsuperscript{1/2}. This difference can be exploited for separation by PV. Solubility parameter values of most of the polymers used as membrane material lie in the range\textsuperscript{[486]} of 21–26 (J/cm\textsuperscript{3})\textsuperscript{1/2}. Thus, membranes made from these polymers afford good selectivity for thiophenic sulfur. Apart from various homopolymers, chemically and physically modified polymers have also been used for pervaporative desulfurization. Some of these modifications include using different types and amounts of cross-linkers, blending two polymers, and copolymerization. Composite and treated ionic membranes have also been tried for this separation. Polymer membranes tried for this separation include PDMS/PAN, PDMS/PEI, PDMS/PES, PDMS/ceramic, polyetherimine (PI)/polyester, PEG/PES, and PU/PTFE.\textsuperscript{[486]}

#### 8.4.3.1.2 Operating Parameters

Permeation rate, enrichment factor, and selectivity of organosulfur compounds under various process conditions
like feed concentration and type of organosulfur; feed flow rate; feed temperatures; permeate pressure; presence of other components, that is, alkanes and alkenes; and aromatics have been studied in great details with various membranes. Some of these results are shown in Figure 8.4a and b.\textsuperscript{187} It appears that for low feed concentration of thiophene in isooctane, the copolymer membrane can selectively remove thiophene.

Two commercial processes based on PV have been reported: (1) S-Brane\textsuperscript{®} technology\textsuperscript{488} of W.R Grace and Co. and (2) Transsep technology\textsuperscript{60188} of Trans Ions Corporation. Table 8.5 gives a summary of the literature investigations on organic–organic separations.

The early enthusiasm for PV was a result of its various advantages vis-à-vis distillation. This was evident from the fact that most majors like Exxon, Standard Oil, British Petroleum, and Texaco established research groups devoted to PV. The group at Exxon made a concerted effort for developing membranes for separating close boiling aromatic/aliphatic compounds. However, the selectivities obtained with the optimized membranes were not good enough to encourage a change over from distillation. Indeed, these rather unsuccessful efforts eventually resulted in closure of many groups. Currently, only a small number of companies (Sulzer, Chemtech, Ube, Mitsui, MTR, Permionics, Nanotech, etc.; information about list of companies in America, Europe, and Asia with its membranes, modules, and application areas are available in www.pervaporation.org.) are active in this area. Thus, despite the advantages of PV and its potential applicability to a wide range of organic–organic separations of great industrial interest, there are very few commercial examples. Steinhauser et al.\textsuperscript{196} have described the separation of an azeotrope of trimethyl borate and methanol using VP unit. VP is the analog of PV wherein the feed is vapor instead of liquid. Another documented application is in the manufacture of MTBE and ethyl tertiary butyl ether (ETBE). Both these ethers form an azeotrope with the alcohol. In a detailed engineering study, Hommerich\textsuperscript{190} has shown that PV can be advantageously used in a large-scale plant with significant savings in operating costs.

With the rising cost of crude oil and energy, distillation may be placed at a greater disadvantage because of its energy-intensive nature. PV, with its low operating costs, is most likely to receive a revived interest. Particularly important applications of interest will be separation of organic azeotropes and close boiling mixtures. A concerted effort is needed to develop membranes with higher selectivities than the currently available to ensure that PV does not remain a small-scale application.\textsuperscript{59}

\subsection*{8.4.4 Cost and Longevity of Pervaporation Plant}

There are few reports available on cost and longevity of PV membrane on industrial scale. Normal lifetime for PV membrane is 2–4 years\textsuperscript{176} depending on the type of membrane and the nature of application. Higher extent of cross-linking of the membrane results in increased selectivity and longer membrane life. However, this is at the expense of flux. Lipnizki et al.\textsuperscript{182} studied the effect of membrane life and membrane cost on annual cost of a batch and continuous PV plant for recovery of natural aroma in food industries. It was found that reduction of membrane lifetime from 24 to 6 months (by replacing a new membrane module after 6 months) increased membrane cost by 3% and a 5% increase in membrane replacement cost led to marginal (only 0.3%) increase in annual cost of a semibatch-type PV plant. This may be ascribed to the fact that a small membrane area is required for semibatch process. However, for a continuous PV plant, this increase was quite significant (around 30%) because of much higher membrane area. It must be stated here that the application studied by Lipnizki et al.\textsuperscript{176} related to recovery of high-value components in which the value of the recovered material masks other costs. This analysis is unlikely to apply to low-value compounds like ethanol and \textit{i}-propanol.
<table>
<thead>
<tr>
<th>System</th>
<th>Membrane Used</th>
<th>Remark</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butadiene is separated from its mixture with trans-2-butene.</td>
<td>Polybenzimidazole membrane</td>
<td>$\beta = 4.9$.</td>
<td>[191]</td>
</tr>
<tr>
<td>1,3-Butadiene is separated from its mixture with trans-2-butene.</td>
<td>PVC membrane</td>
<td>Separation of dienes from mono-olefins.</td>
<td>[192]</td>
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<tr>
<td>Toluene/heptane.</td>
<td>PAN composite membrane</td>
<td>High selectivity and high permeate fluxes were obtained.</td>
<td>[194]</td>
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<tr>
<td>Separation of alcohol toluene mixture.</td>
<td>$N$-Acetylated chitosan membrane</td>
<td>Additional acetyl groups in the membrane decreased the flux but increased $\alpha$.</td>
<td>[195]</td>
</tr>
<tr>
<td>$n$-Butyl acetate–$n$-butanol–methyl acetate–methanol.</td>
<td>Sulzer Pervap-2255 membrane</td>
<td>Combination of reactive distillation and PV allowed 100% conversion.</td>
<td>[196]</td>
</tr>
<tr>
<td>Ethyl acetate–isoctane mixtures.</td>
<td>Commercial PolyAn GmbH, Germany</td>
<td>Separation factor of 22.34 with a total permeate flux of 6.3 kg/m$^2$ h at 30°C and a feed concentration of 25 wt% ethyl acetate. Membrane preferentially permeated ethyl acetate.</td>
<td>[197]</td>
</tr>
<tr>
<td>$n$-Octane/thiophene.</td>
<td>PDMS/ceramic composite membrane</td>
<td>At 303.15 K, the composite membrane exhibited high performance with the total flux of 5.37 kg/m$^2$ h and the corresponding sulfur enrichment factor of 4.22 for 400 μg/g sulfur in feed under 210 Pa.</td>
<td>[198]</td>
</tr>
<tr>
<td>Toluene–methanol.</td>
<td>PDMS–polyimide IPN membrane</td>
<td>The membranes preferentially permeated toluene depending on the amount of polyimide present in the IPN.</td>
<td>[199]</td>
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<tr>
<td>Methanol–benzene.</td>
<td>RC (cellophane), (PVA), CA, cellulose tri-acetate (CTA), two blends of CTA (B1 and B2) with acrylic acid, poly(dimethylsiloxane) (PDMS), and low-density polyethylene (LLDPE) membrane</td>
<td>Methanol selectivity PVA &gt; CA &gt; CTA &gt; B1 &gt; B2. The influence of the membrane material with varying solubility parameter is investigated.</td>
<td>[24]</td>
</tr>
<tr>
<td>Methanol–toluene.</td>
<td>RC (cellophane), (PVA), CA, cellulose tri-acetate (CTA), two blends of CTA (B1 and B2) with acrylic acid, poly(dimethylsiloxane) (PDMS), and low-density polyethylene (LLDPE) membrane</td>
<td>The IPA selectivity performance was cellophane &gt; PVA &gt; CA &gt; CDA &gt; CTA.</td>
<td>[26]</td>
</tr>
<tr>
<td>Methanol–toluene.</td>
<td>AN-based copolymer membrane</td>
<td>The permeation, selectivity and flux variation with methanol concentration have been explained using the solubility parameter approach.</td>
<td>[15]</td>
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<tr>
<td>Sorption and diffusion of gasoline components.</td>
<td>HEC membrane</td>
<td>The difference of sorption/diffusion rates between sulfur and nonsulfur compounds increased with increasing cross-link density, predicting that permeation flux decreased but sulfur enrichment factor increased.</td>
<td>[199]</td>
</tr>
<tr>
<td>Pervaporative desulfurization.</td>
<td>Poly(dimethyl siloxane) (PDMS)/poly(oligosilsesquioxanes) (POSS) composite membrane</td>
<td>Composite membranes are found to be promising for the separation of thiophene from $n$-heptane.</td>
<td>[200]</td>
</tr>
</tbody>
</table>

**Special Applications**

**Petroleum Industries**

- **Design and analysis of combined distillation and PV processes for methanol/DMC, methanol/MTBE, and IPA/water**
  - Cross-linked PVA (Pervap 1510) and plasma-polymerized Pervap 1137
  - Hybrid PV + distillation has better economics particularly in terms of low premium energy requirement.

- **Sulfur removal from gasoline**
  - Copolymers of AN with HEMA/MMA
  - $\beta$ ranging from 1.5 to 15.  

(Continued)
Pervaporation

NOMENCLATURE

- \( a_i \): Activity of component \( i \)
- \( A_{ii}, A_{ij}, A_{ji}, B_{ij}, B_{ji} \): Diffusional interaction parameters in Section 8.2
- \( A_i \): Plasticization coefficient (m\(^3\)/mol\(^n\)) in Equations 8.15 and 8.17
- \( C_{(r, o)} \): Molar concentration at the pore outlet (mol/m\(^3\))
- \( C_{(r, z)} \): Molar concentration in the cylindrical pore at a point (mol/m\(^3\))
- \( C_{bi} \): Concentration of component \( i \) in the bulk in Equation 8.6 (mol/m\(^3\))
- \( C_{ai} \): Concentration of selectively permeating solute \( i \) in the feed in Equation 8.28 (mol/m\(^3\))
- \( C_{pi} \): Membrane phase concentration of “i” in the permeate side in Equation 8.28 (mol/m\(^3\))
- \( C_{mi} \): Concentration of a component \( i \) in the membrane in Equation 8.6 (mol/m\(^3\))
- \( C_m \): Membrane phase concentration of the solute in Equations 8.7 and 8.8 (wt. fraction)
- \( C_b \): Bulk liquid phase concentration of the solute in Equation 8.8 (wt. fraction)
- \( C_T \): Total concentration of the solute in the membrane in Equation 8.7 (mol/m\(^3\)) (wt. fraction)
- \( C_z \): Wt. fraction of solute in zeolite phase
- \( D \): Diffusion coefficient (m\(^2\)/s)
- \( D_i \): Diffusion coefficient of component \( i \) (m\(^2\)/s)
- \( D_{io} \): Diffusion coefficient of component \( i \) at infinite dilution (m\(^2\)/s)
- \( D_{jo} \): Diffusion coefficient of component \( j \) at infinite dilution (m\(^2\)/s)
- \( D_p \): Diffusion coefficient of component \( j \)
- \( d_{pore} \): Pore diameter (m)
- \( \Delta H_f \): Heat of fusion of polymer in Equation 8.13 (kJ/kmol)
- \( H_M \): Henry’s constant in Equation 8.8
- \( J_i \): Flux of component \( i \) (kg/m\(^2\) s), (mol/m\(^2\) s)
- \( k \): Sorption coefficient for the solute in the polymer in Equation 8.6
- \( K_L \): Mass transfer coefficient for the boundary layer (m/s)

TABLE 8.5 (Continued)
Organic–Organic Separation

<table>
<thead>
<tr>
<th>System</th>
<th>Membrane Used</th>
<th>Remark</th>
<th>References</th>
</tr>
</thead>
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<tr>
<td>General and Review Articles</td>
<td>Polymeric and ceramic membranes</td>
<td>Review (German).</td>
<td>[202]</td>
</tr>
<tr>
<td>Development in membrane technology</td>
<td>Polymer grafted membrane</td>
<td>An overview of selected membrane techniques for environmental applications.</td>
<td>[203]</td>
</tr>
<tr>
<td>PV and other membrane separations</td>
<td>PEI-based polymer film of 40 μm thickness</td>
<td>Measured fluxes are independent of severe fouling and virtually independent of concentration up to 100 g/L total solids.</td>
<td>[204]</td>
</tr>
<tr>
<td>Production of desalinated water from highly contaminated water</td>
<td>PDMS composite membrane</td>
<td>With the increase of glucose concentration from 0 to 100 g/L, the total flux decreases by 25%, but the separation factor for ethanol increases from 7.7 to 10.</td>
<td>[205]</td>
</tr>
<tr>
<td>Separation of ethanol from a real yeast solution</td>
<td>Polymeric membrane</td>
<td>Review (Chinese).</td>
<td>[206]</td>
</tr>
<tr>
<td>Solvent recovery</td>
<td>Facilitated transport supported liquid membrane (FTSLM)</td>
<td>Some examples of separation of organic compounds from mixtures (p-xylene/m-xylene, benzene/cyclohexane) were discussed, including separation of organic gases, wastewater, and organic solutions.</td>
<td>[207]</td>
</tr>
<tr>
<td>Separation of organic mixtures</td>
<td>Dehydration of organics and organic removal from aqueous streams</td>
<td>Review in Chinese.</td>
<td>[208]</td>
</tr>
<tr>
<td>Organic–water</td>
<td>Application of PV and VP</td>
<td>General review, examples of polymers for membrane preparation, and performance parameters of PV and VP membranes are described.</td>
<td>[209]</td>
</tr>
<tr>
<td>Separation of liquid mixture</td>
<td>Zeolite molecular sieve membrane</td>
<td>It is found that zeolite membranes, disk, and coating show high performance or potential as catalysts compared with conventional catalysts.</td>
<td>[210]</td>
</tr>
</tbody>
</table>
Handbook of Membrane Separations: Chemical, Pharmaceutical, Food and Biotechnological Applications

Overall mass transfer (m/s)

\( k_o \)

Overall mass transfer coefficient in Equation 8.29 (m/s)

\( K_o \)

Fluid to membrane mass transfer coefficient in Equation 8.29 (m/s)

\( k_d, k_j \)

Constants in Equations 8.18 through 8.21

\( L \)

Thickness of membrane in Equation 8.28

\( M_c \)

Molecular weight between two cross-links

\( M_v \)

Molecular weight of repeating unit of polymer (kg/mol)

\( n \)

Constant in Equation 8.15

\( n_1, n_2 \)

Number of moles of component 1 and 2, respectively, in Equation 8.4

\( n_i \)

Ratio of molar volume of polymer to solute in Section 8.2

\( \rho_i^c \)

Critical (partial) vapor pressure of component i in Equation 8.1

\( \rho_i^p \)

Partial pressure of component i at equilibrium state in Equation 8.1

\( \rho_2 \)

Effective pressure (atmospheric pressure/RO pressure) of A and B at the pore inlet in Equation 8.1

\( \rho_1 \)

Effective pressure (atmospheric pressure/RO pressure) of A and B at the pore outlet in Equation 8.1

\( r, z \)

Cylindrical coordinates (m)

\( R \)

Universal gas constant (8.314 kJ/kmol K)

\( S \)

Sorption coefficient in Equation 8.29

\( S_A \)

Sorption coefficient for A

\( S_B \)

Sorption coefficient for B

\( T \)

Temperature (K)

\( T_m \)

Melting temperature of the crystalline phase (K)

\( V \)

Solution velocity in pore (m/s)

\( V_i \)

Molar volume of component i (cm³/mol)

\( V_1, V_2 \)

Molar volumes of components 1 and 2, respectively, in equations in Section 8.2 (m³/mol)

\( \delta_p \)

Contribution of polar forces towards solubility parameter (MPa)½

\( \Phi_p \)

Volume fraction of the polymer

\( \eta \)

Solution viscosity in the pore (Pa s)

\( \lambda \)

Fraction of noncrystalline polymer in Equation 8.13

\( \Delta \mu \)

Chemical potential difference between the two phases in Equation 8.10

\( \rho_p \)

Polymer density (kg/m³)

\( \sigma_p \)

Surface tension of liquid in pore (N/m) in Equation 8.1

ABBREVIATIONS

A  Solute, A

ABE  Acetone–butanol–ethanol

AN  Acrylonitrile

B  Solute, B

CA  Cellulose acetate

CDA  Cellulose diacetate

COD  Chemical oxygen demand

CP  Concentration polarization

CPI  Chemical process industries

CTA  Cellulose triacetate

EA  Ethyl acetate

EB  Ethyl butyrate

EGDM  Ethylene glycol dimethacrylate

EP  Ethyl propionate

EPDM  Ethylene propylene diene monomer

ETBE  Ethyl tertiary butyl ether

FTSLM  Facilitated transport supported liquid membrane

HEMA  Hydroxyethyl methacrylate

IPN  Intercalated polymer networks

LDPE  Low-density polyethylene

MARS  Membrane aromatic recovery system

MF  Microfiltration

MMA  Methyl methacrylate

MS  Mild steel

MTBE  Methyl tertiary butyl ether

NBR  N-butyl rubber

NR  Natural rubber

NRS  Nonrenewable resources

PAA  Poly(acrylic acid)

PCE  Perchloroethylene

PDMS  Poly(dimethyl siloxane)

PEBA  Poly(etherimide block polymer)

PMMA  Poly(methyl methacrylate)

POMS  Poly(octyl methyl siloxane)

PP  Polypropylene

PSI  Pervaporation separation index

PV  Pervaporation

PVA  Poly(vinyl alcohol)

PVC  Polyvinyl chloride

RO  Reverse osmosis

RTV  Room temperature vulcanization

SBR  Styrene butadiene rubber

Δ  Signifies difference in two properties

GREEK LETTERS

\( \alpha_s \)

Sorption selectivity

\( \alpha_d \)

Diffusional selectivity

\( \alpha_s \)

Overall selectivity

\( \beta \)

Separation factor defined by Equation 8.33

\( \chi_{AB}: \chi_{AM} \)

Friction constants between A

\( \chi_{ip} \)

Interaction parameter for component i

\( \sigma \)

Overall solubility parameter (MPa)½

\( \delta_p \)

Length of the pore (m) in Equation 8.1

\( \delta_p \)

Contribution of dispersive force towards solubility parameter (MPa)½

\( \delta_h \)

Contribution of hydrogen bonding towards solubility parameter (MPa)½
REFERENCES

Pervaporation


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188. Web information (http://www.pervaporation.com)


