Reviews

Separation of liquids by pervaporation through polymeric membranes

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Fundamental and applied aspects of liquid separation by means of pervaporation through polymeric membranes are considered. The review gives the state of the art as well as prospects of development of this branch of membrane science and technology.

Key words: polymeric membranes, pervaporation.

Introduction

In the 70's and 80's, membrane methods for separating liquids and gases formed an exceedingly important and dynamically developing field, which presumably will determine scientific and technical progress in a number of spheres. The main features of membrane methods are as follows: low energy and material consumption, the continuous character of the processes, and simplicity and flexibility of control.

Recently, the method of separating liquid mixtures by pervaporation through polymeric membranes has been one of the fields of membrane science and technology that has been developed especially successfully. This technique attracted the attention of specialists in the chemical, biochemical, and petrochemical industries, and elsewhere first and foremost as an energy saving environmentally friendly technology with little if any waste. Additionally, unlike traditional distillation, it can be used for the separation of azeotropic mixtures, mixtures of isomers, as well as mixtures of compounds with close boiling points or of compounds that are thermally unstable.

It was noted more than a hundred years ago that the content of ethanol in wines and liquors can increase with time when they are stored in certain clay vessels. This seemingly contradicted the phenomenon that one observed in evaporation from the open surface of liquid mixtures: in this case the more volatile component, ethanol, evaporates with a higher rate and, hence, the remaining liquid is depleted in ethanol. This unusual behavior was first attributed to features of the porosity of the clay vessels used. That were assumed to affect the volatility of the components of the mixture. Now we understand that the reason for the behavior is the phenomenon of pervaporation through the walls of "a membrane" in the form of a clay vessel.

The first qualitative results on separation of hydro-

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carbons and alcohols by pervaporation through rubbery membranes were reported as early as 1906 by L. Kahlenberg,[1] while the first quantitative data on the separation of organic mixtures using a microporous glass wall as a membrane were published by D. H. Hederbaumer and K. Kammermeyer[2] in 1955. However, pervaporation attracted the serious interest of researchers only in the 1960's. Dense (homogeneous) polymer films were used as membranes, and high fluxes and degrees of separation were obtained for numerous organic mixtures.[3–7] For example, R. C. Binning *et al.* published a number of papers (see, *e.g.*, Refs. 3,4) and issued several patents[8–10] including some dealing with design of a module and with the procedure for membrane manufacturing. However, this method failed to obtain any industrial application at that time.

Only in the early 80's were the first practical advances[11] in this field achieved when the GFT Co. in Germany developed a composite membrane based on cross-linked polyvinyl alcohol (PVA) coated on a porous polyacrylonitrile (PAN) support.[12] This membrane happened to be very efficient for the removal of water, by means of pervaporation, from water-organic mixtures.[13] Several technical companies first in Western Europe, and then in Japan commenced the development of industrial pervaporation plants based on the GFT-membrane.[14–16]

Fundamentals

Pervaporation is a membrane process of liquid separation where a liquid mixture (feed stream) is in contact with one side of a selectively permeable nonporous membrane, and the components that penetrate through the membrane (permeate stream) are removed as vapor from the opposite side of the membrane. It should be noted that the term "pervaporation" (a combination of words "permeation" and "evaporation" coined by P. A. Kober[17] as early as in 1917) is not yet widely accepted in Russian scientific literature where it competes with the older term "evaporation across a membrane". However, in many cases and, in particular, when describing special types of "pervaporation membranes" it is certainly simpler and more convenient.

Membrane separation can occur provided a driving force has been created and sustained. In the more general case, a gradient of chemical potential across the membrane thickness serves as this driving force. Hence, for pervaporation it can be written

$$\frac{d\mu_i}{dx} = \frac{d(RT\cdot\ln a_i)}{dx}, \qquad (1)$$

$$a_i = p_i/p_i^0, \qquad (2)$$

where x is the coordinate perpendicular to the membrane, a_i is the thermodynamic activity of component i, p_i and $p^0{}_i$ are the partial equilibrium pressure over the liquid phase and the saturated vapor pressure of pure component i at temperature T, respectively. Thus, Eq. (1) indicates that a driving force appears in the systems when there is a gradient of activity and/or temperature across the membrane. Usually, it is the gradient of activity that acts as the driving force. This can be realized by decreasing the vapor pressure of the separated liquid mixture in the downstream part of the apparatus by evacuation, by sweeping the vapor by an inert gas, or by condensation of the vapor on a cold surface. A schematic presentation of a vacuum-type pervaporation apparatus is given in Fig. 1.

Only the first method has found practical application, mainly due to economic considerations, in large pervaporation plants (at least, for the dehydration of organic solvents). In such plants, the permeate is continuously condensed on the surface of a cold heat-exchanger introduced into the vacuum system and is removed from the system. Two other techniques are more widely used in laboratory experiments. The principle of liquid separation by means of pervaporation, in spite of the diversity of technical solutions and designs, is the same in all of the pervaporation processes and has the following features:

1. In contrast to many membrane processes, the "liquid to vapor" phase transition "liquid to vapor" takes place in the process of mass transfer of the components to be separated from the upstream side of the apparatus to the downstream side. Accordingly, pervaporation is particularly efficient as an energy saving process for the isolation of minor components of a liquid mixture when both enriched and depleted streams can be considered as targets.

2. The membrane includes a nonporous separating layer.

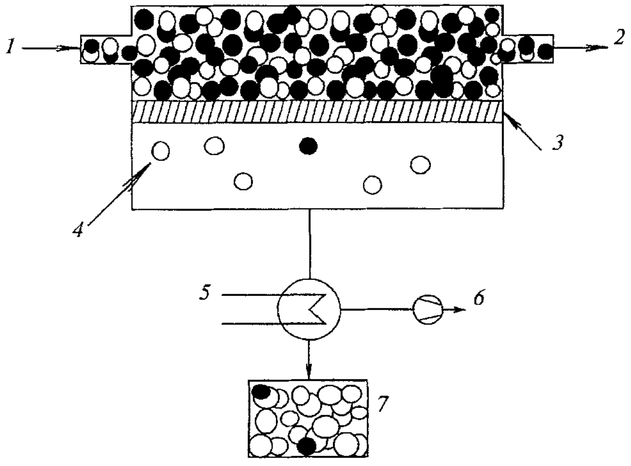

Fig. 1. The scheme of a vacuum regime of pervaporation: *1*, liquid feed; *2*, retentate; *3*, membrane; *4*, permeate vapor; *5*, condenser; *6*, vacuum pump; *7*, liquid permeate.

3. As a rule, the nonporous separating layer is in contact with the liquid mixture to be separated.

4. Activity or temperature gradients across the membrane serve as the driving force of the process.

Bearing in mind the practical aspects of pervaporation and the complex of requirements applied to membrane materials, the problems that can be solved can be divided into three large groups:

— removal of water from organic solvents and their mixtures;

— separation of organic components from aqueous media;

— separation of liquid organic mixtures.

These three problems will be considered separately since the methods used for their solution, the degree of scientific and technical maturity, as well as the tendencies of technical developments are different in all three cases.

Model approaches

Quantitative theoretical analysis of pervaporation mass transfer is a complicated problem due to the strong and nonlinear gradients of many of the parameters across the thickness of a membrane. In pervaporation processes, the mechanism of transport of low molecular weight compounds through nonporous polymeric membranes is the same as that in membrane gas separation: it involves the sorption of penetrant molecules on the upstream side of the membrane, diffusion along the membrane material, and desorption from the downstream membrane surface (Fig. 2, *a*, *b*). This is the so-called solution-diffusion mechanism.[18,19]

Due to the considerable thermodynamic affinity of membrane materials for the components of the liquid mixture to be separated, anisotropic swelling of the membrane polymer is characteristic for pervaporation. The extent of swelling varies from the equilibrium state at the boundary upstream layer of the membrane to the practically dry polymer at the downstream layer contacting the vapor phase (Fig. 2, *b*). The concentration of a particular component C^{M}_{i} on the upstream side of the membrane,which is in contact with the feed stream, depends on its equilibrium sorption from the liquid phase. When the effect of concentration polarization is not substantial, it is very close to the concentration that can be observed when equilibrating the membrane material with a mixture of the same composition as the feed stream. The concentration of any component in the downstream layer of the membrane is negligible because a sufficiently low partial permeate vapor pressure is maintained under the standard conditions of pervaporation. The rates of transport of the components i and j of a binary mixture across this nonuniformly swollen separating layer of the membrane is determined by the local diffusion coefficients D_i and D_j and the corresponding concentration gradients.

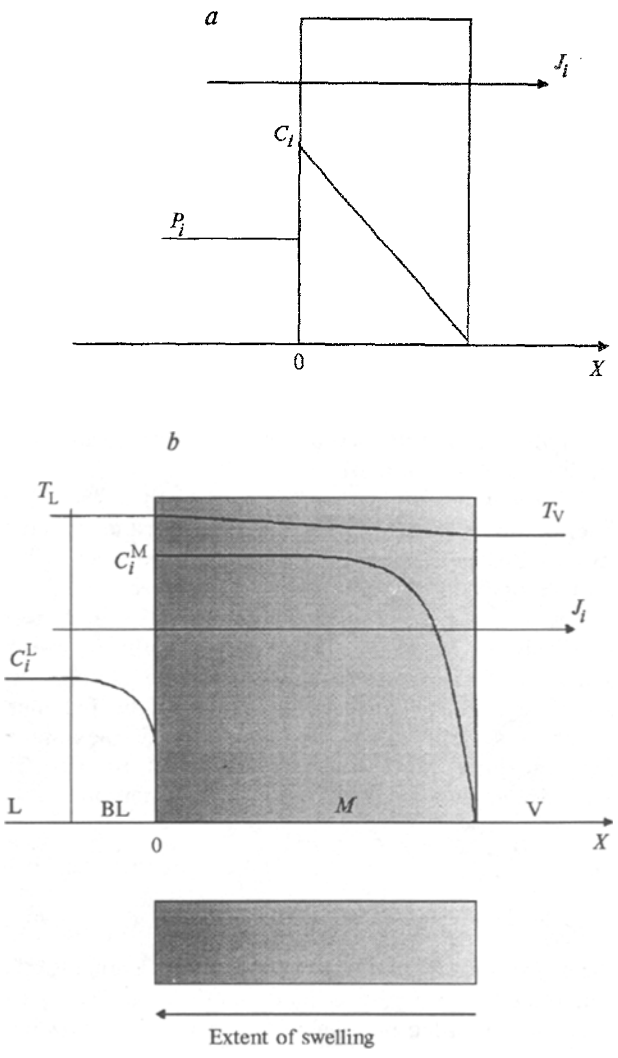

Fig. 2. Concentration profile of a "fast" component of a mixture to be separated under steady state conditions of: (*a*) gas separation and (*b*) pervaporation: L, liquid phase; BL, liquid — membrane boundary layer; M, membrane; V, vapor.

Thus, in contrast to the majority of gas separation processes where nonporous membranes are also used, the following features are characteristic for mass transfer across a pervaporation membrane:

— strong affinity between the components of the liquid mixture to be separated and the polymeric membrane material;

— anisotropic swelling of the separating layer of the membrane;

— highly nonlinear concentration profile across the membrane;

— significant concentration dependence of the local diffusion coefficients of the components of the liquid mixture within the membrane.

Therefore, under the conditions of steady state vacuum pervaporation the flux of each individual component can be given by the following integral expression of Fick's first law

$$J_i = \frac{1}{L}\int_0^{C_i^M} D_i(C_i,C_j)\mathrm{d}C, \qquad (3)$$

where J_i is the steady state flux of the component i (kg m^{-2} s^{-1}); C_i^M is the concentration of the component i on the upstream side of the membrane; $D_i(C_i,C_j)$ is the local diffusion coefficient of the component i in the swollen component at the point where the concentrations of the components are C_i and C_j respectively; L is the thickness of the membrane under the steady-state conditions of pervaporation.

Different molecular models have been proposed to describe mass transfer across a membrane and the concentration dependence of the diffusion coefficients. The most recognized is the Rautenbach—Albrecht model,[20] which is based on equations that had been derived previously.[21] The model implies that the diffusion coefficients D of the permeating components i and j are determined by the local composition of the polymer-penetrant system at any point within the membrane. The concentration dependences for the diffusion coefficients are given by the following linear equations

$$D_i = D_i^0(A_{ii}C_i + A_{ij}C_j), \qquad (4)$$

$$D_j = D_j^0(A_{jj}C_j + A_{ji}C_i), \qquad (5)$$

where D_i^0 and D_j^0 are the diffusion coefficients of the components i and j at infinite dilution (C_i, $C_j \Rightarrow 0$); A are the so-called parallel and cross coefficients which describe the plastisization action of every component exerted over its own diffusion rate (A_{ii}, A_{jj}) or the rate of diffusion of the other component (A_{ij}, A_{ji}).

Substitution of Eqs. (4) and (5) into Fick's Eq. (3) and integration for the conditions of steady-state mass transfer yields a rather complicated expression. Its numerical solution can be obtained for the fluxes J_i and J_j if the values of the parallel and cross coefficients at the membrane surface are known. However, the predictive ability of the Rautenbach—Albrecht model is limited, because the A_{ij} and A_{ji} values can be considered only as adjustable parameters since they can be estimated now only in experiments of pervaporation of this binary mixture. Moreover, linear Eqs. (4) and (5) do not always describe adequately the concentration dependence of the diffusion coefficients that is observed experimentally.

Accordingly, the six-parameter exponential model for the concentration dependence of D:

$$D_i = D_i^0\exp(A_{ii}C_i + A_{ij}C_j), \qquad (6)$$

$$D_j = D_j^0\exp(A_{jj}C_j + A_{ji}C_i), \qquad (7)$$

has been used in a number of papers.[22—25] If the composition of the feed stream strongly influences the component fluxes and the selectivity of the pervaporation process, the nonlinear model given by the Eqs. (6) and (7) is more general and is much more efficient than the aforementioned linear model.

However, it has a disadvantage: it only allows one to calculate the parameters of isothermic pervaporation, although the temperature gradient within the membrane can amount to several degrees depending on the conditions of the process. This is induced by the local cooling of the downstream side of the membrane and the appearance of a temperature gradient across the membrane due to the evaporation of the components penetrating through the membrane (see Fig. 2, *b*). The magnitude of this effect is a function of many parameters: the rate of mass transfer across the membrane, the composition of the feed, and the thermodynamic parameters of its components (such as enthalpy of evaporation, heat capacity), *etc.* The latter circumstance should be taken into account when deriving the equations of mass transfer.[25] In some cases, electroheated membrane units were employed to control these effects.[26,27] Among the other reported models of pervaporation mass transfer, those by M. H. V. Mulder and C. A. Smolders *et al.*,[28,29] M. Fels and R. Y. M. Huang,[30,31] S. F. Timashev and Yu. K. Tovbin,[32] and E. P. Ageev *et al.*[33,34] should be mentioned.

When the efficiency of the pervaporation process is assessed on the whole, many authors emphasize the relevant role of the hydrodynamic resistance of the boundary layer between the liquid and the membrane (see Fig. 2, *b*), which often causes an essential reduction in the pervaporation selectivity.[35—37] The phenomenon, which is observed at the liquid—membrane boundary, is known as concentration polarization. It has been long accepted that this effect, in contrast to separations by means of porous membranes, must not affect membrane gas separation or pervaporation owing to the relatively low rate of mass transfer across a membrane in comparison with those in gas and liquid phases. However, recently it was reported [35—37] that one cannot *a priori* neglect this phenomenon. Moreover, in many practically important cases of pervaporation, *e.g.*, in the treatment of waste waters containing less than 0.001 % (v/v) of an organic component, it significantly affects the overall flux of the target component.

Proceeding from the compositions of the feed and permeate streams, one can calculate the selectivity of pervaporation of a mixture of two liquids i and j by means of the separation factor α_{ij}

$$\alpha_{i,j} = \frac{(C_i/C_j)''}{(C_i/C_j)'} = \frac{C_i''/C_i'}{C_j''/C_j'} = \frac{(P_i/P_j)''}{(P_i/P_j)'}, \qquad (8)$$

and the enrichment factor β

$$\beta = C_i''/C_i', \qquad (9)$$

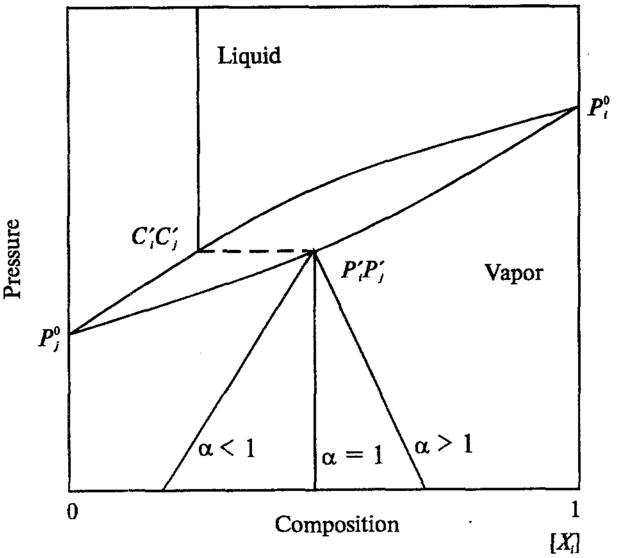

Fig. 3. Thompson's diagram. Schematic representation of the effect of permeate pressure at the downstream side of a membrane on the permeate composition. X_i is the mole fraction of component *i*.

where *i* is the "rapid" or prevailingly permeating component, and the superscripts (") and (') refer to permeate and feed stream, respectively.

As can be seen from Eqs. (8) and (9), factors α and β are dimensionless. The difference between the separation and enrichment factors is that the former is independent of the selection of the units for concentration.

Whereas in a distillation process the vapor phase can be enriched only in the more volatile component of a binary mixture, in pervaporation the permeate can be enriched in both the more and less volatile components depending on the properties of the membrane. This statement can be illustrated by the so called Thompson's diagram[38] shown in Fig. 3. It shows schematically the dependence of the composition of the permeates, on the pressure attained and maintained during pervaporation for membranes with different selectivity α. The upper part of the diagram shows the composition of the feed stream, while the lower part indicates the permeate composition.

As is seen in Fig. 3, the permeate composition depends essentially on the pressure in the downstream part of the pervaporation unit. Depending on the properties of the membrane the pressure can produce additional enrichment ($\alpha > 1$) or depletion ($\alpha < 1$) of the vapor phase in the more volatile component (*i*) compared with the equilibrium evaporation (distillation) of the liquid mixture to be separated. If $\alpha = 1$ or the working permeate pressure is close to the equilibrium pressure, the selectivities of distillation and pervaporation coincide.

Following is a list of the best known examples of pervaporation processes where a less volatile component is concentrated in the permeates:

1. Exhaustive dehydration of organic solvents (ethanol, 2-propanol, tetrahydrofuran, *etc.*) having boiling points below that of water. [11–16,39–42] In these cases, the depleted stream (retentate) serves as the target product, whereas the permeate is water vapor practically free of any organic material. It is this process that first made it possible to demonstrate the feasibility of liquid separation by means of pervaporation on an industrial scale.

2. Treatment of waste and/or recycling water streams with the aim of removing the high-boiling components such as phenol and its derivatives.[27,43,44]

In the following processes, the permeates are enriched in the more volatile components of the feed streams:

3. Continuous removal of ethanol and other oxygenates during the fermentation of a biomass.[39,45–49]
4. Removal of low-boiling organic solvents such as chloroform, dichloromethane, *etc.* from waste waters.[35,50–55]
5. Drying high-boiling (>100 °C) organic compounds, *e.g.*, aliphatic amines.[40]

Processes 1 and 2 can be performed by means of water selective (usually hydrophilic) membranes; on the other hand, membranes based on hydrophobic, organoselective (organophilic) polymers are used for accomplishing processes 3 to 5.

A general approach to the selection of pervaporation membrane materials

Pervaporation characteristics, like those of any separation process using nonporous polymeric membranes, are determined by the differences in the rates of mass transfer across a membrane. On the other hand, the permeability of the membrane can be represented as a function of the solubility and diffusion coefficients of the penetrant in the material of the separating layer of the membrane. As has been noted, the mechanism of mass transfer of low-molecular-weight compounds across nonporous polymeric membranes is the same for gas separation and pervaporation. It includes the following steps: sorption of the penetrant molecules on the upstream side of the membrane, diffusion through the bulk of the membrane, and desorption from the downstream boundary of the membrane (see Fig. 2, *a*, *b*). If one deals with the permeability of permanent gases at moderate pressures, the equilibrium sorption and diffusion obey Henry's and Fick's laws, respectively. It can be easily shown that

$$P = S \cdot D, \qquad (10)$$

where *P* is the permeability coefficient, *S* is the solubility coefficient, and *D* is the diffusion coefficient.

The selectivity of permeation of components *i* and *j* (α_P) can be given by the ratio of the permeability coefficients

$$\alpha_P = \frac{P_i}{P_j} = \frac{S_i}{S_j} \cdot \frac{D_i}{D_j} = \alpha_S \cdot \alpha_D \qquad (11)$$

Equation (11) shows that the selectivity of permeation involves both a thermodynamic component (the selectivity of dissolution α_S) and a kinetic component (selectivity of diffusion α_D). A similar approach can be very efficient in considerations of the regularities of selective mass transfer in pervaporation.[57–58] However, one should bear in mind that the prediction of the selectivity of separation of a real liquid mixture by pervaporation using the ratio of the permeability coefficients of the individual components can be considered, in contrast to gas separation, to be only a first approximation.[57]

V. Volkov *et al.*[59–61] proposed to use the slopes of the linear correlations of the solubility coefficients versus the Lennard—Jones potential parameter ε/k and the slopes of the gas and vapor diffusion coefficients versus d^2 where d is the gas kinetic collision diameter of a penetrant molecule, as the most general quantitative criteria for the assessment of α_S and α_D for polymers (Fig. 4, *a*, *b*). Thus, as can be seen from Fig. 4, *a*, the S_1/S_2 ratio in semilogariphmic coordinates is given by the difference in logarithms of the solubility coefficients of components *1* and *2*, and log α_S is determined by the slope of the linear correlation. The higher this slope, the greater the selectivity of gas and vapor dissolution in the polymer. Similar considerations are applicable to the linear correlation of the diffusion coefficient and the size of the penetrant shown in Fig. 4, *b*.

It should be noted that ε/k and d for gases and liquids correlate with each other as well. Hence, when passing from one sort of molecules to another, an increase in the values of ε/k is accompanied, as a rule, by an increase in the values of d. When no strong specific interaction takes place in the "liquid-membrane" system the following regularity is obeyed: the component of a binary mixture that has greater thermodynamic affinity for the polymeric material of the membrane (component *1* in Fig. 4, *a* for which $(\varepsilon/k)_1 > (\varepsilon/k)_2$) will be preferentially sorbed by the membrane material ($S_1/S_2 = \alpha_S > 1$). On the other hand, owing to its larger size the rate of diffusion of component *1* (see Fig. 4, *b*) would be lower that that of component *2* ($D_1/D_2 = \alpha_D < 1$). Therefore, in the general case of the absence of specific interactions, the thermodynamic (sorption) and kinetic (diffusion) contributions of selective permeability tend to act in the opposite direction, *i.e.*,

$$\log\alpha_P = |\log\alpha_S| - |\log\alpha_D|, \qquad (12)$$

where $\alpha_P = P_1/P_2 = S_1D_1/S_2D_2$ (see Fig. 4, *a*, *b*).

The selectivity of dissolution α_S is determined by the thermodynamic affinity of the components of a liquid mixture for the membrane material.[62–65] As is evident from Fig. 5, in the absence of strong specific interactions in a penetrant-membrane system, α_S increases as the dispersion-induction component of cohesion energy density of a sorbing medium increases both for polymers (*e.g.*, polytetrafluoroethylene (PTFE), polydimethylsilox-

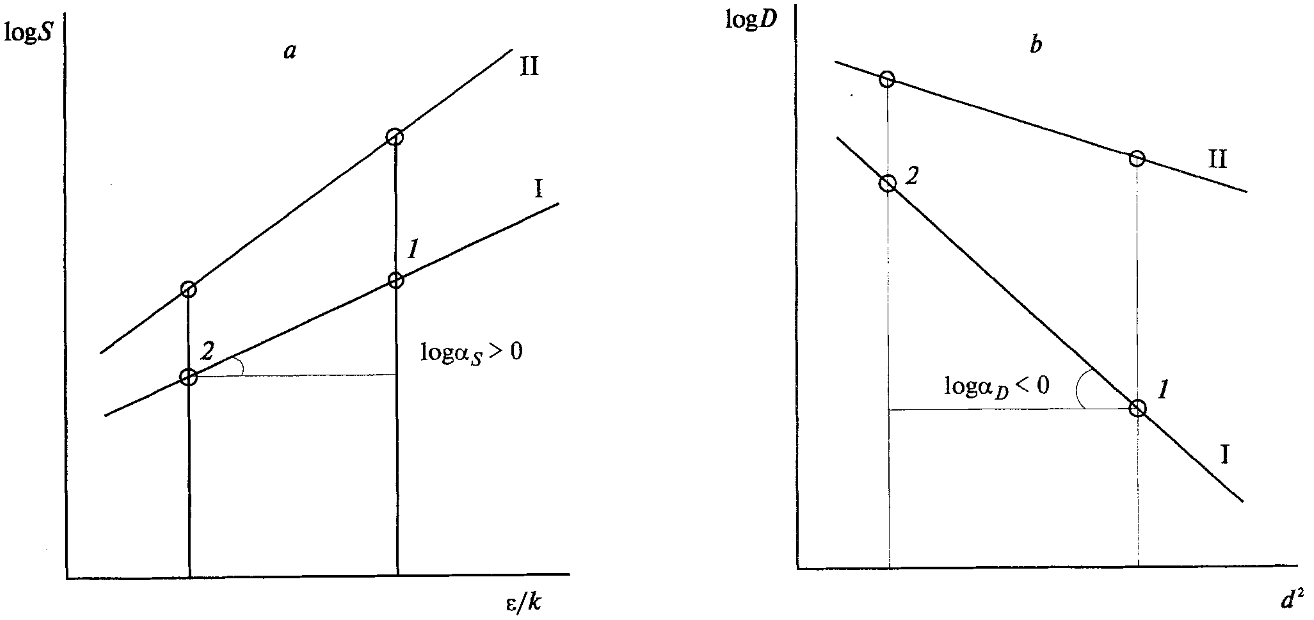

Fig. 4. Schematic representation of the correlations of solubility coefficients (*a*) and diffusion coefficients (*b*) of components *1* and *2* in polymers I and II.

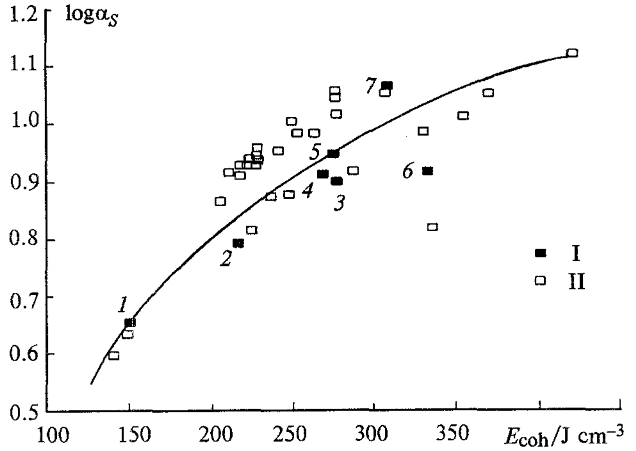

Fig. 5. Correlation of the selectivity of solubility of gases and vapors with the dispersion—induction component of cohesion energy density of polymers (I) and liquids (II): *1*, PTFE; *2*, PDMS; *3*, PVTMS; *4*, PE; *5*, NR; *6*, PVC; *7*, PEMA.

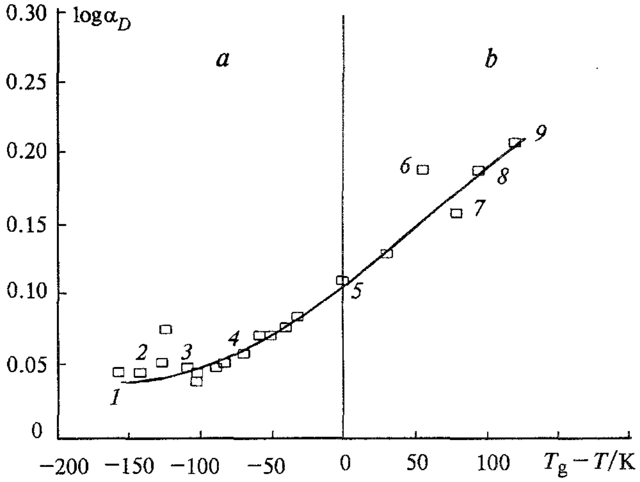

Fig. 6. Diffusion selectivity for gases and vapors as a function of the difference of the glass transition temperature T_g and the temperature of measurement: *a*) rubbery state, *b*) glassy state; *1*, PDMS; *2*, PE; *3*, NR; *4*, PB; *5*, poly-4-methylpentene-1; *6*, polystyrene; *7*, polycarbonate; *8*, polyethylene terephthalate; *9*, PVTMS.

ane (PDMS), poly(vinyl chloride) (PVC), poly(ethyl methacrylate) (PEMA)) and for liquids.[58] On the other hand, the selectivity of diffusion α_D increases with the rigidity of the polymeric matrix (*cf.* Fig. 6).[58,59] A general feature of this dependence is that polymer glasses have higher diffusion selectivity than rubbers. However, there are some important exceptions that will be dealt with later, namely, highly permeable polymer glasses with mass transfer parameters higher than those of the most permeable rubbers.

1. *The diffusion mechanism of separation prevails providing the following inequality holds*

$$|\log\alpha_S| < |\log\alpha_D| \tag{13}$$

In this case, the separation is governed primarily by the geometry of the molecules to be separated: as a rule, the component with the smaller molecules preferentially penetrates through the membrane during pervaporation (component *2*, Fig. 4, *a*, *b*). This regularity is typical mainly of polymer glasses with low permeability and is used in the processes of pervaporation dehydration of organic solvents involving such polymers as polyimides,[66] PAN[67] and its copolymers.[68]

When inequality (13) holds, the fluxes across the membranes and the selectivities of separation are clearly inversely interrelated. In other words, any changes in the structure of a membrane resulting in an increase in its selectivity are inevitably accompanied by a reduction in its productivity.

2. *The sorption mechanism of separation prevails providing the following inequality holds*

$$|\log\alpha_S| > |\log\alpha_D| \tag{14}$$

In this case,the separation is governed by the principle of thermodynamic affinity between the molecules of the liquid mixture and the polymeric material of the membrane. These conditions can be realized both in the absence and in the presence of strong specific interactions in the system.

When interactions between a component of the binary liquid mixture and the membrane polymer are absent, the inequality (14) holds only when the selectivity of diffusion α_D is low. This is characteristic, as can be seen from Fig. 6, for rubbers with low glass transition temperatures (PDMS, PB, *etc.*) and, as we shall see later, for highly permeable microporous polymer glasses (*e.g.*, for poly(trimethylsilyl propyne (PTMSP)). Components with larger molecules preferentially penetrate through the pervaporation membrane in all these cases (for example, component *1* shown in Fig. 4, *a*, *b*). In practice, this is the mechanism that occurs in the enrichment of organic components from aqueous solutions using hydrophobic nonporous membranes (see the classification of pervaporation problems given above).

If a component is present that is able to exhibit strong reversible specific interactions with the material of the membrane (*e.g.*, donor—acceptor interactions or hydrogen bonding), then inequality (14) will always hold, and this component will prevail in the permeate stream. Dehydration of organic solvents by means of hydrophilic polyelectrolyte "Symplex" membranes are examples of the practical application of this mechanism.[69]

In the pervaporation processes that proceed according to the sorption mechanism, we meet, as a rule, a favorable combination of a simultaneous increase in both the selectivity and the flux of the "rapid" component, which is observed for the membranes with different characteristics. This is typical both of the systems

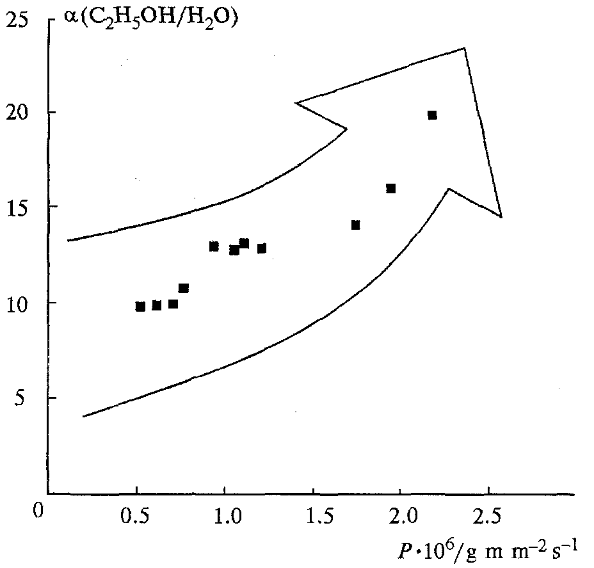

Fig. 7. Interrelation of selectivity and permeability in the pervaporation of a 7 % solution of ethanol in water through PTMSP films with different histories at 25 °C.

with strong specific interactions (*e.g.*, hydrogen bonding in the hydrophilic polyelectrolyte—water system[69]) and systems where such interactions are absent. The latter case is illustrated in Fig. 7 for the pervaporation enrichment of ethanol from its aqueous solutions by means of PTMSP films with different histories.

Polymers and membranes for pervaporation processes

Modern pervaporation membranes are structures containing dense separating layers (asymmetric or composite membranes). Figure 8, for example, is a schematic representation of a flat multilayer composite membrane. Membranes of this kind contain, as a rule, no less than three different layers of different materials. An ultrafilter of a polymeric material is formed on the surface of woven or nonwoven cloth by the phase inversion method. A thin defect-free layer of another polymer is coated over the ultra-filter. The upper coating may be prepared from several superimposed layers as well.[50,70,71]

Since the difference in vapor pressure of the components to be separated at the upstream and downstream sides of the membrane units is the driving force of pervaporation,this must be kept as high as possible. This is achieved by maintaining a sufficiently high temperature in the feed stream. Therefore, stability of membrane materials towards the components of a mixture to be separated at elevated temperatures is necessary for pervaporation membranes.

In contrast to distillation, pervaporation can result, as has been mentioned above, in concentration of the more volatile or the less volatile component of the liquid feed stream including azeotropic mixtures. Thus, pervaporation allows one both to dehydrate water-organic mixtures (preferential diffusion of water through a membrane) and to extract organic components. The choice of membrane material determines the direction of the process in both cases.

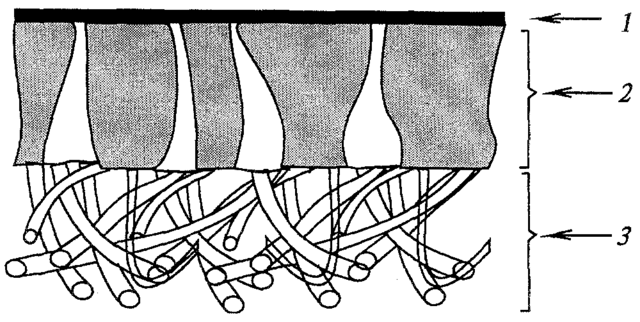

Fig. 8. Schematic representation of a multilayer composite membrane: *1*, dense nonporous layer with thickness 0.05—3 μ; *2*, ultrafilter with open porosity and asymmetric morphology (thickness 100 μ); *3*, nonwoven or woven polymeric cloth.

1. Separation of water-organic mixtures

In the framework of the sorption—diffusion mechanism, this group of mixtures is characterized by the following features:

— water is a polar compound that tends to form hydrogen bonds;

— the nonspecific or dispersion-induction component of the solubility parameter of water is significantly lower than those of organic compounds;

— water molecules are substantially smaller than molecules of organic compounds.

Removal of water from organic solvents and their mixtures

This field of pervaporation can be characterized today as the most thoroughly studied from the practical point of view. An enormous number of polymers and membranes has been tested since the advent of pervaporation, however, today only several of them satisfy the requirements necessary for an industrial application. The membranes must possess both high permeance and selectivity combined with good chemical and mechanical stability at elevated temperatures (about 100 °C). In addition, their cost must be reasonable. The first membrane to satisfy all these demands was a composite PVA/PAN membrane developed by the GFT company.[11,12] This was the first pervaporation membrane that appeared on the market in the mid-80's.

This membrane consists of three layers made from different polymers. The upper nonporous, dense layer is made of partially crosslinked PVA with a thickness of

0.5 μ. An ultrafilter made of PAN with a thickness of 100 μ serves as the middle layer. It has an asymmetric structure with open porosity. The bottom layer is made from a polyester nonwoven filter that has a thickness of 100 μ and provides additional mechanical strength to the whole membrane. This membrane allows one, for example, to perform one-stage dehydration of ethanol at 95—100 °C, increasing the alcohol content from 94 to 99.8 vol. %. Using this membrane, even minute quantities of water in chlorinated hydrocarbons can be reduced to the level of 10^{-3} vol. %.

CM-Celfamembranetrenntechnik AG now produces good water-selective membranes based on physically and/or chemically cured PVA coated on a PAN ultrafilter.[72] X-ray scattering, DSC, and IR-spectroscopy have indicated that a high content of oriented microcrystallites of PVA seems to be the main feature of these membranes responsible for their excellent operating characteristics.

The pervaporation parameters of these membranes indicate that their behavior is in agreement with the classical resistant model of Henis and Tripody proposed for composite membranes.[73,74] Indeed, the decisive contribution to the resulting selectivity of the membrane is provided by the ultrafilter material (in this case, PAN), on which the upper thin dense layer is coated. Therefore, most likely, the separation of liquid mixtures through PVA/PAN-based membranes proceeds via the diffusion mechanism. This is also confirmed by the inverse dependence of fluxes through the membranes in various technological regimes and their selectivities.[12,75,76]

Texaco (USA) has developed a very interesting series of chemically stable, high-flux, selective membranes for the removal of water and methanol from their mixtures with ethers, acetates, aromatics, and other organic compounds.[40,41,77] The separation layer of these membranes consists of either crosslinked PVA or an ion-exchange "Nafion" membrane. The former is very similar to a composite PVA/PAN membrane.

Composite membranes obtained by deposition of plasma-polymerized coatings on porous supports form a novel class of hydrophilic membranes.[78] Due to the high degree of cross-linking, these membranes are chemically very stable and exhibit a rare combination of high selectivity and permeance. The properties of these membranes can be varied over a wide range, which makes it possible to dehydrate alcohols and organic acids and recover methanol from mixtures.

Continuous removal of water from reaction mixtures with the aim of shifting thermodynamic equilibria to the final products is a novel and promising field of the application of water-selective membranes.[66,79] Indeed, it was shown that a regime that includes a pervaporation stage allows one to significantly shift the extent of ester formation from organic acid and alcohol.[79] To optimize the efficiency of the work in such a system it is necessary to select the ratio of the membrane's surface area to the reaction volume in an appropriate way. An increase in this ratio results in an increase in the yield of the final product.

Recovery of organic components from aqueous media

This field of pervaporation is now being developed especially actively, both in the fundamental and applied aspects. Practically, it is related, first and foremost to environmental protection problems: pervaporation recovery of traces of hazardous organic compounds from waste waters of different chemical and refinery plants, etc. Accordingly, numerous rubbery polymers have been tested as potential membrane materials. Excellent results have been achieved with composite membranes having cross-linked polydimethylsiloxane as the upper separative layer.[70,71,80]

The degree of enrichment in these processes depends on the type of organic solvent. Thus, the concentration of ethanol, methanol, acetone, and other polar compounds can be increased by a factor of 5—40. Nonpolar solvents such as ethyl acetate and chloroform can be enriched 50—300-fold. Pervaporation of such hazardous organic components as trichloroethylene, chloroform, dichloromethane, dichloroethane, benzene, toluene, phenol, methyl ethyl ketone, and so on is being studied. There are strict regulations for the content of these compounds in both industrial waste water and in subsoil water used for potable water.

Highly permeable polymer glasses like PTMSP are special types of organoselective membranes.[81,82] Their characteristic features are exceedingly high permeability and diffusion coefficients of small molecules combined with low diffusion selectivity comparable with that of PDMS. The latter can be explained by the structural organization of the free volume in this polymeric glass. According to data from Refs. 83, 84, PTMSP has a very high fractional nonequilibrium (or nonrelaxed) free volume, which can be as high as 20—26 %. This forms a network of interconnecting micropores within the polymer matrix with the narrowest diameters 4—5 Å, which is comparable to the collision diameters of the molecules of organic liquids.

This approach made it possible to explain for the first time[84] the dramatic reduction in the selectivity (down to 9.4) observed by Y. Fujii *et al.*[85] in the recovery of *tert*-butyl alcohol from its aqueous solutions in pervaporation through PTMSP films as compared with the corresponding selectivities of separation of less branched or bulky isomers. The drastic (by an order of magnitude) decrease in the permeability coefficient of isobutane in comparison with those of normal alkanes (ethane, propane, *n*-butane)[86] can also be considered to be a manifestation of this structural features. These, at first sight, unusual phenomena of the mass transfer of organic compounds through PTMSP films are easily explained by the microporous nature of this highly permeable glass.

Indeed, since the cross sections of the molecules of 1-butanol, 2-butanol, and isobutanol oriented along the coordinate of the diffusion transport are lower than the intrinsic size of the narrowest sections of the interconnected micropores of PTMSP, the permeability coefficients of these compounds are high and do not depend strongly on the structure of the alcohol. The observed pervaporation permeabilities are equal to 6.408, 8.431, and 7.025 mol m^{-2} h^{-1} for 1-butanol, 2-butanol, and isobutanol, respectively.[85] When passing to bulkier *tert*-butyl alcohol, the size of which is larger than the intrinsic size of the pores, a decrease by an order of magnitude in permeability of PTMSP with respect to this alcohol (0.729 mol m^{-2} h^{-1}) and in the selectivity of pervaporation are observed.

The effect of blocking diffusion channels when binary mixtures are transported through PTMSP films described earlier by S. Auvil *et al.*[83] can also be observed for *tert*-butyl alcohol although the nature of this phenomenon is different in the case of pervaporation. A reduction in the permeation rate of water from binary mixtures with C_4 alcohols is observed only in the case of *tert*-butyl alcohol. The values of water permeability are as follows: 8.548, 8.548, 8.104, and 5.717 for *n*-butanol, 2-butanol, isobutanol, and *tert*-butyl alcohol, respectively.[85]

2. Separation of organic mixtures

In spite of the essential practical importance and some preliminary positive results on a laboratory scale (see for example, Refs. 3,4,8—10,75), this field of pervaporation involving fractionation of organic mixtures has not yet reached a maturity that would allow industrial applications. As a single exception, one can mention, perhaps, the successful separation of mixtures containing methanol. Because methanol is a highly polar molecule of small size, it can readily penetrate through pervaporation membranes that are used for dehydration. Thus, pervaporation has been used in the process of manufacturing dimethyl carbonate (DMC) for overcoming the region of the compositions where the DMC-methanol azeotrope can be formed by distillation of this mixture.[77] The binary mixture containing about 70 % methanol (while the azeotrope contains 67 % methanol) is sent to a pervaporation unit. The retentate stream containing 55 % methanol is directed to subsequent distillation while the permeate stream with 99 % methanol is recycled to the DMC synthesis reactor.

Removal of excess methanol from reactor wastes in the manufacturing of methyl *tert*-butyl ether (MTBE) is another successive application of pervaporation.[87] The pervaporation unit allows one to increase the methanol content, as compared with the traditional process, in the feed directed into the reactor and, therefore, to increase by 5 % the conversion rate without any negative accompanying effects on the work of the existing distillation plant.

State of the art in industrial pervaporation

If we compare pervaporation with such processes as reverse osmosis, ultrafiltration, dialysis, and electrodialysis from the standpoint of industrial application, we can conclude that pervaporation is a membrane process that is still in the very early stage of its development. During the last decade it proved to be a reliable technological process for liquid separation, especially for the separation of azeotropic mixtures of organic solvents and water and dehydration of organic solvents.

Now pervaporation is considered as a component of many processes in the chemical industry. In the market, a number of pervaporation membranes are available and there is good potential for the diversification and expansion of their uses in the near future. More than 90 industrial pervaporation plants of different scales now exist in the world. Table 1 summarizes the fields of application, the numbers of different pervaporation plants that use PVA/PAN membranes from the GFT Co., and their outputs.[88] It is seen that the most numerous are plants of modest output of the order 10 t per day of a product.

Pervaporation processes can be successfully used as an alternative to traditional methods of separation in the following continuous hybrid processes:

Novel hybrid process	Traditional process
1. Distillation/ pervaporation	Distillation/ azeotropic distillation
2. Distillation/ pervaporation/ distillation	Distillation/ extractive distillation

Pervaporation proved to be very successful not only in separation of binary azeotropic mixtures, but also in dehydration of solvent mixtures containing components with boiling points both lower and higher than water. Here distillation is practically excluded since the

Table 1. Pervaporation plants for dehydrating organic solvents using water-selective GFT membranes

Organic solvent	Output /m^3 per day	Number of plants
Ethanol	Pilot	4
	< 10	9
	< 100	6
	> 1000	1
2-Propanol	Pilot	4
	< 10	3
	> 10	2
Ethyl acetate	< 10	3
Diverse mixtures	Pilot	15
	< 10	7
	> 10	2

individual components form azeotropic mixtures with water.

Pervaporation is especially efficient, from an economic standpoint, when periodic dehydration of different solvents or their mixtures is necessary. Multipurpose pervaporation plants are much more advantageous than the traditional ones, if the latter can be employed at all.

As for the isolation of organic components from aqueous media by pervaporation, the scale currently attainable is only at the level of pilot plants, in spite of extensive studies in this field. No industrial-scale separation process has yet been reported.

The design of membrane modules and technological schemes continues to be perfected. Thus, in addition to plate-and-frame modules, spiral wound and hollow fiber modules are being successfully developed for industrial processes. The greatest practical progress will be achieved when an appropriate combination of this novel method with traditional methods of separation is found.

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