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REVIEW

Pervaporation Membranes

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ABSTRACT

Pervaporation processes are a basic unit membrane operation for the separation of liquid mixtures. They are an alternative for the separation of liquid mixtures which are difficult or impossible to separate by conventional methods. The interest in these processes in research institutions and industrial firms has resulted in an increasing number of publications of relevant work (including research papers and industrial patents) in the last decade. In this paper, some recent works on developments in pervaporation processes are reviewed and discussed.

INTRODUCTION

Pervaporation (PV) as a membrane process is today considered a basic unit operation with significant potential for the solution of various environmental and energetic processes (1). In the pervaporation operation, the feed mixture is maintained in contact with one side of a membrane and the permeate is continuously removed from the other side in vapor form by a vacuum pump (Fig. 1). A selective dense membrane can alter the vapor–liquid equilibrium that can be established among the components of the feed solution as the ternary solvent in extractive distillation. For this reason, the pervaporation process is considered as an alternative for the separation of liquid mixtures which are difficult or not possible to separate by conventional distillation methods. Many binary mixture pairs

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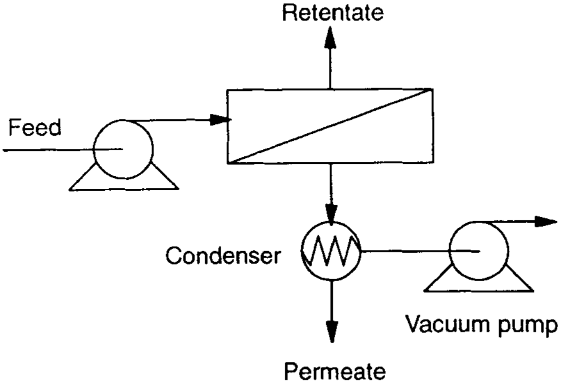

FIG. 1 Principle of pervaporation.

have been studied, and some separation pervaporation separation systems have been suggested or realized.

Although the pervaporation process was suggested early in the 1950s, there was no great progress in fundamental research and application studies for this separation technique until the end of the 1970s. Since then, many research papers have been published and industrial patents have been issued. The International Conference on Pervaporation Processes in the Chemical Industry has been held six times since 1986. The number of works on pervaporation cited in *Chemical Abstracts* indicates the increasing interest in pervaporation processes by both research institutions and industrial firms. Figure 2 shows the works on pervaporation cited in *Chemical Abstracts* from 1983 through 1992. In 1983, only six works (five research papers and one industrial patent) were cited. Ten years later, in 1992, there were 199 works (135 research papers, 11 reviews, and 53 industrial patents) cited. Before 1992, pervaporation appeared as a secondary subject entry in the general subject *permeability and permeation* in the Volume Index of *Chemical Abstracts*. Since then, the term has appeared as a new general subject.

Because of the energy-saving potential of pervaporation processes, much attention has been paid to research and development of the technique. In March 1988 the first large-scale plant for the dehydration of ethanol by the pervaporation technique was established by GFT mbH at Betheniville (France) (2). Since then, other industrial companies have built their own pervaporation units. Very selective and solvent stable membranes are commercially available, using materials such as poly(vinyl alco-

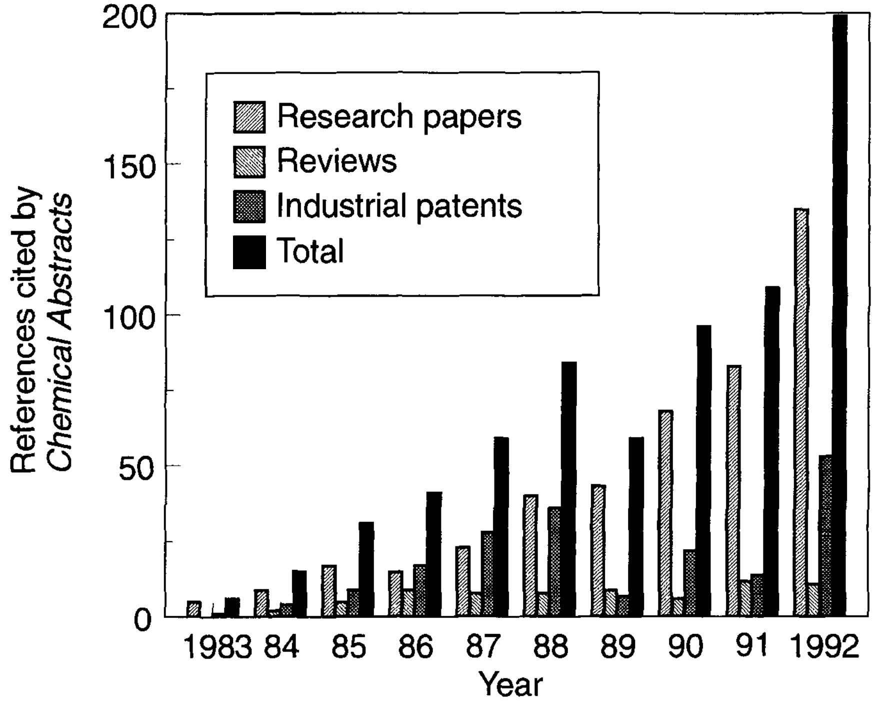

FIG. 2 Pervaporation-related references cited in *Chemical Abstracts*.

hol), polydimethylsiloxane, polyacrylate, chitosan, etc. More than 90 industrial units were in operation worldwide in 1992 (3).

Although there have been commercial successes and intensive worldwide research continues, the actual picture of the potential of pervaporation is still not clear. On the one hand, new membrane materials exhibiting good permselectivity should be developed for given separation problems; some aspects (e.g., coupling phenomena) of the permeation mechanism of liquid molecules through a polymeric membrane are not well understood. On the other hand, the potential of existing membranes has not yet been fully explored; the module and process design should be further developed. In recent years, many research results have been reported on membranes, module design, and case studies. There have been some reviews on module and process development (1, 3–6), and in this paper some recent works on the development in pervaporation are reviewed and discussed.

FUNDAMENTALS OF PERVAPORATION

In the pervaporation operation, only the dense layer of the membrane contributes to separation of the mixture. Mass transport in pervaporation is generally described by a solution–diffusion mechanism (1, 6). The model consists of three consecutive steps: 1) solution of the liquid feed penetrant molecules at the upstream surface; 2) diffusion through the membrane; 3) desorption of the permeate in vapor form at the downstream surface of the membrane. The *driving force* of permeation is the concentration gradient of the penetrants across the membrane. Due to the different properties of the penetrants and the membrane, the concentration gradient exhibits different modes, like those shown in Fig. 3. Mode I is the case of low swelling of penetrants in the membrane. In this case the concentration gradient is linear through the membrane and the use of a dense membrane is very effective. Mode II is the case where moderate swelling takes place and the effective thickness of the membrane is thinner than the total membrane thickness. Mode III is the case of a highly swollen membrane and the effective thickness is very thin. In both Modes II and III the effective thickness is very difficult to estimate. The diffusivity of the penetrants in a swollen region is not important unless the evaporation rate is not high enough on the surface of the permeate side. The diffusion coefficient in the active layer, which is normally concentration-dependent, is another factor that governs the permeation rate and the selectivity (6).

Based on the solution–diffusion mechanism, the permeation rate (J_i) of a single component (i) through a membrane in pervaporation can be

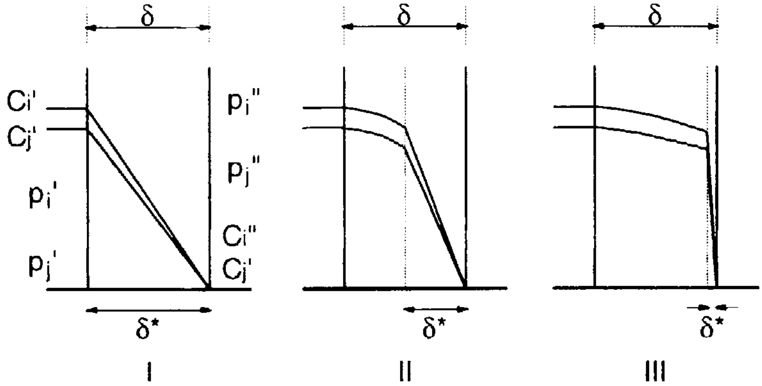

FIG. 3 Different models of the concentration gradient in pervaporation.

described by Fick's first law:

$$J_i = -D_i \frac{dC_i}{dx} \tag{1}$$

where D_i is the diffusion coefficient and C_i is the concentration of the component (i) in the membrane. Accordingly, the permeation rate can be described by

$$J_i = D_i \frac{C_i' - C_i''}{\delta} \tag{2}$$

where

$$C_i' = S_i p_i'; \qquad C_i'' = S_i p_i'' \tag{3}$$

where C' and C'' are the concentrations of the component, p' and p'' are the vapor pressures in the upstream and downstream, respectively; and S is the solubility coefficient. Thus,

$$J_i = \frac{P_i}{\delta}(p_i' - p_i'') \tag{4}$$

where

$$P_i = D_i S_i \tag{5}$$

is the permeability coefficient. Considering that pervaporation is generally operated under very low downstream pressure (the customary situation), i.e., $p' \gg p'' \rightarrow 0$, $C' \gg C'' \rightarrow 0$, and the upstream vapor pressure is the saturated vapor pressure p_i^0, Eqs. (2) and (4) reduce to

$$J_i = D_i C_i'/\delta \tag{6}$$

and

$$J_i = \frac{P_i}{\delta} p_i^0 \tag{7}$$

The separation factor $\alpha_{i/j}$, defined as the concentration ratio in the permeate (y_i/y_j) divided by the ratio in the feed (x_i/x_j), i.e.,

$$\alpha_{i/j} = \frac{y_i/y_j}{x_i/x_j} = \frac{J_i/J_j}{x_i/x_j} = \frac{P_i}{P_j}\frac{p_i^0/p_j^0}{x_i/x_j} \tag{8}$$

may be expressed as the product of solubility selectivity and diffusivity selectivity according to Eq. (6):

$$\alpha_{i/j} = \alpha_{i/j}^{S}\alpha_{i/j}^{D} \tag{9a}$$

where

$$\alpha_{i/j}^{S} = \frac{C_i'/C_j'}{x_i/x_j} \tag{9b}$$

and

$$\alpha_{i/j}^{D} = D_i/D_j \tag{10}$$

are the solubility-selectivity and diffusivity-selectivity, respectively.

Matsuura et al. (7–9) developed a new transport mechanism for pervaporation, the pore flow model. The mechanism consists of three consecutive steps: 1) liquid transport from the pore inlet to the liquid–vapor phase boundary; 2) evaporation at the phase boundary; and 3) vapor transport from the phase boundary to the pore outlet. From the model they have established the transport equations and discussed the predictability of the equations for pervaporation. The membranes used in this model were mainly microporous, and the permeation seems in substance to be *vacuum membrane distillation* rather than pervaporation.

For multicomponent transport, the coupling effect takes place due to strong interaction between penetrant molecules and membrane. The coupling phenomena are difficult to measure quantitatively, and it is also difficult to estimate beforehand the extent of the phenomena in relation to the separation properties. However, it is possible to get indirect information from flux measurement or sorption and desorption experiments. Some approaches for explaining coupling phenomena have been published based on pure component transport (10), Flory–Huggins theory (11), and the thermodynamics of irreversible processes (12). Some works focus on simulation of the pervaporation of a binary liquid mixture. For instance, Shelden and Thompson (13) established a semiempirical thermodynamic-diffusive model to numerically simulate the nonideal hexane/heptane/polyethylene system in which the dependence of activity and diffusivity of the penetrants on the upstream and downstream pressures were processed. A "six-coefficient exponential model," proposed by Brun et al. (14), computed the dependence of permeation rates and selectivity on feed composition and downstream pressure by using some experimental data and assuming an ideal moderate swelling of the membrane.

Considering that mass transport in pervaporation is basically the motion of individual molecules, the authors introduced (15, 16) a deviation coefficient (ϵ) and a molar normalized permeation rate (J^n) to describe the coupling effect.

$$\epsilon_i = \frac{J_i}{J_i^0 x_i} = \frac{J_i^n}{J_i^0} \tag{11}$$

where

$$J_i^n = J_i/x_i \tag{12}$$

are the molar normalized permeation rates.

The dimensionless deviation coefficient (ϵ) can be used to describe the actual permeation of a binary liquid mixture system. When ϵ is equal to unity, $J^n = J^0 =$ constant, pervaporation is under the ideal permeation situation. When $\epsilon > 1$, the interaction between membrane and penetrants accelerates the permeation of the penetrant; when $\epsilon < 1$, the interaction hinders the permeation. When $\epsilon > 1$ for both components, the permeation is enhanced transport; conversely, when $\epsilon < 1$ for both components, inhibited transport takes place. The normalized permeation rates are available to explain the coupled transport when one or two permeation rates of the pure component cannot be measured experimentally. As an example of the use of the deviation coefficient, the deviation coefficients $\epsilon_{\text{pyridine}}$ and ϵ_{water} for water/pyridine mixtures through an ion-exchange membrane are shown in Fig. 4 as a function of feed composition (16). It can be seen that the interaction speeds up pyridine permeation and slows down water permeation for both membranes. When the mole fraction of a component is high, its deviation coefficient varies a little; when its concentration is

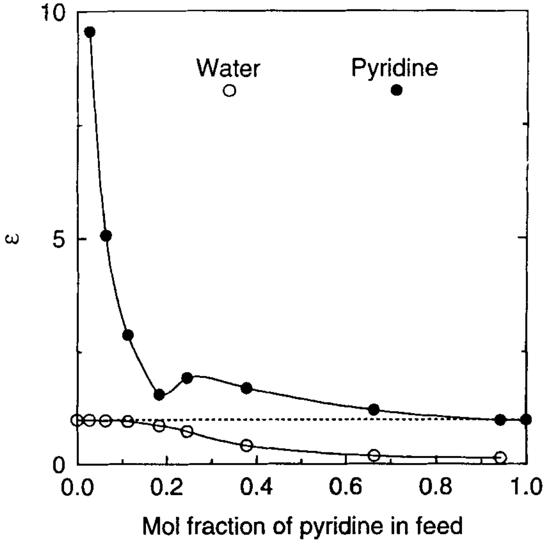

FIG. 4 Plot of deviation coefficients versus feed composition of water/pyridine mixtures through an ion-exchange membrane (16).

low, the interaction brings about a great change from pure component transport. In particular, at low pyridine concentration, $\epsilon_{\mathrm{pyridine}}$ increases significantly with a decrease of its mole fraction in the feed. This behavior can explain the permeation properties.

Although the permeability coefficient (P) is present in mass transfer equations for pervaporation, the concept has rarely been used because of the difficulty in determining partial vapor pressures in liquid mixtures. The permeation rate is sufficient for the comparison with permeation through other membranes; however, it becomes less comparable when the comparison is with different feed compositions and different operation temperatures for a given membrane. Zhang et al. (17) estimated the vapor pressures of water–ethanol mixtures and calculated the permeability coefficients for the permeation of water/ethanol mixtures through a chitosan membrane (Fig. 5). $P_{\mathrm{H_2O}}$ decreases with decreasing water fraction in the feed while P_{EtOH} Is always greater than P^0_{EtOH}. These results are attributed to plasticization and to dual-mode sorption of the penetrant molecules in the glassy polymer.

Interface resistance plays an important role in the pervaporation process. Bode et al. (18) considered the interface resistance in permeation through dense membranes. A theory which uses flux balance equations and split equations has been developed to describe transport across an

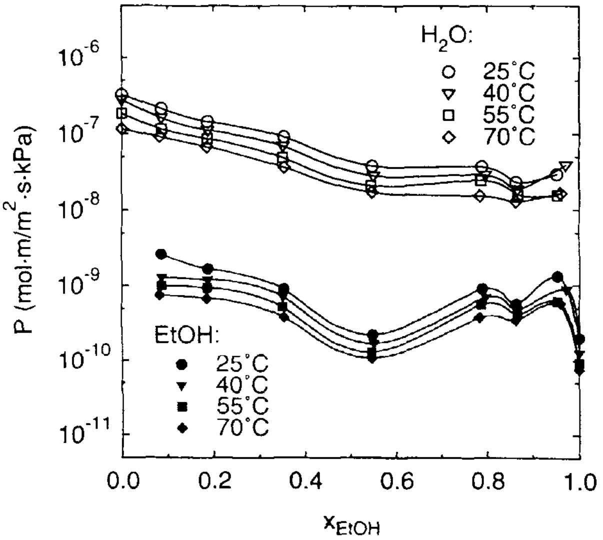

FIG. 5 Effect of feed composition on permeability coefficients of water/ethanol mixtures through a chitosan membrane (17).

interface between polymer and vapor, the step between the vapor and the adsorbed state being rate determining. Raghunath et al. (19) discussed the correlation of liquid boundary layer resistance in the pervaporation of dilute volatile organic compounds, and the relevant equations were established.

DESIGN AND CHOICE OF MEMBRANE MATERIALS FOR PERVAPORATION

For the practical application of pervaporation, the membrane must have a high permeation rate and a large separation factor. To obtain a higher permeation rate, an improved permeability coefficient is necessary (Eq. 7). Although a so-called trade-off relationship exists between permeability and selectivity, i.e., high selectivity is generally accompanied by low permeability, acceptable membrane materials with both high permeability and high selectivity may be synthesized by polymer design. According to the solution–diffusion mechanism, $P_i = D_iS_i$. While the separation factor is the product of solubility selectivity and diffusivity selectivity (Eq. 9), enhancement of the solubility and the diffusivity for the fast component and reduction for the slow component are required. Generally, diffusion of small molecules through a dense membrane is favored, and the solubility of a compound in a polymer is governed by the chemical affinity between the penetrant and the membrane. Therefore, when the difference of molecular size of two components to be separated in a mixture is large, permeation through the membrane may be preferential for the small component, although the solubility of the big component in the membrane is large. For this reason, many polymers are preferentially permeable to water rather than organic components because the water molecule is much smaller than the organic molecules. An organic selective membrane must have very high solubility for organic molecules.

Some work on the design of membrane materials has been published. Yamada and Nakagawa (20) discussed the swelling ratio or concentration in a membrane and the separation behavior of an alcohol solution with dense membranes such as silicone rubber blends, neutral and charged copolymers composed of hydrophilic and hydrophobic monomers, cross-linked and modified PVC, etc. They found that the permeation rates vary in proportion to degree of swelling, and that the separation factors are independent of concentration in membranes in most cases. Maeda et al. (21) investigated the relationship between the permeation properties and the polymer structure of water–alcohol and water–acetic acid mixtures through aromatic polymer membranes (Fig. 6). Poly(parabanic acid) (which has an excellent heat- and solvent-resistant nature) was a good

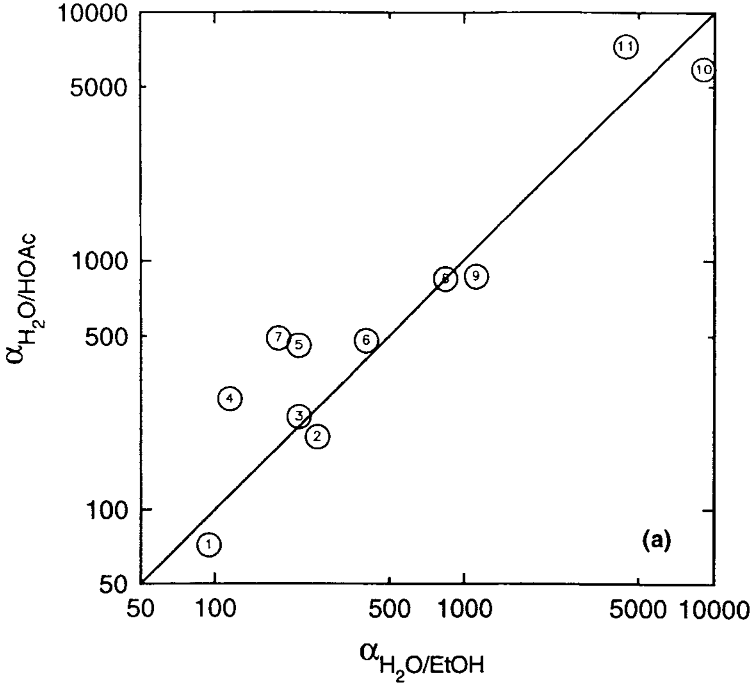

FIG. 6 Relationship between pervaporation properties through some aromatic polymer membranes. Pervaporation conditions: 70°C, 80 wt% acetic acid or ethanol aqueous solution (After Ref. 21). (a) Correlation of separation factors between water/acetic acid and water/ethanol mixtures. (b) Correlation of permeation rates between water/acetic acid and water/ethanol mixtures. (c) Separation factor for water/acetic acid plot against He or H_2 permeability. Indicators: 1: polyarylate U-polymer (PAR); 2: poly(parabanic acid) SOLLAC MF (PPA-MF); 3: polycarbonate (PC); 4: poly(2,6-dimethyl-1,4-phenylene oxide) (PPO); 5: poly(parabanic acid) SOLLAC TMF (PPA-TMF); 6: polyetherimide ULTEM 1000 (PEI); 7: PSF = polysulfone P-1700 (PSF); 8: polyamideimide TORLON 4000-T (PAI); 9: polyethersulfone P-300 (PES); 10: polyimide (benzophenone tetracarboxylic dianhydride/1,4-phenyl diisocyanate) (PI); 11: polyimide PI-2080 (PI-2080); 12: polyimide UPILEX-R (PI-R); 13: polyimide KAPTON 100-H (KAPTON).

membrane material for the separation of water–alcohol and water–acetic acid mixtures; the correlation between separation factor and gas permeability supported the separation mechanism of the aromatic polymer in which separation mainly occurred through the diffusivity differences.

Some of the most investigated polymers for pervaporation are given in Table 1. Because of addition to membranes of low content components (like crosslinking agents, selective adsorbents), different formation methods of membranes, different thicknesses of the dense layer, and different

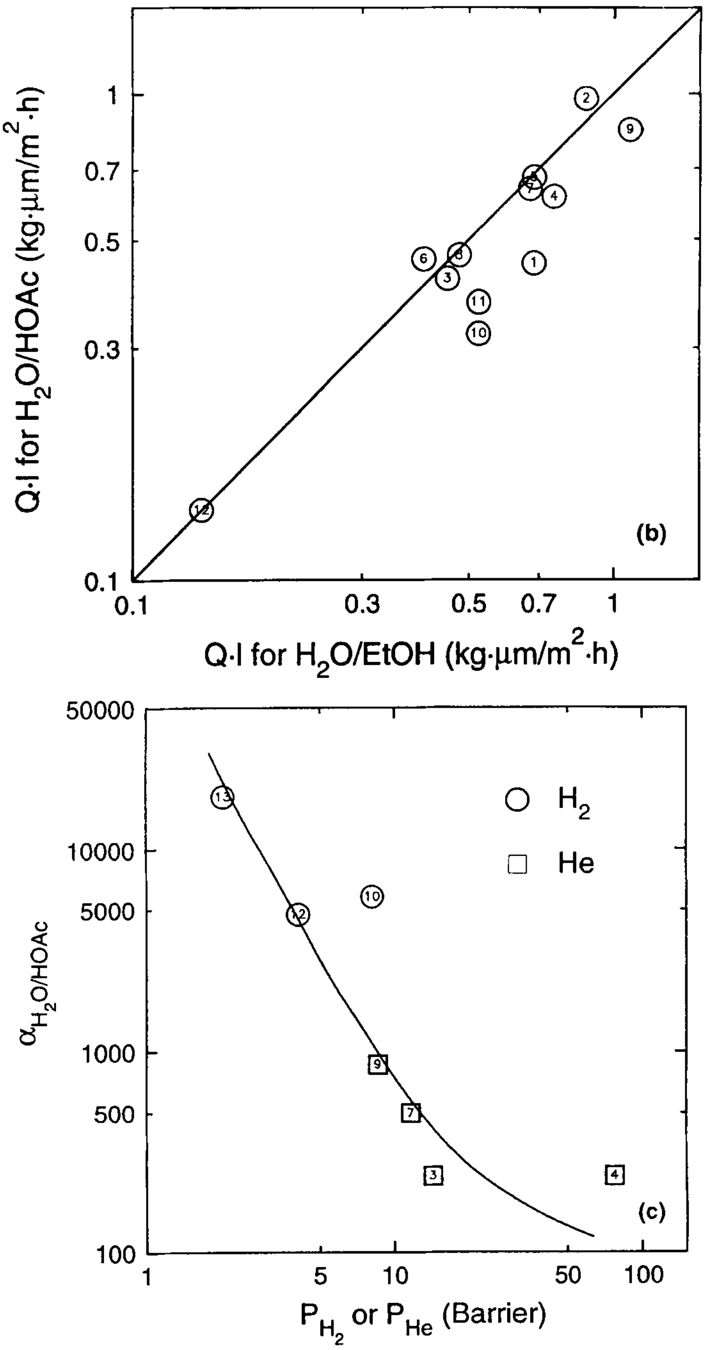

FIG. 6 Continued.

TABLE I
Polymers for Pervaporation[a]

Polymer	Application
Cellulose and derivatives	Extraction of water from an aqueous solution of ethanol, separation of benzene/cyclohexane mixtures
Chitosan	Extraction of water from an aqueous solution of ethanol
Collagen	Extraction of water from aqueous solutions of alcohols and acetone
Cuprophane	Extraction of water from an aqueous solution of ethanol
Ion-exchange resins (Nafion, etc.)	Extraction of water from an aqueous solution of ethanol, pyridine
LDPE	Separation of C_8 isomers
NBR	Separation of benzene/*n*-heptane
Nylon-4	Extraction of water from an aqueous solution of ethanol
PA	Extraction of water from an aqueous solution of ethanol, acetic acid
PA-*co*-PE	Separation of dichloroethane/trichloroethylene mixtures
PAA	Extraction of water from an aqueous solution of ethanol, acetic acid
PAN	Extraction of water from an aqueous solution of ethanol
PAN-*co*-AA	Extraction of water from an aqueous solution of ethanol
PB	Extraction of 1-propanol, ethanol from an aqueous solution
PC	Extraction of water from an aqueous solution of ethanol, acetic acid
PDMS filled with silicalite, molecular sieves, etc.	Extraction of alcohols from an aqueous solution, separation of butanol from butanol/oleyl alcohol mixture
PEBA	Extraction of alcohols and phenol from an aqueous solution, recovery of natural aromas
PI	Extraction of water from an aqueous solution of ethanol, acetic acid; separation of benzene/cyclohexane and acetone/cyclohexane mixtures
Plasma polymerized fluorine-containing polymers	Extraction of ethanol from an aqueous solution
Plasma polymerized PMA	Separation of organic/organic mixtures
Polyion complexes	Extraction of water from an aqueous solution of ethanol
Polysulfones	Extraction of water from an aqueous solution of ethanol, acetic acid
POUA	Separation of benzene/*n*-hexane mixtures
PP	Separation of xylene isomers
PPO	Extraction of water from an aqueous solution of alcohols, separation of benzene/cyclohexane mixtures
PTMSP/PDMS composite	Extraction of ethanol from an aqueous solution
PTMSP and derivatives	Extraction of ethanol from an aqueous solution
PUR	Extraction of ethanol from an aqueous solution
PVA	Extraction of water from an aqueous solution of alcohols, acetic acid, ethers, pyridine, etc.
PVC	Extraction of water from an aqueous solution of ethanol
Silicone rubber (PDMS, etc.)	Extraction of alcohols, ketones, hydrocarbons, halogenated hydrocarbons, amines, acetic acid, natural aromas, etc., from an aqueous solution

[a] AA: acrylic acid; LDPE: low density polyethylene; NBR: poly(butadiene–acrylonitrile); PA: polyamide; PAA: poly(acrylic acid); PAN: polyacrylonitrile; PB: polybutadiene; PC: polycarbonate; PDMS: polydimethylsiloxane; PE: polyester; PEBA: polyetheramide-block-polymer; PI: polyimide; PMA: poly(methyl acrylate); POUA: poly(oxiethylene urethane acrylate); PP: polypropylene; PPO: poly(phenylene oxide); PTMSP: poly(trimethylsilylpropyne); PUR: polyurethane; PVA: poly(vinyl alcohol); PVC: poly(vinyl chloride).

permeation conditions in characterization, the permeation performance varies in different researchers' reports. Thus, only the separation mixtures are presented.

FABRICATION OF MEMBRANES FOR PERVAPORATION

According to Eq. (7), an effective means for increasing the permeation rate is by reducing the thickness of the membrane for a given membrane material. Either a composite or asymmetric membrane in which the porous support or sublayer offers the mechanical strength of the membrane can be the membrane candidate. Since only the dense layer controls the separation property as in the separation of pressure-driven membrane operation, any method which can produce a thin or ultrathin defect-free dense layer can be used in the fabrication of a pervaporation membrane. Direct coating, transfer coating, in-situ formation or modification, spreading of polymer solution on water surface, plasma polymerization, and chemical vapor deposition and polymerization are some examples for the preparation of defect-free dense layer membranes. In the paper of Heinzelmann (22), the formation of dense membrane layers on porous supports by coating and in-situ polymerization methods was described; the posttreatment of membranes was also discussed. The membrane may be in a flat sheet, spiral and wound, or capillary and hollow fiber form. For examples, the GFT system at Betheniville (France) is equipped with flat sheet PVA composite membranes used for the dehydration of ethanol (1); Sampas PV modules are based on silicone rubber capillary membranes used for the removal or recovery of organic solvents from wastewater (23); and Tokuyama Soda's dewatering systems are equipped with chitosan hollow fiber membranes (24).

SEPARATION OF DILUTE ORGANIC AQUEOUS SOLUTIONS

The separation of dilute organic aqueous solutions is an important area of pervaporation in chemical and biochemical industries. It concerns the treatment of industrial wastewater, the recovery of noble substances in aqueous solution, the improvement of biofermentation processes, and the production or recovery of aromas from fermentation broths. Many studies have focused on these areas.

For the enrichment or removal of organic compounds from their dilute aqueous solutions, the more convenient separation is extracting the organic compounds from the bulk solutions; therefore, organophilic or hydrophobic membranes are used. Since water molecules are very small in comparison with organic molecules, diffusion through polymeric matrices is preferential for water and so the diffusion selectivity organic/water is less than unity. Therefore, the membrane materials must possess very high affinity to organic molecules in order to govern the permselectivity. Silicon-containing polymers generally exhibit good organophilicity, and silicon rubber (mainly polydimethylsiloxane, PDMS) based membranes have been the most investigated for many organic–water mixture systems such as alcohols, ketones, phenols, hydrocarbons, chlorohydrocarbons, etc. Crosslinked PDMSs are reported to have good stability in organic solutions and quite good permselectivity for organic compounds. Commercial hydrophobic membranes based on silicon rubbers are now available. Watson and Payne (25) and Blume et al. (26) reported the sorption and permeation properties of organic compounds through PDMS membranes.

To improve the selectivity, hydrophobic adsorbents such as molecular sieves have been entrapped in PDMS matrices. The adsorbents used have good solubility to organics and may create new permeation "tunnels," for the penetrants. The filled membranes show a higher separation factor for organics on water with no loss or enhancement of permeation rate in comparison with the bulky PDMS membrane (27, 28).

In 1986 a series of backbone-unsaturated silicon-containing polypropynes [for instance, polytrimethylsilylpropyne (PTMSP) and its derivatives] was reported to have high permeable to gas; the same materials have been found interesting for pervaporation (29–31). PTMSP has a very high permeation rate but it is not stable for gas permeation.

For the extraction of alcohols from aqueous solution, Jopski et al. (32) systematically studied the permeation properties of ethanol–water mixtures by pervaporation with silicon-containing polymer membranes: pure, silica filled, blocked, and blended PDMS membrane. Interpenetrating networks (IPN) of acrylates in PDMS gum were also investigated. Slater et al. (33) studied the pervaporation performances of ethanol, *n*-butanol, and *t*-butanol dilute aqueous solutions through PDMS, PTMSP, and poly(methoxy siloxane) (PMS) membranes. As in the case of gas permeation, the loss of permeability of an organic liquid with operation time was also observed in pervaporation processes. Volkov et al. (34, 35) investigated the pervaporation properties of ethanol and acetone aqueous solutions through polyvinyltrimethylsilane (PVTMS), PVTMS–PDMS block copolymers, PVTMS–polybutadiene (PB) block copolymers, MDK and MDK-U, and other modified PTMSP membranes. Gudernatsch et al. (36) reported the influence of a composite membrane structure on pervaporation: they used Kirchhoff's resistance theory to model the pervaporation performances of ethanol/water mixtures through polyethersulfone and PDMS-coated composite membranes.

Plasma polymerization or modification and radiation curing are very effective methods to prepare defect-free ultrathin membranes. This technique can polymerize any type of monomer including saturated small molecules which cannot be polymerized at normal conditions. Masuoka et al. (37) studied plasma polymerization to prepare silicon-free organophilic membranes: they used a cold plasma method to prepare perfluoropropane composite membranes on a polysulfone porous support and discussed the effect of pore size of porous support, carrier gas, and treatment time on the pervaporation properties of an ethanol/water mixture through the composite membrane. Scholz et al. (38) investigated radio-cured PDMS and molecular-sieve-filled PDMS membranes; the effect of the porous support layer on the permselectivity of ethanol–water mixtures indicated that the nature of the porous support plays a very important role on the separation factor.

For the dehydration of nonalcohol organic aqueous mixtures, Kujawski et al. (39) and Drioli et al. (15) separately studied the pervaporation of pyridine/water mixtures. The former reported the pervaporation performances of pyridine/water mixtures through cation-exchange membranes and a neutral PVA membrane; a hybrid large-scale pervaporation process combined with conventional distillation was suggested. The latter reported the direct recovery of pyridine from dilute aqueous solution using three types of membranes (selective to low-content pyridine mixture, pyridine/water azeotrope, and high-concentrated pyridine solution). Deng et al. (40) studied the separation of acetic acid/water mixtures by pervaporation using the PDMS membrane. Dettwiler et al. (41) reported the recovery of acetoin by pervaporation in the bioproduction of acetoin and butanediol.

Nonsilicon synthetic membranes have also been reported in recent years (37, 42–46). The most investigated is the polyetheramide block polymer (PEBA), used for the extraction of alcohols and aromatic hydrocarbons; the membrane exhibits good selectivity for high boiling bioproducts. Böddeker et al. (42) studied the pervaporation of isomeric butanols; they characterized some silicon-containing and PEBA polymeric membranes and a supported liquid membrane for the pervaporation of isomeric butanol and benzyl alcohol aqueous mixtures. Matsumoto et al. (47) reported the pervaporation of phenol–water mixtures through PEBA membranes: the individual permeation rates of phenol and water in the mixtures and their solubility in the membrane showed similar tendency with feed composition; the diffusion rate of phenol in the pervaporation of the mixtures was not affected by the presence of water.

Peterson et al. (48) reported a study on the removal of halogenated hydrocarbons from waste streams by pervaporation or gas permeation through poly[bis(phenoxy)phosphazene] membranes, showing high separation factors for removing chlorinated hydrocarbon contaminants from water and nitrogen: 84 for methylene chloride from nitrogen, 27 for carbon tetrachloride from nitrogen, and about 10,000 from water. Roizard et al. (49) reported some results of sorption and pervaporation experiments for single solvents: small swelling value and low permeation rate were found for weakly polar organic solvents (alcohols, alkanes) and water; large swelling value and high permeation rate for strongly polar organic solvents (ethers, acetone, EtOAc).

Using suitable membranes, pervaporation can be used to extract the low-content component from a liquid mixture, proving the applicability of the technique for the removal of volatile pollutants in wastewater treatment. Many research reports have been published in recent years. Lipski and Côté (50) established a model of the process design for the removal of organic contaminants from water; PDMS hollow fiber modules were characterized for the pervaporation of synthetic wastewater containing trichloroethylene, and the costs (capital, operation, energy, etc.) of the process were compared with those of conventional technologies. Nakagawa et al. (51) studied the pervaporation enrichment of chlorine-containing organic hydrocarbons (1,1,2-trichloroethane, trichloroethylene, and tetrachloroethylene) from dilute aqueous solution through poly(acrylate-*co*-acrylic acid) composite membranes crosslinked with (*N*,*N*,*N*′,*N*′-tetraglycidyl metaxylenediamine); high selectivity and an acceptable permeation rate for the chlorohydrocarbons were obtained. Clément et al. (52) studied the extraction of ethyl acetate from aqueous solutions by pervaporation. Batch-type pervaporation of aqueous solutions of ethyl acetate was performed, and the process was modeled. A new method for the rapid determination of membrane characteristics was also proposed.

SEPARATION OF WATER FROM ORGANIC AQUEOUS SOLUTIONS

Since the size of water molecules is smaller than that of organic molecules, the diffusion of water molecules through a dense membrane is faster than that of organic molecules although the solubility is higher for the organic molecules. For this reason, many polymers are preferentially permeable to water rather than to organic components. However, it is better to use hydrophilic polymers as membrane materials in order to get a high water/organic separation factor.

Poly(vinyl alcohol) (PVA) is one of the most important materials in the chemical industry. Although pure PVA (100% or partially hydrolyzed) is soluble in water, it cannot be directly used in pervaporation for the extraction of water from organic aqueous solution. The hydroxyl group (—OH) in the polymer chain makes the modification of PVA very easy with many chemical reagents. GFT water selective membranes are made of chemically crosslinked PVA and used for the dehydration of alcohols and organic acids. Many researchers have also investigated this polymer. Yamada et al. (53) investigated the pervaporation of water–ethanol mixtures through PVA crosslinked with formaldehyde and glutaraldehyde: they found that the intermolecular bridges in polymer matrices of longer glutaraldehyde molecules caused a higher water/ethanol separation factor and that the crosslinking degree also influenced the permeation properties. Huang and Yeom published a series of papers discussing the pervaporation separation of aqueous mixtures using crosslinked PVA membranes (10, 54, 55): they used amic acid as a crosslinking reagent to prepare a modified PVA membrane, and they studied the pervaporation performances of ethanol and acetic acid aqueous mixtures.

Chitosan is a type of polysaccharide having good chemical resistance, and it easily forms membranes. Like PVA, this polymer must be modified with crosslinking reagents because of its instability in acidic solutions. The selectivity may also be improved by modification. Some researchers have reported modified chitosan membranes used for the pervaporation separation of water/ethanol mixtures (56–58). Watanabe and Kyo prepared a PAN porous supported chitosan hollow-fiber composite membrane which had good permselectivity (J_{total} = 0.6 kg/m^2·h and $\alpha_{\text{water/ethanol}}$ = 5000 at an ethanol concentration of 95%) for the dehydration of ethanol. Pratowidodo et al. (59) reported the pervaporation of ethanol–water mixtures using chemically modified algenate and chitosan membranes. Crosslinking with glutaraldehyde increased the water/ethanol selectivity and decreased the permeation rate for a chitosan membrane but did not improve the selectivity for an algenate membrane. Uragami et al. (60) reported the characteristics of permeation and separation for aqueous ethanol solutions through a glutaraldehyde (GA) crosslinked chitosan membrane in vapor permeation. They found that both the permeation rate and the separation factor of water/ethanol increased with increasing crosslinked GA content in the membrane. They gave the reason for the increase of the degree of swelling of the penetrants in the membrane and the decrease of chitosan crystallinity as GA crosslinking.

Aromatic polymers have been found to have excellent chemical and heat resistance. The systematic study on these polymers has established the relationship between the permselectivity and the polymer structure. Maeda et al. (21) studied a series of aromatic polymer membranes for the separation of water–ethanol and water–acetic acid mixtures; the relationship between separation factor and permeability, a comparison of the H_2O/HAc separation factor versus the H_2O/EtOH separation factor, and the H_2 or He permeability were reported (Figs. 4 and 5).

Tsuyumoto et al. (61) developed a hollow fiber membrane composed of a polyion complex (PIC) consisting of polyacrylic acid and a polycation. By varying the hydrolysis conditions and optimizing the posttreatment, they designed a 6-m^2 module with excellent permselectivity ($J_{\text{total}} \approx 400$ g/m^2·h and $\alpha_{\text{water/ethanol}} > 5000$ for 95 wt% ethanol at 60°C). Maser et al. (62) studied crosslinked collagen (a natural protein polymer) membranes for the pervaporation of ethanol, isopropanol, ethylene glycol, and an acetone aqueous mixture, indicating that the membranes are highly selective and permeable to water at low temperature, which provides the possibility of economically concentrating aqueous solutions of compounds which are sensitive to heat, such as fruit juice aroma and alcoholic beverages. Hanemaaijer and Versteeg (63) reported a vapor permeation method for IPA dehydration; they used some extremely hygroscopic salt (e.g., LiBr, LiBr/$ZnBr_2$/$CaBr_2$, TEG) solutions instead of a vacuum pump to take up the permeate (water). This resulted in a vacuum- and refrigeration-free operation. By using cascade hollow fiber modules (equipped with a PPO membrane, permeation membrane area 3–50 m^2), a production of 185 kg/h of 98% IPA was obtained at the end retentate with a feed of 230 kg/h of 85% IPA. Ping et al. (64) reported the concentration of inorganic acids by pervaporation: ion-exchange membranes were used for the purpose, and hydrochloric acid, sulfuric acid, and phosphoric acid were pervaporated. Sulfonic-acid-type membranes (such as a Nafion-like membrane) showed excellent pervaporation performances for these acids. As a example, the Nafion-like membrane can successfully break the azeotrope (20 wt% of HCl) of the hydrochloric acid/water system. Some works have been concerned with polyurethane (65), nylon-4 (66), cuprophane (67), ternary- and multi-component systems (68), etc.

SEPARATION OF ORGANIC–ORGANIC MIXTURES

For the pervaporation of water-free organic mixtures, some researchers studied the pervaporation of aromatic C_8-isomers. Wessling et al. (69) reported the pervaporation of ethylbenzene/xylenes and *p*-xylene/*o*-xylene mixtures through polyethylene membranes; the modeling of the process from the mass transport of pure components to the coupling phenomenon were discussed. Wytcherley and McCandles (70) studied the pervaporation separation of *m*-xylene/*p*-xylene mixtures through a polypropane membrane in the presence of CBr_4; they found that the pervaporation process was quite selective to *m*-xylene at temperatures below about 5°C and in the presence of 24 mol% CBr_4 in the feed, and that the separation factor ($\alpha_{p/m}$) varied from 1.2 to 0.05 depending on the temperature and feed composition. Sheng (71) reported the separation of dichloroethane/trichloroethylene mixtures by pervaporation; sorption experiments were carried out for a series of polymeric materials and membranes in order to screen suitable membrane materials, and Pebax (a block polymer of polyamide and polyether) was chosen for pervaporation of the given liquid pair. The Pebax 6312 and 5533 membranes showed high permeability but low preferential selectivity for dichloroethane. Tanihara et al. (72) reported the pervaporation performances of benzene/cyclohexane and acetone/cyclohexane mixtures through polyimide mixtures. The polyimides were synthesized from the condensation of BPDA and/or BTDA and/or 6FDA with TMPD and/or PD and/or DABA. The membranes were permeable preferentially to benzene and acetone. Photocrosslinked membranes had good selectivity and durability, but the permeability decreased. Yamaguvhi et al. (73) reported poly(methyl acrylate) prepared by plasma-graft polymerization for the pervaporation of organic–liquid mixtures: the stability of the membrane was tested for more than 50 organic solvents and water. The pervaporation properties showed that the membrane possessed high permselectivity for benzene/cyclohexane, chloroform/*n*-hexane, methyl acetate/cyclohexane, chloroform/CCl_4, and acetone/CCl_4 mixtures.

APPLICATIONS OF THE PERVAPORATION PROCESS

Theoretically, the pervaporation technique can be applied for the separation of any type of liquid mixture by changing the nature of the membrane in all concentration ranges. In practice, most research efforts have been concentrated on the separation of azeotropic mixtures, close boiling-point mixtures, structural isomers, removal of low-content components in a mixture, recovery or removal of trace substance, and to replace the equilibrium of chemical reactions. In Table 2, some applications of pervaporation and their state of the art are listed.

Such industrial companies as Deutsche Carbone (GFT), BP International (Kalsep), Lurgi, Sempas, MTR, Separex, Mitsui, Daicell, and Tokuyama Soda, are taking part in the industrial applications of the pervaporation process. Of these, Deutsche Carbone GmbH (the former GFT mbH) is the biggest producer in the world of pervaporation membranes and equipment. The 55 units for the dehydration of organic solvents built by Deutsche Carbone are summarized in Table 3. The membranes used in this equipment are in composite form with the selective layer made of

TABLE 2
Applications of Pervaporation Processes

Applications	State of the art
General applications:	
Dehydration:	
Alcohols: MeOH, EtOH, PrOH, BuOH	Industrially realized
Ketones: acetone, methyl ethyl ketone	Industrially realized
Acids: acetic acid, chlorinated acetic acid, sulfuric acid, sulfonic acid, hydrochloric acid	Pilot test
Amines: pyridine, cyclohexanamine	Pilot test
Extraction of organics from aqueous solutions:	
Removal of toxic components: hydrocarbons, halogenated hydrocarbons, amines, phenols	Partially industrially realized
Recovery of natural aromas in agro-food industry	Pilot test
Recovery of trace components: perfumery	Pilot test
Azeotropes, close boiling-point mixtures:	
EtOH/water, *i*-PrOH/water	Industrially realized
Pyridine/water	Pilot test
Organic mixtures:	
Ailphatic/aromatic: benzene/hexane, benzene/ethanol, benzene/cyclohexane	Laboratory tested
Isomers: butanols, C_8 isomers (xylenes, ethylbenzene)	Laboratory tested
Halogenated HCs: dichloroethane/trichloroethylene	Laboratory tested
Others: alcohol/ester, chlorohydrocarbons	Laboratory tested
Hybrid applications	
PV aimed chemical/biochemical reactors:	
Esterfication: ethyl acetate, butyl acetate	Laboratory tested, pilot tested
Continuous membrane fermenter separator (CSFR): EtOH, MeOH, perfumery, analcoholic beverage	Laboratory tested
Processing of vegetable/animal fats	Laboratory tested, pilot tested
Fine chemistry: synthesis of dimethylurea	Laboratory tested
PV aimed distillation:	
Alcohols: ethanol, isopropanol, etc.	Industrially realized
Pyridine	Laboratory tested

modified poly(vinyl alcohol). The technical data for some units are summarized in Table 4.

Reactors Incorporating Pervaporation

Since pervaporation can extract designated components from a liquid mixture by using a suitable membrane, it is possible to incorporate the technique into chemical or biochemical reactors. Therefore, the reaction

TABLE 3
Pervaporation Units for Dehydration by Deutsche Carbone (GFT)

Organic solvent	Capacity	Number of applications
Ethanol	Pilot plant	4
	<10 m^3/d	9
	<100 m^3/d	6
	>100 m^3/d	4
Isopropanol	Pilot plant	4
	<10 m^3/d	3
	>10 m^3/d	2
Ethyl acetate	<10 m^3/d	3
	>100 m^3/d	1
Multipurpose	Pilot plant	15
	<10 m^3/d	7
	>10 m^3/d	2

TABLE 4
Technical Data of Some Pervaporation Units by Deutsche Carbone (GFT)[a]

Code	Place	Membrane area (m^2)	Solvent	Flow rate (kg/h)	Concentration		Consumption	
					Inlet (%)	Outlet (%)	Stream (kg/h)	Power (kW)
PVA1	Betheniville, France	2100	Ethanol	5000	96	99.8	560	200
				3000	96	99.95	500	
PVA2	Provins, France	480	Ethanol	1195	85.7	99.8	195	85
				1500	93.9	99.8	110	
				840	85.7	99.95	145	
				970	93.9	99.95	83	
PVA3	ICI, Australia	210	Isopropanol	500	96	99.9	30	−10
PVA4	BASF, USA	60	Solvenon	75	55	98	204	5
PVA5	Nattermann, Germany	28	Ethanol	2600	96	96.4	70	7
PVA6	ALKO, Finland	12	Ethanol	19	94.5	99.8	—	11
PVA7	?, Germany	80	Ethyl acetate	250	96.5	99.8	25	5

[a] Source: *Product Bulletin*, Deutsche Carbone GmbH.

equilibrium can be replaced and the reaction efficiency can be improved. Consequently, the consumption of reagents and energy might be reduced. Figure 7 shows a schematic diagram of a pervaporation integrated reactor. Some examples of pervaporation integrated reactors are given in what follows.

In many organic reactions, the presence of a by-product (e.g., water) inhibits the reaction. In order to obtain high conversion, it is necessary to remove the by-product from the reactor. Bitterlich et al. (74) studied pervaporating-aided esterification of butanol, where pervaporators were introduced into the reaction units in order to remove water; as a result, they obtained higher concentration of butyl acetate in the product (Fig. 8). Hodges et al. (75) also studied pervaporation-aided esterification. Nafion-H^+ and Nafion-H^+/Cs^+ tubular membranes were used both as a means of immobilizing the catalyst and to selectively remove products from the reaction mixture. A proton counterion in Nafion can be used as a catalyst for the reaction, and the transport properties of the membrane are utilized to selectively remove the by-product water in the reaction. For the reaction of acetic acid and butanol to butyl acetate, a conversion of more than 90% was obtained in less than an hour compared to the 70% achieved without a membrane. A cesium-cation-incorporated Nafion membrane had a greater selectivity but a lower overall permeability compared to Nafion in the acid form, leading to a longer reaction time. Schaet-

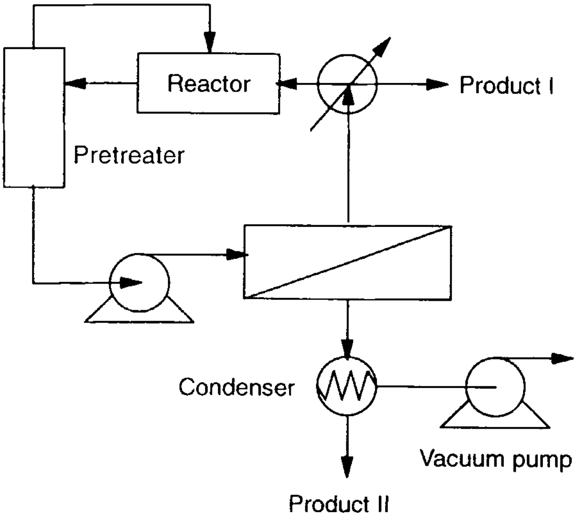

FIG. 7 Schematic diagram of a reactor incorporating pervaporation.

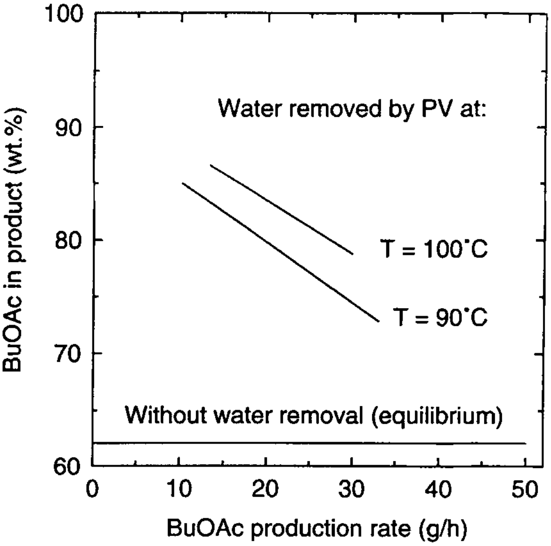

FIG. 8 Concentration of butyl acetate in the product of pervaporation-aimed esterification (after Ref. 74).

zel et al. (76) reported ion-exchange resin-catalyzed esterification aided by pervaporation: a batch reactor for esterification of propionic acid by 1-propanol in combination with and without pervaporation was investigated, and a model combining the rate equation of esterification, the water flux equation through the membrane, and the diffusion equations in the heterogeneous catalyst to describe the evolution of the pervaporation-aided process with time was developed. Dams and Krug (77) reported the production of ethyl acetate in a batch process; a pervaporator equipped with a 250 m^2 PVA membrane was integrated in the reactor. The energy costs for different dehydration methods (shown in Fig. 9) are estimated in comparison with a distillation alone process. As shown in Table 5, the energy cost for dehydration in a pervaporation-incorporated membrane reactor was only 7% of that in conventional distillation. In a reactor for the synthesis of dimethylurea from methylamine and carbon dioxide, Herion et al. (78) introduced a pervaporation unit for removing water and achieved a 90% lower NaOH consumption.

In other organic reactions, the presence of product also inhibits the reaction; for instance, in fermentation the enzyme is active when the ethanol concentration is less than 5 wt%. In order to maintain enzyme activity and to achieve high conversion, the product ethanol must be removed continuously. Cho and Hwang (79) studied a continuous membrane

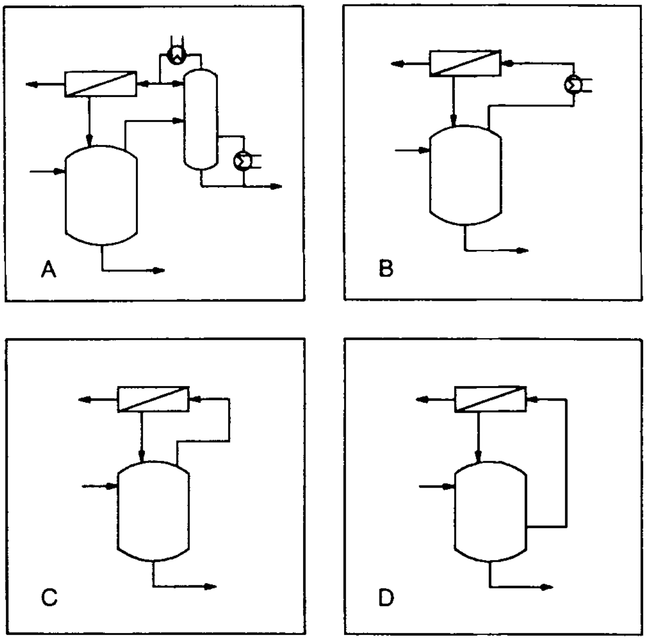

FIG. 9 Processes incorporating pervaporation for the esterification of ethanol and acetic acid (after Ref. 77). See Table 5.

fermentor separator (CMFS) for ethanol fermentation; compared to conventional continuous fermentation, the performance of CMFS results in high yeast cell densities, reduction of ethanol inhibition, longer residence time of substrate, more glucose consumption, and recovery of clean and concentrated ethanol.

By introducing the pervaporator in chemical/biochemical reactors, the composition of one or more reagents in the reaction may be controlled in

TABLE 5
Relative Energy Costs for Dehydration by Different Configurations in an Esterification of Ethanol and Acetic Acid (77)

Code in Fig. 9	Configuration mode	Cost
	Distillation only	100
A	Pervaporation + distillation	42
B	Pervaporation	22
C	Vapor permeation	22
D	Membrane reactor	7

order to keep the reaction up to optimum condition. For example, in the processing of oils, the enzyme possesses the highest activity at a water concentration of about 1–2 wt%. Cuperus and Derksen (80) reported the processing of oils from new crops (which contain erucic acid and dimorphecolic acid); they used a pervaporation unit (membrane: PAN, 70 m^2) to control water concentration in the oils in order to get high enzyme activity and a high esterification rate. By controlling the water concentration to abut 1–2 wt%, 1000 kg oil/day was processed with a conversion of 96%.

ECONOMICS OF PERVAPORATION

As an alternative to the conventional separation means for liquid mixtures, a practical pervaporation plant must be economically competitive with conventional separation plants. The conventional methods commonly have difficulty in the separation of azeotropic mixtures, close-boiling point mixtures, structural isomers, removal of low-content components in a mixture, and the recovery or removal of trace substance. The processes are therefore quite complicated and expensive. Pervaporation processes appear very attractive in these areas.

The cost of a pervaporation plants is composed of two parts: capital and operating costs. The individual costs can be written as follows (81):

$$\begin{aligned}\mathrm{COST}_{\text{capital}} &= \mathrm{COST}_{\text{membr.}} + \mathrm{COST}_{\text{fee pump}}\\ &\quad + \mathrm{COST}_{\text{vacuum pump}} + \mathrm{COST}_{\text{condn. pump}} \qquad (13)\end{aligned}$$

$$\begin{aligned}\mathrm{COST}_{\text{treatment}} &= \mathrm{FRACTION}_{\text{amortization}} \times \mathrm{COST}_{\text{capital}} + \mathrm{FRACTION}_{\text{labor}}\\ &\quad \times \mathrm{COST}_{\text{capital}} + \mathrm{COST}_{\text{membr. replacement}} + \mathrm{COST}_{\text{energy}} \qquad (14)\end{aligned}$$

with

$$\mathrm{COST}_{\text{energy}} = \frac{E_{\text{feed}}}{e_{\text{feed}}} + \frac{E_{\text{vacuum}}}{e_{\text{vacuum}}} + \frac{E_{\text{condn.}}}{e_{\text{condn.}}} \qquad (15)$$

where e_i are the individual efficiency factors.

As an example, an economic estimation for the removal of trichloroethylene (TCE) from water mixture by pervaporation (81) is presented in Table 6. The results shows that the total cost for TCE removal is dependent on the membrane configuration and the thickness of the selective layer. The lowest cost was 0.56 USD/m^3 for the transversal flow module. In comparison with the conventional method, the cost is 0.75 USD/m^3 for air stripping and both liquid- and vapor-phase granular activated carbon

TABLE 6
Costs for Extraction of Trichloroethylene from Water by Pervaporation through SR Membrane

Work time	16 h/d, 300 d/yr
TCE concentration	10 mg/L
TCE removal	99%
Flow rate	10 m^3/h
Temperature	25°C
Membrane cost	200 USD/m^2 in module

Membrane module type	Inside flow (narrow bore)	Inside flow (wide bore)	Spiral-wound	Transversal flow
Dense layer thickness (μm)	75	10	30	30
Membrane area (m^2)	357	463	160	96
Reynolds number	500	4000	700	250
Capital cost (10^3 USD)	482	193	140	69
Energy cost (USD/m^3)	0.26	0.30	0.15	0.07
Total cost (USD/m^3)	3.80	1.41	1.1	0.56

methods, and 0.80 USD/m^3 for the liquid-phase granular activated carbon method.

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