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Resistance model approach to asymmetric polyetherimide membranes for pervaporation of isopropanol/water mixtures

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Abstract

The resistance model approach to asymmetric membranes for pervaporation was attempted. It was shown that the selectivity achievable in an asymmetric membrane is influenced not only by the relative resistance of the skin layer and the substrate but also by the relative resistance of the polymer matrix and the pores in the substrate. Based on this approach, the pervaporation data of the asymmetric polyetherimide membranes for the separation of isopropanol/water mixtures were analyzed, and the resistances lying in the path of mass transport through the membranes were quantified on a relative basis. The intrinsic permeability data involved in the resistance model were determined by conducting pervaporation experiments with a dense membrane. The asymmetric membranes used here were not prepared under optimum conditions, but membranes of better performance can be obtained by appropriate control of the preparation parameters.

Key words: pervaporation; resistance model; asymmetric membrane; liquid permeability and separations

Introduction

For membrane controlled systems, in order to achieve a high permeation flux, the thickness of the selective layer of the membrane should be reduced to low levels. One way to do this is to make a membrane with an asymmetric structure in which a thin selective skin layer is supported on a relatively thick microporous substrate. Integrally skinned asymmetric membranes have been widely used in reverse osmosis and gas separations [1], but their applications in pervaporation are less developed [2]. Recently, asymmetric aromatic polyetherimide membranes have been prepared and tested in our laboratory for the dehydration of aqueous isopropanol solutions. A permeation flux of 2.5 mol/(m^2-hr) and a separation factor of 173 was achieved for breaking the isopropanol–water azeotropic composition at room temperature, and a higher separation ($\alpha = 384$) with a lower flux [0.8 mol/(m^2-hr)] was also observed when the feed concentration was 0.96 mole fraction isopropanol [3].

It is well known that the substrate in an asymmetric or composite membrane influences the overall separation performance of the membrane. The resistance model, first pro-

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posed by Henis and Tripodi [4], and its appropriate variations have been widely used for the analysis of gas permeation through composite membranes [5–7]. The influence of the composite membrane structure on the pervaporation performance was analyzed by Gudernatsch et al. [8] on the basis of the resistance model. Recently, Fouda et al. [9,10] have modified the model to describe gas separation by membrane laminates. In all the aforementioned composite membranes, the skin layer and the substrate are formed separately and hence the substrate can be characterized individually, whereas it is difficult to determine the individual resistances of the skin layer and the substrate in an asymmetric membrane since they are formed simultaneously during the phase inversion process. Using the relative resistance of the skin layer and the substrate, Pinnau and Koros [11] applied the resistance model to gas separations by asymmetric membranes and demonstrated the high dependence of membrane selectivity on the substrate resistance.

In the present study, we attempt to use the resistance model approach to asymmetric polyetherimide membranes for the pervaporation of isopropanol/water mixtures. The asymmetric structure of the membranes will be illustrated by using scanning electron microscopy. Note that the resistance model approach, though not a mechanistic approach to membrane separation, has practical utility to membrane development because it correlates membrane selectivity and the resistance components lying in the path of mass transport through the membrane and offers a means of determining these resistances qualitatively, at least in relative terms. It, however, needs to be mentioned that when the concentration polarization effect is significant, the mass transport resistance of the boundary layer should also be taken into account to best illustrate the overall separation performance [12].

Theoretical

The basic equation for mass transport of a permeating component in membrane pervaporation can be written phenomenologically as

$$[PR]=KA\frac{\gamma p_s X-pY}{l} \tag{1}$$

where $[PR]$ is the permeation rate, γ is the activity coefficient, A and l are the area and thickness of the membrane, respectively. K is the effective permeability coefficient that accounts for non-ideal behaviour of the feed mixture. X and Y are the mole fractions of the permeating species in the feed and the permeate, respectively; p and p_s refers to the permeate pressure and the saturated vapour pressure, respectively. Defining the membrane resistance (R) and the driving force (ΔU) for the permeation as

$$R=l/(KA) \tag{2}$$

$$\Delta U=\gamma p_s X-pY \tag{3}$$

eqn. (1) becomes

$$[PR]=\Delta U/R \tag{4}$$

which is in analogy to Ohm's law in an electric circuit. Thus the permeability coefficient K can be understood as a specific conductivity for mass flow. Equation (4) can be applied to each permeating species and to each resistance component in the path of mass flow through a membrane.

Consider the pervaporation through an asymmetric membrane shown in Fig. 1. The mass flow can be considered analogous to an electric flow in a circuit consisting of three resistance components in a series–parallel configuration. A permeating species must first pass through the skin layer and then through the pores and the polymer matrix in the substrate. The overall permeation resistance R_t is given by

$$R_t = R_1 + R_2R_3/(R_2+R_3) \qquad (5)$$

where R_1 is the resistance of the skin layer; R_2 and R_3 are the resistances of the pores and the polymer matrix, respectively, in the porous substrate. They can be written in a form similar to eqn. (2) as

$$R_1 = \frac{l_1}{K_1A} \qquad (6)$$

$$R_2 = \frac{l_2}{K_2A\epsilon} \qquad (7)$$

$$R_3 = \frac{l_2}{K_3A(1-\epsilon)} = \frac{l_2}{K_1A(1-\epsilon)} \qquad (8)$$

where l_1 and l_2 are the thickness of the skin layer and the substrate, respectively; K_1 and K_2 are the effective permeability coefficients through the polymer solid and the pores, respectively; and ϵ is the area porosity of the substrate.

Now let us consider the permeability coefficients K_1 and K_2. K_1 can be determined from pervaporation experiments using a dense membrane, and usually it is expressed as a polynomial function of feed concentration to characterize its concentration dependence. The pores in the substrate are assumed small enough for Knudsen flow to apply; this assumption is normally satisfactory because the mean free path of a gas molecule under vacuum is relatively large. Further assumptions are cylindrical pores and uniform pore size distribution in the substrate. Then K_2 can be expressed by

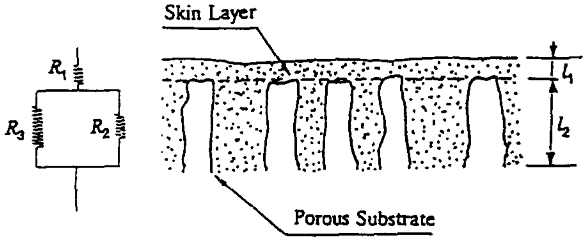


Fig. 1. Schematic cross section of an asymmetric membrane and the mass transport resistance configuration.

$$K_2 = r\left(\frac{32}{9\pi MR_gT}\right)^{1/2} \qquad (9)$$

where r is the radius of the pores, and M is the molar mass of the permeating component. Thus eqn. (7) can be rewritten as

$$R_2 = \frac{l_2}{A\epsilon r}\left(\frac{9\pi MR_gT}{32}\right)^{1/2} \qquad (10)$$

As an illustration, consider the permeation of a binary mixture of water and isopropanol, where water is the preferentially permeating species. The resistance ratio for each resistance components can be written as

$$\frac{(R_1)_{IPA}}{(R_1)_{H_2O}} = \frac{(K_1)_{H_2O}}{(K_1)_{IPA}},$$

or

$$(R_1)_{IPA} = \frac{(K_1)_{H_2O}}{(K_1)_{IPA}}(R_1)_{H_2O} \qquad (11)$$

$$\frac{(R_2)_{IPA}}{(R_2)_{H_2O}} = \sqrt{\frac{(M)_{IPA}}{(M)_{H_2O}}},$$

or

$$(R_2)_{IPA} = \sqrt{\frac{(M)_{IPA}}{(M)_{H_2O}}}(R_2)_{H_2O} \qquad (12)$$

$$\frac{(R_3)_{IPA}}{(R_3)_{H_2O}} = \frac{(K_1)_{H_2O}}{(K_1)_{IPA}}$$

or

$$(R_3)_{IPA} = \frac{(K_1)_{H_2O}}{(K_1)_{IPA}}(R_3)_{H_2O} \qquad (13)$$

The total resistance for water permeation is, from eqn. (5),

$$(R_t)_{H_2O} = (R_1)_{H_2O} + \frac{(R_2)_{H_2O}(R_3)_{H_2O}}{(R_2)_{H_2O} + (R_3)_{H_2O}} \qquad (14)$$

Similarly, the total resistance for isopropanol permeation is

$$(R_t)_{IPA}=(R_1)_{IPA}+\frac{(R_2)_{IPA}(R_3)_{IPA}}{(R_2)_{IPA}+(R_3)_{IPA}} \qquad (15)$$

Substituting eqns. (11) to (13) into eqn. (14) yields

$$(R_t)_{IPA}=\frac{(K_1)_{H_2O}}{(K_1)_{IPA}}\times\left[(R_1)_{H_2O}+\frac{(R_2)_{H_2O}(R_3)_{H_2O}}{(R_2)_{H_2O}+\frac{(K_1)_{H_2O}}{(K_1)_{IPA}}\sqrt{\frac{(M)_{H_2O}}{(M)_{IPA}}}(R_3)_{H_2O}}\right] \qquad (16)$$

By definition the separation factor can be expressed by

$$\alpha=\frac{Y_{H_2O}/Y_{IPA}}{X_{H_2O}/X_{IPA}}=\frac{[PR]_{H_2O}/[PR]_{IPA}}{X_{H_2O}/X_{IPA}} \qquad (17)$$

When the permeate pressure p is sufficiently low so that $\gamma p_s X \gg pY$ for both permeating species, eqn. (17) can be simplified to the form

$$\alpha=\frac{\gamma_{H_2O}(p_s)_{H_2O}(R_t)_{IPA}}{\gamma_{IPA}(p_s)_{IPA}(R_t)_{H_2O}} \qquad (18)$$

For a dense membrane where $\epsilon=0$, we have

$$\frac{(R_t)_{IPA}}{(R_t)_{H_2O}}=\frac{(R_1)_{IPA}}{(R_1)_{H_2O}}=\frac{(K_1)_{H_2O}}{(K_1)_{IPA}} \qquad (19)$$

Thus the intrinsic separation factor α_{int} can be written as

$$\alpha_{int}=\frac{\gamma_{H_2O}(p_s)_{H_2O}(K_1)_{H_2O}}{\gamma_{IPA}(p_s)_{IPA}(K_1)_{IPA}} \qquad (20)$$

Dividing eqn. (18) by eqn. (20) and using eqn. (16) gives

$$\frac{\alpha}{\alpha_{int}}=\left[R_1+\frac{R_2R_3}{R_2+\frac{(K_1)_{H_2O}}{(K_1)_{IPA}}\sqrt{\frac{(M)_{H_2O}}{(M)_{IPA}}}R_3}\right]\times\left[R_1+\frac{R_2R_3}{R_2+R_3}\right]^{-1} \qquad (21)$$

where R's are the resistance components for water and, for convenience, the subscript H_2O for resistance has been dropped. Usually, for a hydrophilic membrane,

$\frac{(K_1)_{H_2O}}{(K_1)_{IPA}}>\sqrt{\frac{(M)_{IPA}}{(M)_{H_2O}}}$ (=1.827.) Thus, the intrinsic selectivity of a membrane material, which is controlled by the physicochemical interactions in the membrane–permeant system, is larger than the Knudsen flow selectivity which is determined by the relative molar mass of the permeating species to be separated. Equation (21) shows that the selectivity achievable in an asymmetric membrane depends on the resistance components on a relative basis.

Note that whether or not the assumption of cylindrical pores with uniform pore size distribution is strictly applicable, the foregoing analyses are still valid with an appropriate correction of R_2 for geometric factors of the porous structure as long as the pore sizes are small for the Knudsen flow to be applicable.

Experimental

Materials

Aromatic polyetherimide was kindly supplied by GE Plastics Canada. The polymer material was thoroughly dried before use. N,N-dimethyl acetamide supplied by BDH Chemicals was used as the solvent for the preparation of membrane casting solution. Isopropanol was obtained from J.T. Baker Chemical Company. Both chemicals were of reagent grade and used without further purification. Water was deionized and distilled before use.

Membrane preparation

Asymmetric polyetherimide membranes were prepared by the phase inversion technique [3]. The casting solution consisted of polyetherimide 25 wt.% and N,N-dimethyl acetamide 75 wt.%. The polymer solution was cast on Pyrex glass plates to an equal nominal thickness of 275 μm. The casting atmosphere was ambient. Immediately after casting, the cast film was gelled in ice-cold water, and the membrane so produced is designated as PEI-W. Two other membranes, designated as PEI-DW and PEI-D, were prepared by evaporating the solvent within the cast films at 80°C for 2 and 10 min, respectively, before being gelled. All the membranes were finally air-dried. In fact, the PEI-D membrane is a dense membrane, as will be shown later.

Dense membranes of various thickness were prepared by completely evaporating the solvent at elevated temperatures. These membranes were used to measure the intrinsic pervaporation properties of the polymer material.

Pervaporation

The pervaporation experiments were performed in a static permeation cell. The membrane was cut into coupons and mounted in the cell. The equipment and the experimental procedure have been described elsewhere [3,13]. The permeation rate was determined gravimetrically by weighing the permeate sample collected for a predetermined period of time, and the permeate composition was determined by either refractometric analysis or gas chromatographic analysis, depending on the permeation rate and the permeate concentration.

In all the experiments the downstream pressure was maintained below 133 Pa and the temperature was kept at 25°C.

Results and discussion

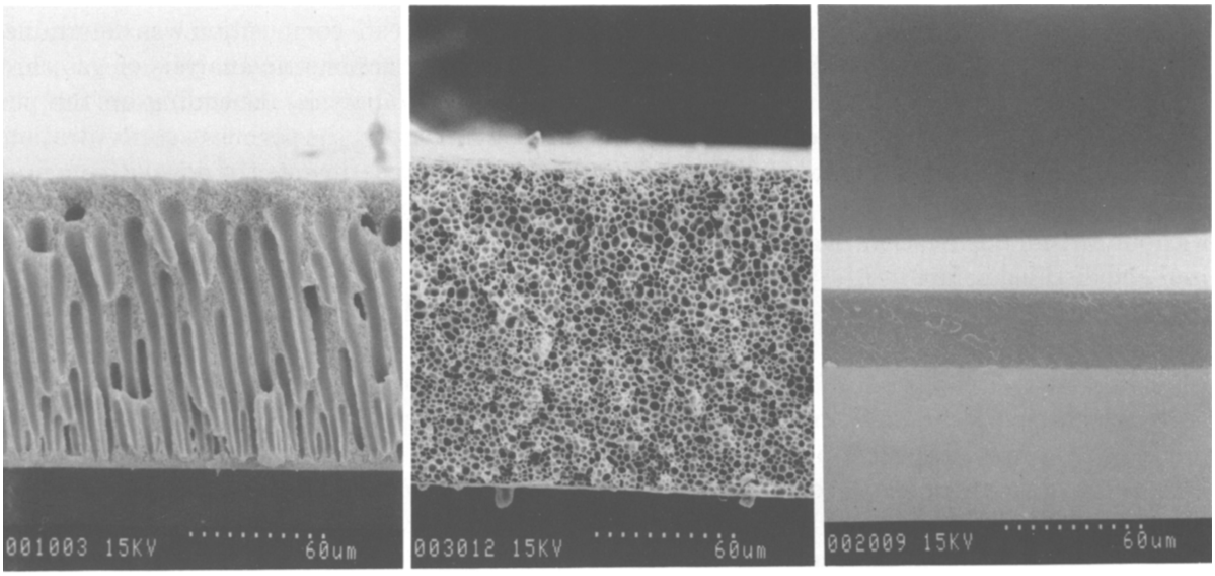
Membrane morphologies

The cross sections of the membranes were examined by using scanning electron microscopy in a Hitachi S-570 microscope. The physical strength of the membranes were very high even at liquid nitrogen temperature, and the specimens were prepared by cutting the membranes at the cryogenic temperature. The micrographs of the membrane cross sections taken at the same magnification are presented in Fig. 2.

Figure 2(a) shows that the PEI-W membrane is featured with a thin skin layer and a finger-like porous substrate. The finger-like pores do not penetrate the entire cross section, and the pore inlets and outlets are connected to the finely porous polymer matrix.

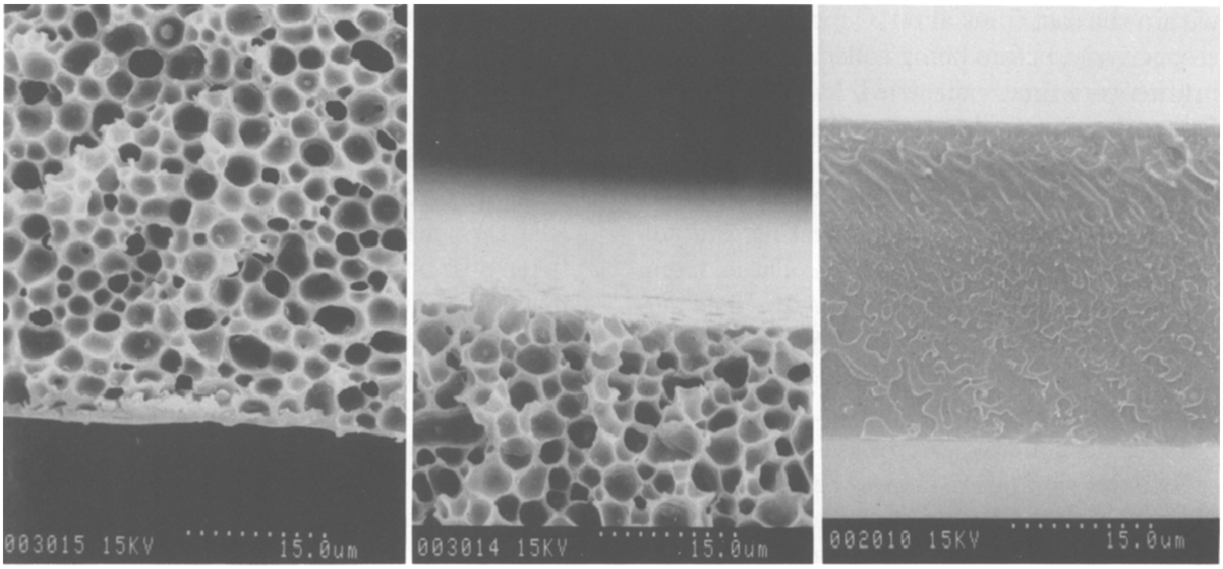
Figure 2(b) shows the micrograph for the PEI-DW membrane. Micrographs were also taken near both sides of the membrane at higher magnification, as shown in Figs. 3(a) and (b). It is very clear that the membrane consists of a dense skin layer and a sponge-like porous substrate, and that the substrate underneath the skin has a relatively uniform pore size distribution over the entire cross section.

Unlike the PEI-W and the PEI-DW membranes that are structurally asymmetric, no visible pores are observed in the cross section of the PEI-D membrane, as shown in Figs. 2(c) and 3(c), at least at the resolution level of the electron microscope. The rough appearance in the membrane cross section is believed to arise



(a) (b) (c)

Fig. 2. Scanning electron micrographs of membrane cross sections for membranes (a) PEI-W, (b) PEI-DW, and (c) PEI-D. The membrane skins in (a) and (b) are at the bottom in the micrographs.



(a) (b) (c)

Fig. 3. Scanning electron micrographs of membrane cross sections for membranes (a) PEI-DW near skin side, (b) PEI-DW near substrate side, and (c) PEI-D.

from the intermolecular association of the polymer material in the casting solution that gives rise to polymer aggregates [14].

Note that the only difference in the preparation conditions for the above mentioned three membranes is in the solvent evaporation step prior to gelation. In the evaporation step, the local concentration of polymer on the surface of the cast polymer film increases due to the loss of solvent. Hence, the coagulation path in the polymer–solvent–nonsolvent ternary diagram, which determines the final membrane composition, or membrane porosity, during the subsequent immersion precipitation will be changed. On the other hand, the evaporation step also influences the kinetic aspect of membrane formation. According to Strathmann [15,16], fast precipitation of polymer solution in a nonsolvent tends to produce finger-like macrovoids, whereas slow precipitation tends to produce sponge-like structure. When the solvent loss on the film surface cannot be compensated by solvent diffusion from the film interior to the surface, phase separation in the surface region takes place. As a result, the resistance to the solvent–nonsolvent exchange in the later gelation step increases and, consequently, polymer precipitation slows down, resulting in a sponge-like structure. This explains the structural difference between the PEI-W and the PEI-DW membranes.

It should be mentioned that if the solvent evaporation time is sufficiently long, a completely dry membrane will be produced, and that the membrane structure may be asymmetric or symmetric, depending on the specific operation conditions. This is the case for the PEI-D membrane, which has a dense structure. In practice, many dense membranes used in laboratory studies are prepared by using the solvent evaporation method.

It is evident that the solvent evaporation step in the membrane preparation procedure has a significant effect on the resulting membrane structure. Simply by varying the solvent evaporation conditions, membranes with totally different structures can be produced from the same polymer.

Intrinsic permeability of polyetherimide (K_1)

The intrinsic permeability of the polyetherimide material can be determined by conducting pervaporation experiments using a dense membrane. Since the permeation rate of the dense PEI-D membrane was very low, thinner membranes were thus prepared. The permeability coefficient is supposed to be independent of membrane thickness. This is illustrated by Fig. 4 where there is a linear relationship between the pure water permeation flux and the reciprocal of the membrane thickness, although the permeation data are less reproducible from coupon to coupon for thinner membranes. The membrane having a thickness of 23 μm was used for the permeability measurements and the experimental data are shown in Fig. 5. The permeability coefficients were cal-

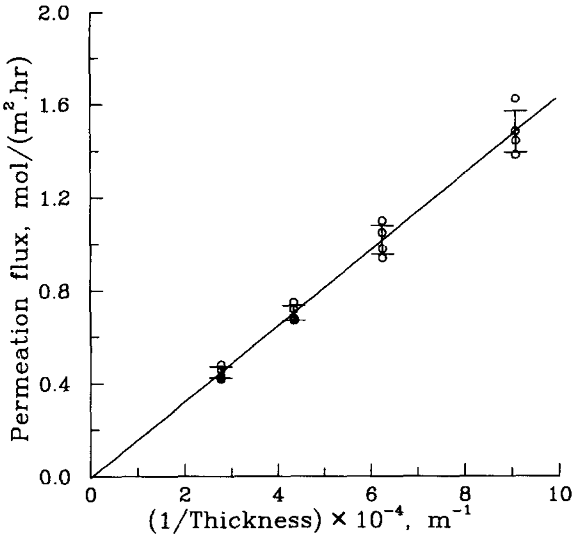


Fig. 4. Pure water flux versus reciprocal thickness of dense membranes. Temperature, 25°C.

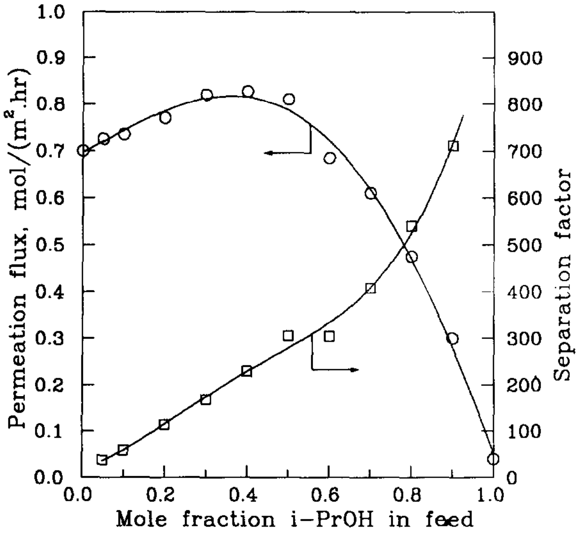


Fig. 5. The permeation flux and separation factor of a dense PEI membrane at 25°C.

culated from these data by using eqn. (1); the activity coefficients involved in the calculation were evaluated on the basis of the Wilson equation using the recommended Wilson parameters [17]. The permeability coefficients versus feed concentration is depicted in Fig. 6 which shows the permeability coefficient of water is approximately two orders of magnitude higher than that of isopropanol. To facilitate the mathematical treatment in the following part of the work, polynomial equations listed in Table 1 were fitted to these data using the least square method, and the curves are also plotted in Fig. 6.

The selectivity achievable in an asymmetric membrane

The influence of the substrate resistance on the selectivity of an asymmetric membrane can be calculated by applying eqn. (21). Figure 7 illustrates the typical results for $\alpha/\alpha_{\text{int}}$ as a function of the relative resistances. Note that the substrate resistance (R_{sub}) constitutes R_2 and R_3, namely $R_{\text{sub}} = R_2R_3/(R_2+R_3)$, and that the skin layer resistance (R_{skin}) is equal to R_1. Clearly, the selectivity–resistance graph can be divided into three regions:

(I)$R_3/R_2 < 10^{-4}$

(II)$10^{-4} < R_3/R_2 < 0.1$

(III)$R_3/R_2 > 0.1$

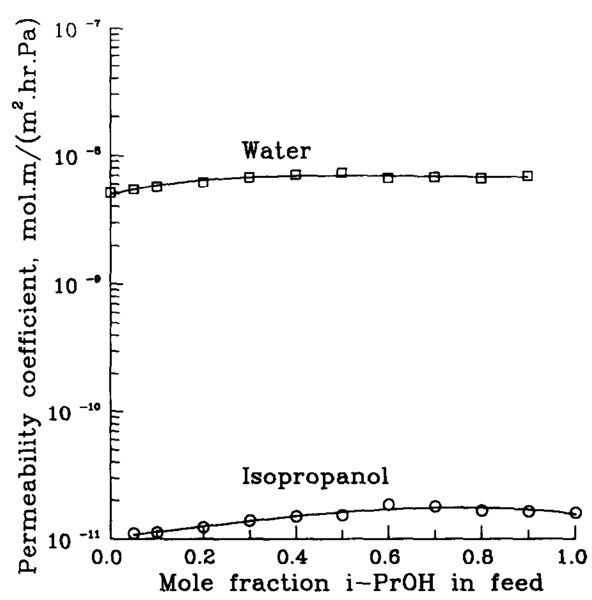


Fig. 6. The permeability coefficients of isopropanol and water through the dense PEI membrane at 25°C.

Consider the mass transport though the substrate. In Region I, less than 0.01% of the permeating molecules pass through the pores (R_2), and the remaining go though the polymer matrix (R_3) which exhibits the intrinsic selectivity. Consequently, $\alpha \approx \alpha_{\text{int}}$, regardless of the relative resistance of the skin layer and the substrate. However, the permeation flux of the asymmetric membrane will be as low as that of a dense membrane of the same thickness under the same operating conditions. Apparently, the permeation flux cannot be enhanced by using such an asymmetric membrane. Nevertheless, this result suggests that when measuring the

TABLE 1

Polynomial expression of permeability coefficient

$(K_1)_{H_2O} = (0.498+1.003X-1.602X^2+0.787X^3)\times10^{-8}$	mol-m/m²-hr-Pa
$(K_1)_{IPA} = (1.039+0.819X-1.604X^2+1.915X^3)\times10^{-11}$	mol-m/m²-hr-Pa
where X = feed isopropanol mole fraction	

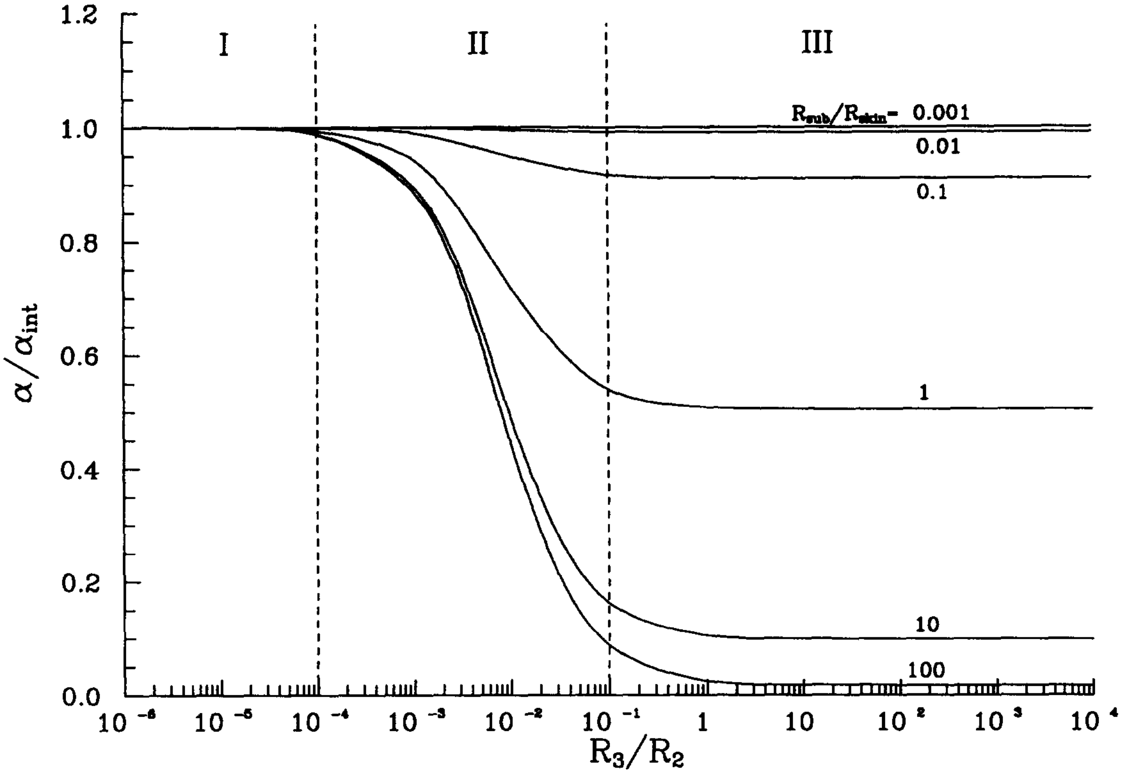


Fig. 7. The results of sample calculation for α/α_{int} as a function of relative resistances. Feed concentration, 0.5 mole fraction isopropanol.

intrinsic permeation properties the membrane does not need to be perfectly dense as long as the resistance of the pores is sufficiently large in comparison to the resistance of the polymer matrix.

Regarding Region II, the membrane selectivity is influenced by both the ratios R_3/R_2 and R_{sub}/R_{skin}. It is shown that the separation factor decreases considerably as R_3/R_2 increases, though R_2 still dominates the overall resistance of the substrate. Further, the selectivity decrease is more significant when the resistance ratio of substrate to skin layer is larger. In Region III, the Knudsen flow in the substrate becomes more important, and the membrane selectivity is determined predominately by R_{sub}/R_{skin}. When the skin layer controls the separation, the membrane selectivity approaches the intrinsic value; otherwise, the selectivity achievable in the asymmetric membrane will be lowered by the presence of the pores in the substrate.

The calculation results show that when the feed concentration increases from 0.1 to 0.9 mole fractions isopropanol, the $\alpha/\alpha_{\rm int}$ values in Regions I and III are essentially constant for a given set of data on R_3/R_2 and $R_{\rm sub}/R_{\rm skin}$, while $\alpha/\alpha_{\rm int}$ in Region II shifts upwards. Hence, only in Region II does the feed concentration affect the extent to which the separation potential of the membrane is utilized. It may also be noted that for a given value of R_3/R_2, the $\alpha/\alpha_{\rm int}$ data in both Region II and Region III decrease gradually with an increase in $R_{\rm sub}/R_{\rm skin}$ when $R_{\rm sub}/R_{\rm skin}$ is lower than 0.1 or larger than 10; the decrease in $\alpha/\alpha_{\rm int}$ is dramatic when $R_{\rm sub}/R_{\rm skin}$ is in intermediate range. The latter predictions from the simple resistance model can be used to explain the experimental observation of Gudernatsch et al. [8] who tested the effects of polymer concentration in casting solution for preparing substrate on the separation performance of silicone coated composite membranes. The higher the polymer concentration, the larger the substrate resistance (which is reflected by the decrease in gas permeation fluxes), and hence the larger the $R_{\rm sub}/R_{\rm skin}$ for the same silicone coating procedure; whereas R_3/R_2 values are essentially constant in the polymer concentration range of 17% to 27% (which can be judged from the constant gas permeability ratio of the substrate). Therefore, when the polymer concentration increases, the membrane selectivity changes from alcohol selective (which is intrinsic to the silicone skin layer) to water selective (which is intrinsic to the substrate polymer). Moreover, the selectivity change is most severe at intermediate polymer concentrations.

On the basis of the foregoing analyses, the following considerations arise:

(1) The overall membrane selectivity is influenced not only by the relative resistance of the skin layer and the substrate but also by the relative resistance of the polymer matrix and the pores in the substrate. Even a defect-free asymmetric membrane may still exhibit a very low selectivity if the resistances offered by the pores and the polymer matrix in the substrate are not well balanced.

(2) The development of high flux membranes should be directed not only at producing a thin skin layer but also at reducing the substrate resistance. Only when a thin skin layer is coupled with a highly permeable substrate will the separation potential of an asymmetric membrane be fully worked out.

(3) Based on the separation system studied here, a $R_{\rm sub}/R_{\rm skin}$ value of less than 0.1 will quarantee the asymmetric membrane to achieve more than 90% of the intrinsic selectivity. However, the effect of substrate resistance on the selectivity is expected to become more pronounced for the membranes produced from polymers of high permselectivities.

(4) There are numerous combinations of R_2 and R_3 for a constant $R_{\rm sub}$. It is not always advantageous to use highly porous substrate (i.e. large R_3/R_2) since $\alpha/\alpha_{\rm int}$ may be shifted from Region II towards Region III. Further, for substrate of a given porosity, the smaller the pore size, the better the separation performance, provided that the overall substrate resistance does not change significantly. This feature is particularly important when one can engineer the substrate precisely.

Analyses of PEI-W and PEI-DW membranes

Let $R_3/R_1=a$, and $R_3/R_2=b/K_1$. Then a and b are two constants for a given asymmetric membrane. Thus eqn. (21) can be rewritten as

$$\frac{\alpha}{\alpha_{\rm int}}=\frac{1+\dfrac{a}{1+0.547b/(K_1)_{\rm IPA}}}{1+\dfrac{a}{1+b/(K_1)_{\rm H_2O}}} \tag{22}$$

The α vs. X data are known from experiments [3], and K's and α_{int} are functions of X that have been obtained previously. The parameters a and b in eqn. (22) can be determined by applying nonlinear least square regression. An iterative estimation technique was used to find the solution, and the results are:

For PEI-DW membrane,

$a=3.086\times10^4$, and $b=8.191\times10^{-5}$ (mol-m/m^2-hr-Pa);

For PEI-W membrane,

$a=67.85$, and $b=6.155\times10^{-9}$ (mol-m/m^2-hr-Pa).

Because the K_1 data for water are not highly dependent on feed concentration (see Fig. 6), for the purpose of calculation we take an average value, which is 6.55×10^{-9} (mol-m/m^2-hr-Pa). Then the above a and b values can be converted into the desired R_{sub}/R_{skin} and R_3/R_2 data as follows

For PEI-DW membrane,

$R_3/R_2=1.25\times10^4$, and $R_{sub}/R_{skin}=2.47$

For PEI-W membrane,

$R_3/R_2=0.94$, and $R_{sub}/R_{skin}=34.9$

These data show that

(1) both membranes fall into Region III in the selectivity–resistance plot;

(2) in the substrate, the resistance of the polymer matrix (R_3) is much larger than that of the pores (R_2) for the PEI-DW membrane, while the two resistances are comparable for the PEI-W membrane;

(3) the substrate of the PEI-DW membrane offers 71% of the overall membrane resistance, while more than 97% of the permeation resistance in the PEI-W membrane is attributed to its substrate.

Since these membranes were not prepared under optimized conditions, the membrane structures are far from ideal in terms of membrane selectivity. Due to the deviation from the assumption of cylindrical pores in membrane substrate, these resistance ratio data so obtained may be considered to be effective or equivalent values. Using the resistance model approach, the membrane structures can be differentiated quantitatively. Note that the simple resistance model analyses developed above apply only to defect-free asymmetric membranes. This condition is satisfied for both the PEI-W and the PEI-W membranes, as indicated by their hydrogen/nitrogen permeation rate ratio of 75.6 and 38.7 (measured at 23°C and under a transmembrane pressure difference of 500 kPa), respectively, which values are much larger than the Knudsen flow selectivity of 3.74. For the cases where the membrane skin layer is defective, the mass transport through the defects should be taken into consideration in formulating the resistance configuration, which represents a further refinement of the resistance model.

It is worth noting that asymmetric polysulfone membranes were recently studied by Koops et al. [18] for the pervaporation of acetic acid/water mixtures. The polysulfone material exhibits good chemical resistance to acetic acid. It, however, is shown that the membrane selectivity is much lower than the intrinsic one, although the gas permeation data indicate the membranes to be defect-free. It was thus hypothesized that the low pervaporation selectivity of these asymmetric membranes was due to the defects introduced during pervaporation. Based on the present study, a more reasonable explanation may be that the substrate resistance influences the overall mass transport significantly.

Conclusions

This study demonstrates the utility of the resistance model approach to the asymmetric polyetherimide membranes for pervaporation. The asymmetric structure of the membranes are examined using scanning electron microscopy. The resistance model approach to the asymmetric membranes leads to a useful analysis on the relationship between membrane selectivity and the resistance components of the membrane. It is shown that not only the relative resistance of skin layer and substrate, but also the relative resistance of the polymer matrix and the pores in the substrate has an important effect on the membrane selectivity. If the resistances of the polymer matrix and the pores in the substrate are not well balanced, even a defect-free asymmetric membrane may still exhibit very low selectivity. The resistance model predictions are useful to the development of high performance asymmetric membranes for pervaporation applications. Based on the simple resistance model, the membrane structures can be differentiated in terms of the relative resistance components in the membrane.

Acknowledgement

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List of symbols

A	membrane area (m^2)
K	permeability coefficient (mol-m/m^2-hr-Pa)
l	membrane thickness (m)
M	molar mass (kg/mol)
p	permeate pressure (Pa)
p_s	saturated vapour pressure (Pa)
$[PR]$	permeation rate (mol/sec)
R	resistance (Pa-sec/mol)
R_g	gas constant (J/mol-K)
R_{skin}	resistance of skin layer (Pa-sec/mol)
R_{sub}	resistance of substrate (Pa-sec/mol)
R_t	overall resistance (Pa-sec/mol)
r	pore radius (m)
T	temperature (K)
ΔU	driving force for permeation (Pa)
X	mole fraction in feed
Y	mole fraction in permeate
α	separation factor
α_{int}	intrinsic separation factor
γ	activity coefficient
ϵ	porosity of substrate

Subscripts

H_2O	water
IPA	isopropanol
1	skin layer
2	pores in substrate
3	polymer matrix in substrate

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