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R. Gref[a]; Q. T. Nguyen[a]; J. Néel[a]
[a] LABORATOIRE DE CHIMIE-PHYSIQUE MACROMOLÉCULAIRE, C.N.R.S.-U.R.A 494, NANCY CEDEX, FRANCE

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Influence of Membrane Properties on System Performances in Pervaporation under Concentration Polarization Regime*

R. GREF, Q. T. NGUYEN, and J. NÉEL
LABORATOIRE DE CHIMIE-PHYSIQUE MACROMOLÉCULAIRE
C.N.R.S.-U.R.A. 494
1, RUE GRANDVILLE, BP 451 - 54001 NANCY CEDEX, FRANCE

Abstract

The concentration polarization phenomenon was studied in the case of the dehydration by pervaporation of octanol in relatively concentrated solutions (up to 47000 ppm of water in *n*-octanol). The dependence of the observed performances on the mass transfer properties of the membrane and the boundary layer is analyzed theoretically. Experiments performed with cellulose acetate membranes of different thicknesses at a variable stirring speed in an agitated cell allowed us to determine the parameters of the theoretical model. It appears that the selectivity in pervaporation may depend in a complex way on the mass transfer in the boundary layer due to the possible concentration-dependent coupling of fluxes in the membrane. Results of the simulations of situations in which the membrane characteristics as well as the mass transfer in the liquid phase were changed are given to illustrate the influence of different parameters on the observed performances.

INTRODUCTION

In many membrane processes, transport through the membrane may not be solely controlled by the membrane but also by the boundary layers that may develop on one side or both sides of the membrane. The mass transfer resistances in the boundary layers reside in the slow diffusion process (external transport) which is not able to keep up with the possible rates of "material consumption" at the interface by permeation through the membrane phase. The phenomenon, known as concentration polarization, may equally occur at the surface of solid catalysts or electrodes due to material consumption by the catalyzed or electrochemical reactions.

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In pervaporation, because of the relatively low permeability of dense membranes, the mass transfer resistance in the external liquid phase is often neglected in the total resistance. However, the importance of concentration polarization will grow because membranes with improved permeability and selectivity are expected to appear on the market. When the component extracted by the membrane in pervaporation is present at trace levels in the bulk of the feed solution, and its flux is sufficiently high, this component may be so depleted at the membrane surface that transport in the boundary layer becomes the rate-limiting step and completely controls the behavior of the membrane system. Such a situation was reported by Psaume et al. (*1*) for the extraction of trichloroethylene traces. These authors succeeded in describing their results by using the Levêque's correlation for the external phase resistance and neglecting any resistance of the membrane itself.

Coté and Lipski (*2*) used the resistances-in-series model to describe the general case in which the membrane, the boundary layer, or both, may control the transport rate, depending on the value of the mass transfer coefficient in the external liquid phase.

However, the reported cases concerned very dilute aqueous solutions of organic components; the pervaporation rates of the nonpreferentially permeating component, water, were always constant (*1*, *2*).

Pervaporation rates of the nonpreferentially permeating component are expected to change with the composition of the liquid at the membrane surface, and therefore, with the degree of concentration polarization when the feed liquid contains substantial amounts of the preferentially permeating component. This is due to the strong interactions that generally exist between solvents molecules and pervaporation membranes: at a sufficiently high concentration of the preferentially permeating compound in the liquid, the upstream part of the membrane becomes swollen to such an extent that the sorption and the diffusion properties of the other component(s) are affected. Such a concentration dependence of the membrane properties are well known in the pervaporation of mixtures of organic solvents with water (*3*, *4*) or with another organic solvent (*5*).

The objective of the present work is to study the influence of the concentration polarization on the performances of the membrane system in the case of dehydration, by cellulose acetate membranes, of octanol–water mixtures containing up to 4.7 wt% water. In the theoretical part, approaches using resistances-in-series and mass transfer equations in the boundary layer are discussed in taking into account the possible variations of membrane properties with the feed composition at the membrane surface.

THEORETICAL

Resistances-in-Series Approach

In order to account for the concentration polarization phenomenon in the frame of this approach, the boundary layer is assumed to be a physical layer with its own permeability to the components in the feed liquid. In spite of the dynamic nature of the boundary layer, i.e., there is a concentration gradient which acts as an additional resistance to the transport of the solute, this approach was successfully used to describe the permeation flux of trace solutes in pervaporation (*1*, *2*) or in gas permeation (*7*). The basic equation in this case is

Total resistance = (resistance of the feed side boundary layer)
+ (membrane resistance)
+ (resistance of the downstream side boundary layer)

In pervaporation, if high vacuum is applied on the downstream side, the resistance to mass transports on this side is negligible compared with the other resistances. An independent estimation of the liquid film resistance can be obtained from mass transfer correlations for different flow regimes in the feed compartment (*2*, *6*). The membrane resistance should be determined either by independent methods or by measurements under negligible concentration polarization.

Coté and Lipski (*2*) proposed the following expression, assuming the downstream side resistance negligible, for the steady-state flux of the solute from the liquid side to the vapor side:

$$J_A = (C_o^A - S_v/S_l C_v^A)/(1/k_l + 1/(S_l k_m)) \qquad (1)$$

where J_A is the mass flux of solute A
C_v^A is the concentration of A in the gas phase
S_l and S_v are the dimensionless equilibrium partitions coefficients at the upstream and downstream interfaces of the membrane,
k_l and k_m are, respectively, the mass transfer coefficients for solute A in the boundary layer and in the membrane

C_v^A is negligible compared with C_o^A in high vacuum pervaporation, hence Eq. (1) can be simplified:

$$J_A = C_o^A/(1/k_l + 1/(S_l k_m)) \tag{2}$$

An objection which can be made is that the extent of concentration polarization must depend not only on the permeability to the preferentially permeating component as indicated if one refers to Eqs. (1) and (2), but also largely on the selectivity. According to these equations, the extent of concentration polarization under given hydrodynamic conditions should be set by the permeability of the membrane to the solute. However, one can imagine that the situation would not be the same if for this permeability to the solute, the membrane exhibited different permeabilities to the solvent. At the extremes, when the solvent flux is negligible compared with the solute flux (membrane with very high selectivity), the concentration polarization should be maximum. On the contrary, when the membrane is not selective (same mass ratio of solvent flux to solute flux as that of the components in the feed mixture), there should be no polarization at all, whatever the absolute flux of the solute.

In fact, Eqs. (1) and (2) do not take into account the contribution of the bulk flow of the fluid, due to permeation through the membrane, to the diffusion transport of the solute in the stagnant layer (polarization layer). The more important this contribution, the more the extent of concentration polarization derived from Eq. (2) with the mass transfer coefficient obtained from known correlations is overestimated. The actual flux of A, J'_A, to the membrane surface in the polarization layer in which there is bulk flow of the fluid is

$$J'_A = (J_A + J_B w_o^A)/(1 - w_o^A) \tag{3}$$

The model would only be used when the solution is dilute ($1 - w_o^A \approx 1$) and when the streaming flux of A due to the flux of B is negligible. We will arbitrarily assume that the contribution due to the bulk flow of the fluid would be negligible if the streaming flux of A due to the flux of B is less than 1% of the flux due to diffusion of A in the stagnant film:

$$J_B w_o^A / J_A < 10^{-2} \tag{4}$$

According to Coté and Lipski (2), the selectivity coefficient α generally used in pervaporation can be expressed as a function of the mass fluxes of components A and B, and the bulk mass fraction of A:

$$\alpha = (J_A/J_B)\,(1 - w_o^A)/w_o^A \tag{5}$$

Equation (3) can be rewritten by taking into account Equation (4):

$$\frac{J_B w_o^A}{J_A} = (1 - w_o^A)/\alpha < 10^{-2} \qquad (6)$$

The condition expressed in Eq. (11) is satisfied when the selectivity coefficient exceeds 10^2 for dilute solutions (e.g., $w_o^A < 10^{-3}$).

Another complication is that in pervaporation, the flux of the solvent (B) may significantly change with the concentration of the preferentially permeating specie (solute A) at the membrane surface. This may occur even if the concentration of solvent B remains quasi-constant (but that of the solute may be drastically reduced) (Fig. 1). This phenomenon is known as the coupling effect (which could be a flux coupling or a sorption for which the selectivity changes with the composition of the liquid phase).

For binary mixtures, if the intrinsic characteristics of the membrane can be obtained at different compositions, it would be possible to express the membrane permeability to each component as a function of the external concentration of the preferentially permeating component (solute A).

Under the conditions that an expression of the permeability (which may be concentration dependent) to solute A as a function of the external concentration of A is obtained, the steady-state conditions imply equal fluxes for the permeation in the boundary layer(s) and in the membrane:

$$J_A = k_l(C_o^A - C_m^A) = PC_m^A \ (= kC_o^A) \qquad (7)$$

where P is the permeance of the membrane to the component A: $P = k_m S_l$.

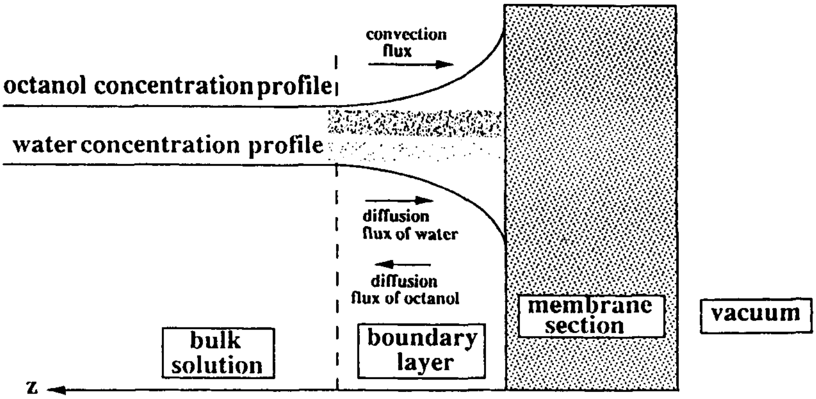

FIG. 1. Concentration profiles in the polarization layer: schematic representation of molecule densities of the preferentially transported component A (minor component) and of the major component B.

There is an "auto-adjustment" of C_m^A in order to satisfy the steady-state conditions, i.e., the equality in Eq. (3) can be simulated by computers, with k_l values calculated from known correlations, to give C_m^A, and therefore J_A.

The flux of B can be derived from the expression that links the permeance of the membrane to the solvent B, to the external concentration of A (the mass conservation in the external phase implies that the sum of concentrations of A and B is constant). The situation is simplified when the permeance of the membrane to the component A is constant:

$$J_A = C_o^A/(1/k_l + 1/P) \tag{8}$$

in which the permeance can be written as a function of the intrinsic permeability P' and the membrane thickness δ:

$$P = P'/\delta \tag{9}$$

The concentration C_o^A can be expressed as a function of the mass fraction of A, w_o^A and the specific mass ρ:

$$C_o^A = w_o^A\rho \tag{10}$$

Equation (7) becomes

$$J_A = \rho w_o^A(1/k_l + \delta/P') \tag{11}$$

The flux of solvent B, which may depend on C_m^A, the concentration of A at the membrane surface, can be calculated from the value of C_m^A obtained from Eq. (7):

$$J_B = P_B(1 - \rho w_o^A) \tag{12}$$

In the presence of a large excess of solvent B, the factor $(1 - \rho w_o^A)$ is practically equal to 1, and J_B depends only on the permeance P_B of the membrane to the solvent B at the composition corresponding to C_m^A. The composition of the permeate is given by the ratio of the flux of the component A to the total flux:

$$w_p^A = J_A/(J_A + J_B) \tag{13}$$

Values for different parameters characterizing the observed selectivity can be calculated from the value of w^A by using the appropriate definition. In our opinion, the enrichment coefficient β, which is defined as the weight fraction of the component A in the permeate to that in the feed, is more appropriate to characterize the selectivity, since it can be used to calculate the productivity of the membrane (*8*). We will therefore use this coefficient to study the influence of the concentration polarization on the selectivity. Equation (13) can be rewritten by taking into account Eq. (2) and the definition of the coefficient β:

$$\beta = w_p^A/w_o^A = \rho_p/[C_o^A + J_B(1/k_l + 1/P)] \qquad (14)$$

This equation is useful when the flux of solvent (component B) remains constant, i.e., in numerous cases reported in the literature (*1*, *2*, *9*). Under this condition, which should be valid for very dilute solutions, the selectivity characteristic can be predicted for different values of boundary layer resistance and membrane resistance.

When the flux of the component B (solvent) depends on the composition of the solution at the membrane surface, i.e., on C_m^A, the value of J_B must be calculated first from the intrinsic correlation of J_B and the composition. The value of C_m^A can be computed from Eq. (15) expressing the steady-state flux of A through the system:

$$k_l(C_o^A - C_m^A) = C_o^A/(1/k_l + 1/P) \qquad (15)$$

i.e.,

$$C_m^A = C_o^A[1 - 1/(1 + k_l/P)] \qquad (16)$$

EXPERIMENTAL

Apparatus and Procedure

Pervaporation of alcohol/water mixtures is performed in a cylindrical, double-walled glass cell fitted out with four baffles and an axial turbine. The stirring speed is controlled by a tachometer (Fig. 2). The membranes, supported by a filter, are clamped at the bottom of the cell and the permeate is collected in traps cooled by liquid air. For the experiments with a conjugate phase (e.g., water–octanol mixtures at 4.7 wt% water), the concentration in the bulk phase is kept constant by circulating the feed mixture in an auxiliary tank in which the two conjugated phases are kept in contact under stirred conditions (Fig. 3). The loss of one component by pervaporation is compensated for by a transfer between the two phases in thermodynamic equilibrium whose concentrations depend only on the tem-

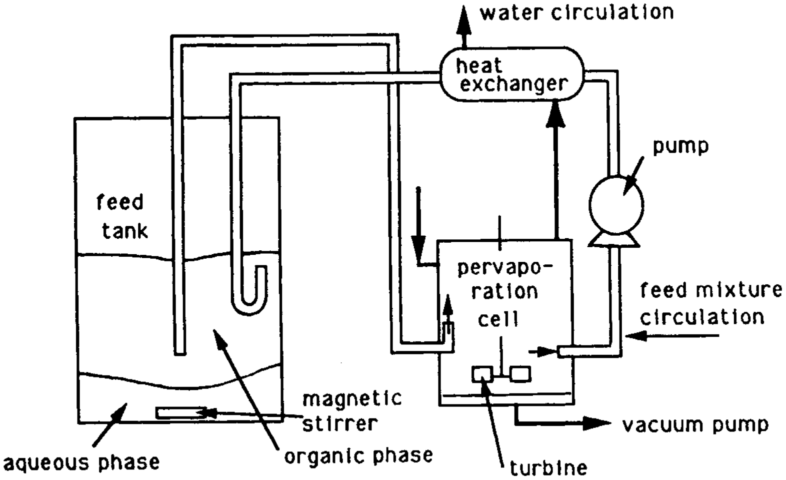

FIG. 2. Schematic representation of the experimental set-up.

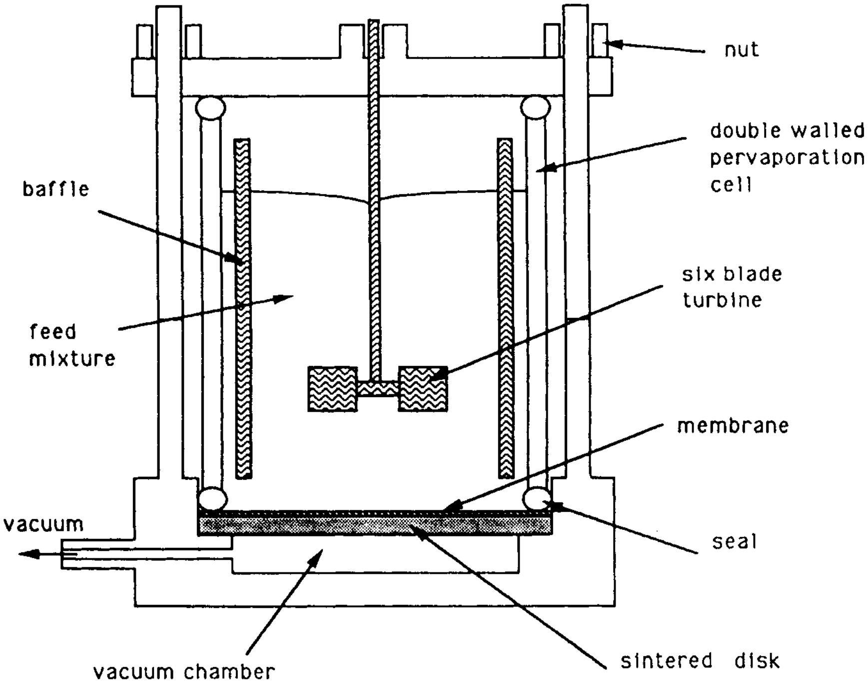

FIG. 3. Details of the pervaporation cell.

perature. The constance of the water content in the cell is determined by Karl-Fischer titration or by gas chromatography.

The measurement of water and alcohol component fluxes was performed by using an automatic apparatus. A well-defined amount of permeate is analyzed by a gas chromatograph controlled by a computer (9).

Membranes

Cellulose acetate of 39.8% acetyl content was obtained from Eastman Kodak. The polymer films were made by casting solutions of cellulose acetate (CA) in acetone at appropriate concentrations on a glass plate by means of a helicoidal rod. The solvent was carefully evaporated first (20 min) at room temperature and afterwards (30 min) in an oven at 60°C. Finally, the CA films were annealed in distilled water at 90°C for 30 min to ensure good reproductiveness of their properties.

RESULTS AND DISCUSSION

Our investigations involving checking the validity of the resistances-in-series model and determining their parameters and then simulating the influence of some parameters on the performances of the pervaporation membrane under the concentration polarization regime. The experiments were performed with the cellulose acetate membrane and the water–octanol mixtures.

Determination of Parameters of the Resistances-in-Series Model for the Water–Octanol–Cellulose Acetate Membrane (CA) System

The cellulose acetate membrane is highly selective to water in this mixture. At low concentration polarization, a permeate containing more than 99 wt% water was obtained from a feed mixture containing 4.7 wt% water (water-saturated octanol), i.e., the value of the enrichment coefficient α exceeds 2000. Due to the high selectivity of the membrane, the system satisfies in all cases the conditions required (Eq. 11) for the application of the resistances-in-series model.

Validation of the Model

The total mass transfer coefficient for water permeation k is plotted as a function of the stirring speed for the CA membranes of different thicknesses in Fig. 4. For the thinnest membrane, k depends strongly on the stirring speed, although the increase in the total mass transfer of water slows down with an increase in the speed. This dependence is reduced when the membrane thickness increases and the total mass transfer of water levels off more and more rapidly. These behaviors clearly indicate the

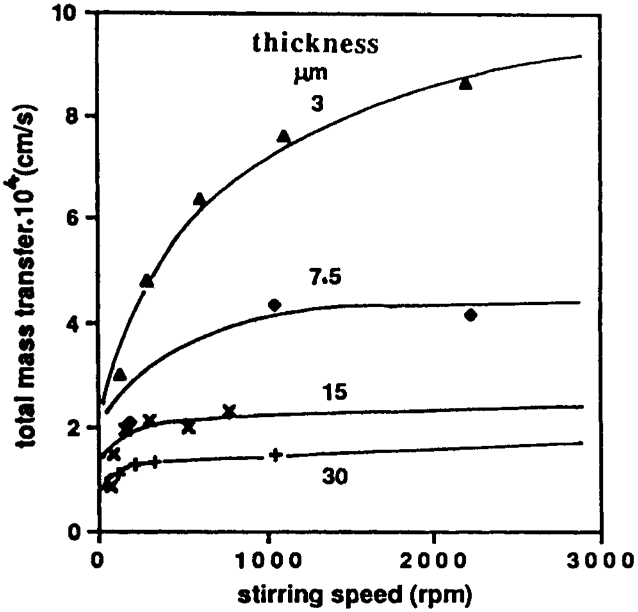

FIG. 4. Total mass transfer coefficient versus stirring speed in the pervaporation of the water–octanol mixture containing 4.7 wt% water with membranes of different thicknesses at 40°C. Solid lines are calculated curves obtained from model fitting.

limitation of water permeation by the concentration polarization, which is more severe for thinner membranes (higher P value) and for lower stirring speeds (higher boundary layer resistance).

A plot of enrichment coefficient versus stirring speed (Fig. 5) also shows a larger negative deviation of the selectivity for thinner membranes at lower stirring speeds. It appears that, contrary to the general opinion, significant concentration polarization can occur even at high feed concentrations (47,000 ppm in the present case) and under turbulent flow, provided that membranes of high selectivity and permeability are available.

The parameters of water permeation which take into account the influence of the stirring speed and the membrane thickness were obtained by a least-square fitting of all the experimental data in Fig. 4. The equations used are Eq. (11) for water permeation and the empirical relationship (17) between the stirring speed and the mass transfer coefficient in a liquid phase under agitation:

$$k_l = a\omega^{(b)} \tag{17}$$

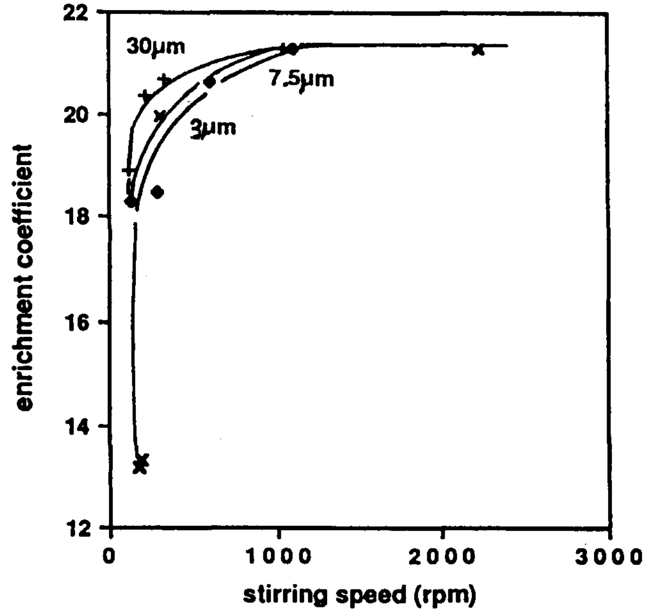

FIG. 5. Enrichment coefficient versus stirring speed in the pervaporation of the water–octanol mixture containing 4.7 wt% water with membranes of different thicknesses at 40°C.

The coefficient a and the exponent b depend on the cell geometry and are determined from the experimental data. Least-square fitting gave the following values:

$$P' = 4.1 \times 10^{-7} \text{ cm}^2/\text{s}$$

$$k_l \text{ (cm/s)} = 2 \times 10^{-5} \, \omega^{0.63} \text{ cm/s}$$

where the stirring speed ω is expressed in revolutions per minute.

The following remarks can be made:

A unique value of the intrinsic permeability coefficient was obtained for different membrane thicknesses. The good agreement between the experimental data and the theoretical curves obtained with these values in Eq. (11) (Fig. 4) allows us to conclude that the model correctly describes the variation of the flux of the preferentially permeated component (water) as a function of the hydrodynamic conditions as well as of the membrane intrinsic properties.

The value 0.63 for exponent b in the stirring speed–k_l mass transfer coefficient correlation is consistent with the values found in the literature, i.e., 0.6–0.65, from other techniques for similar stirred cells (*10*).

Determinations of the Mass Transfer Coefficients k_l and Membrane Permeability

It is not necessary to perform such a series of experiments to obtain the parameters of the model. For a given hydrodynamic condition (the given stirring speed and feed mixture in our cases), k_l and membrane permeability can be obtained by using membranes with different thicknesses. A plot of total transport resistance versus membrane thickness must give a straight line which intercepts the y-axis at the value corresponding to the reciprocal of the liquid phase mass transfer coefficient, and whose slope corresponds to the reciprocal of the permeance. Such a plot (Fig. 6), obtained from independent experiments, gives the same results as previously: $P' = 4.6 \times 10^{-7}$ cm²/s, $k_l = 4.8 \times 10^{-4}$ cm/s at $\omega = 160$ rpm.

It should be noted that the data obtained with stacks of membranes are

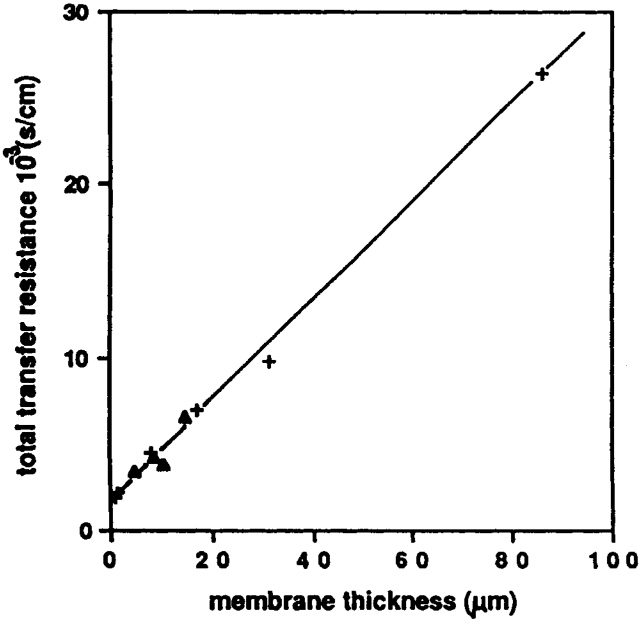

FIG. 6. Variation of the total resistance as a function of the membrane thickness in the pervaporation of the water–octanol mixture containing 4.7 wt% water at a stirring speed of 160 rpm (+, integral membranes; ▲, stacks of membranes).

entirely consistent with those obtained with integral membranes (Fig. 6). Therefore, these parameters can be simply determined by using stacks of the same membrane (with homogeneous properties).

An alternative way to determine these parameters is to measure the water flux of a given membrane at different stirring speeds and to subsequently fit the data with Eqs. (8) and (17). An example is given in Fig. 7 for a 1-μm-thick membrane. Good fitting was obtained with the same values for the correlation between the stirring speed and the liquid phase mass transfer coefficient. However, the value $P' = 1.1 \times 10^{-7}$ cm^2/s obtained for the intrinsic permeability is significantly lower than the one obtained from the data corresponding to Figs. 4 and 6 for the same polymer material ($P' = 4 \times 10^{-7}$ cm^2/s).

Because the membrane thickness was measured with reasonable precision, the lower intrinsic permeability must come from the formation history of this membrane. Indeed, due to its small thickness, the 1-μm-thick mem-

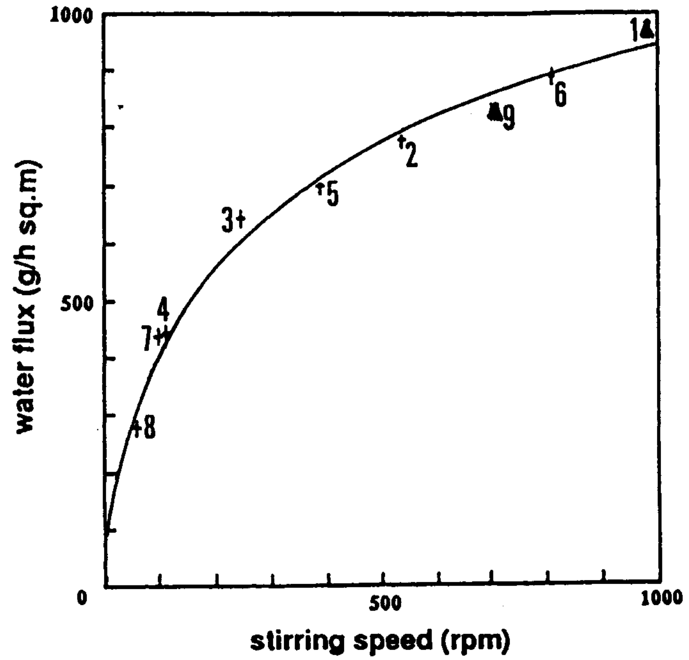

FIG. 7. Variation of the water flux as a function of the stirring speed in the pervaporation of the water–octanol mixture containing 4.7 wt% water from a 1-μm thick CA membrane at 40°C. Numbers are the "run number." The solid curve is the best fit curve obtained with $k_l = 2.2 \times 10^{-5}\ \omega^{0.63}$ cm/s and $P = 1.1 \times 10^{-3}$ cm

brane had to be laid on a porous support (nonwoven paper) during its oven drying and was used with the support without stripping, while the other samples were annealed in hot water in the free standing form. The adhesion of the film on the support prevents its shrinkage in the plane dimension during drying, and the morphology of the polymer should be different. Since cellulose acetate is a semicrystalline polymer, heating of the film under stress leads to a certain degree of crystallinity or chain orientation, and consequently a lower permeability. Nevertheless, the permeation properties of this membrane remained stable during pervaporation, because the water permeability is the same whatever the order of the run.

Influence of the Feed Composition on Water and Organic Fluxes

The water content in the feed mixture was varied in the 1 to 4.7% range, and the permeation fluxes for both components at different stirring speeds were measured (Figs. 8 and 9). The water flux at constant stirring speed is proportional to the water content in the bulk feed (Fig. 8). This behavior means that the water flux is proportional to the water content at the membrane upstream face, as one can deduce from Eq. (8) or (11) in which the

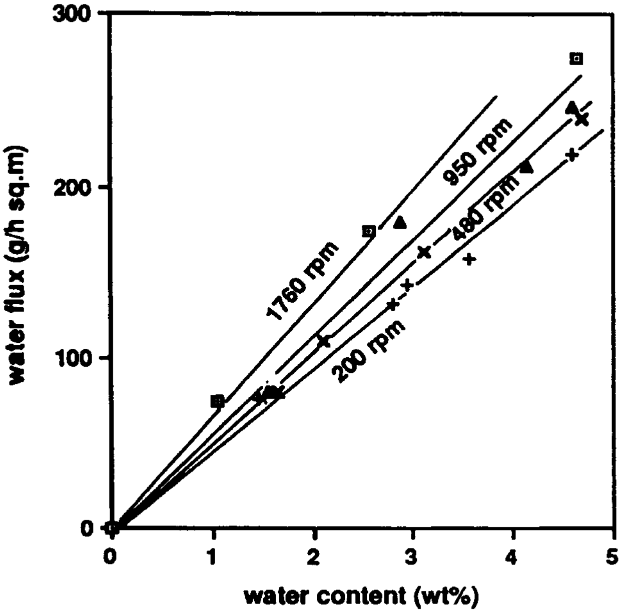

FIG. 8. Permeation flux of water versus water content in the feed in the pervaporation of water–octanol mixtures of different compositions through a 15-μm thick membrane at 40°C.

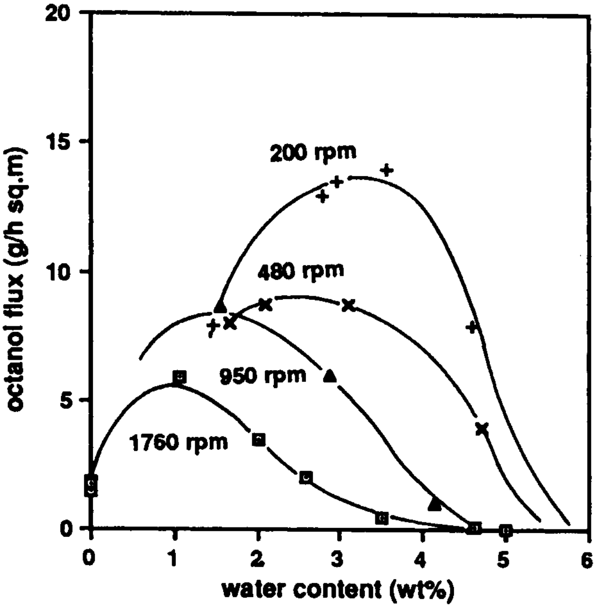

FIG. 9. Permeation flux of octanol versus water content in the feed in the pervaporation of water–octanol mixtures of different compositions through a 15-μm thick membrane at 40°C.

term $1/k_l$ remains constant. In other words, the permeability to water of the cellulose acetate membrane remains constant in this concentration range (Eq. 8), if the mass transfer in the liquid phase at constant agitation does not change significantly with the water content in this range.

On the other hand, the octanol flux increases from practically zero to a maximum, then decreases again (Fig. 9) when the water content increases. The maximum values shift to higher water content when the stirring speed decreases. This behavior indicate a coupling between the octanol flux and the water flux, i.e., octanol alone has a negligible permeation flux and its permeation is caused by the permeation of water. If there were no coupling, the octanol flux would decrease slightly when the water content increased. However, flux coupling is a complex phenomenon in pervaporation.

Flux couplings result from a complex interplay in the interactions between the components themselves and with the membrane, and they therefore depend strongly on the system and its composition. Since no general relationship is available, the variation of the intrinsic octanol flux as a function of the water flux has to be determined experimentally by using the data at the highest stirring speed (i.e., at negligible concentration polarization). The following relationship, valid for concentrations up to 4.7 wt% water, was obtained by least-square fitting:

$$J_B = 1.658 + 0.1028\,w_m^A - 7.856 \times 10^{-4}\,(w_m^A)^2 + 1.9125 \times 10^{-6}\,(w_m^A)^3 - 1.533 \times 10^{-9}\,(w_o^A)^4 \quad (18)$$

Equations (15) and (17) were used for numerical computation of the water content at the membrane surface and the octanol flux for different stirring speeds and water contents in the bulk. Plots of calculated octanol fluxes versus water content (Fig. 10) show a translation of the observed octanol fluxes toward higher water contents when the stirring speed decreases. Qualitatively, this shift of the observed fluxes is consistent with the experimental results and is explained by the fact that the more severe the concentration polarization, the lower the water content that the membrane "sees" at its surface (for a given feed water content), i.e., the membrane really works at a water content lower than the concentration in the bulk

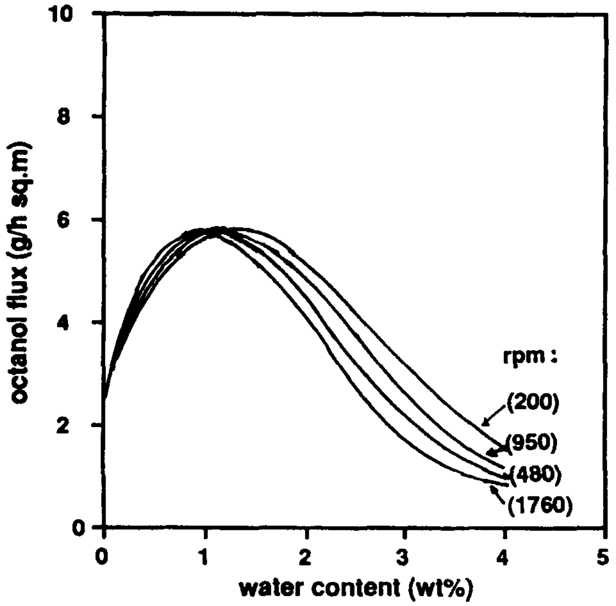

FIG. 10. Calculated octanol flux versus water content in the feed for the case represented in Fig. 9. Curve "1760" rpm was used as the intrinsic octanol flux at different water contents at the membrane upstream face.

phase. This can also be seen in the graphical method which can be used for the determination of the octanol flux (in the absence of temperature effect) under the concentration polarization regime. The graphical method (Fig. 11) involves determining the concentration of the solute (water) at the membrane surface (horizontal line AB starting at the observed water flux at the feed composition and intersecting the intrinsic water flux curve at the membrane surface concentration) and using it to determine the octanol flux which should be observed at this membrane surface concentration; it can be seen that the observed octanol flux lags behind the intrinsic flux. However, the model does not predict the increase in the maximum of the octanol flux in the whole concentration range corresponding to the one-phase mixture of water and octanol when the stirring speed decreases. If the intrinsic membrane properties are constant, the *maximum* of the

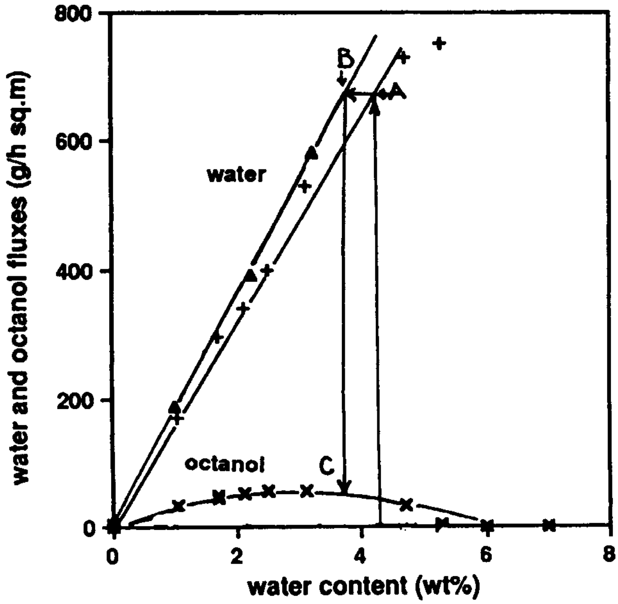

FIG. 11. Graphic method for the determination of the B component flux (octanol) under concentration polarization regime of the A component (water). A: Observed water flux at the considered feed water content. B: Water content in the mixture in contact with the membrane surface; intersection of the water flux level with the plot of intrinsic water flux (no concentration polarization) versus feed water content. C: Octanol flux corresponding to the composition of the mixture at the membrane surface intersection with the plot of intrinsic octanol flux versus feed water content). The method is only valid in the case of concentration polarization alone.

octanol flux should not change with the amplitude of the concentration polarization. Indeed, the octanol flux is an *intrinsic* property of the membrane, which depends *only* on the *temperature* and the *composition* of the mixture with which the membrane surface is in contact, i.e., the *maximum* of the octanol flux in the concentration range depends uniquely on the temperature. Besides, it could not be a change in the membrane structure because we checked that the membrane characteristics were not modified by the pervaporation experiments.

We turn then to the only parameter which can lead to such a change in the maximum of the octanol flux in the concentration range studied. In pervaporation, there is a phase change in the permeation; therefore, there is heat transfer from the bulk liquid phase. The temperature gradient should depend on the stirring speed: the lower the stirring speed, the lower the temperature at the membrane surface. Nevertheless, it is difficult to study the influence of the temperature polarization due to coupling between heat and mass transfers: the observed fluxes would result from both the concentration and temperature polarizations. In order to determine the origin of the deviation, we measured the membrane characteristics at three temperatures under strong stirring. Figure 12 shows the changes in octanol and water fluxes as a function concentration and temperature. Surprisingly, the octanol flux decreases when the temperature increases (Fig. 12, right), while that of water increases (Fig. 12, left).

The increase in pervaporation flux with temperature is well established in the literature and is accounted for by the Arrhenius equation (*11*, *12*). As far as we know, a decrease in pervaporation flux, when the temperature increases, has not been reported. Although such a decrease remains unexplained from the physical point of view, it allows us to interpret the increase in the maximum of octanol flux. When the stirring speed decreases, the temperature polarization as well as the concentration polarization develop further. Along with the decrease in the water content, there is a decrease in the temperature for the mixture in contact with the membrane. As a consequence, the octanol flux does not change from what the flux would be at the composition at the membrane surface but at the temperature of the bulk phase due to a temporary change in the membrane permeability. The larger shifts of the maximum toward higher water content than those given by the model of concentration polarization alone should also be due to the change in the membrane characteristics with temperature. The coupling between mass transfer and heat transfer in the permeation is a complex problem and is beyond the scope of the present paper. In the frame of the model presented in this paper, the concentration polarization alone, although it allows us to account for the experimental data for water permeation, does not mean that there is no temperature polarization. Even

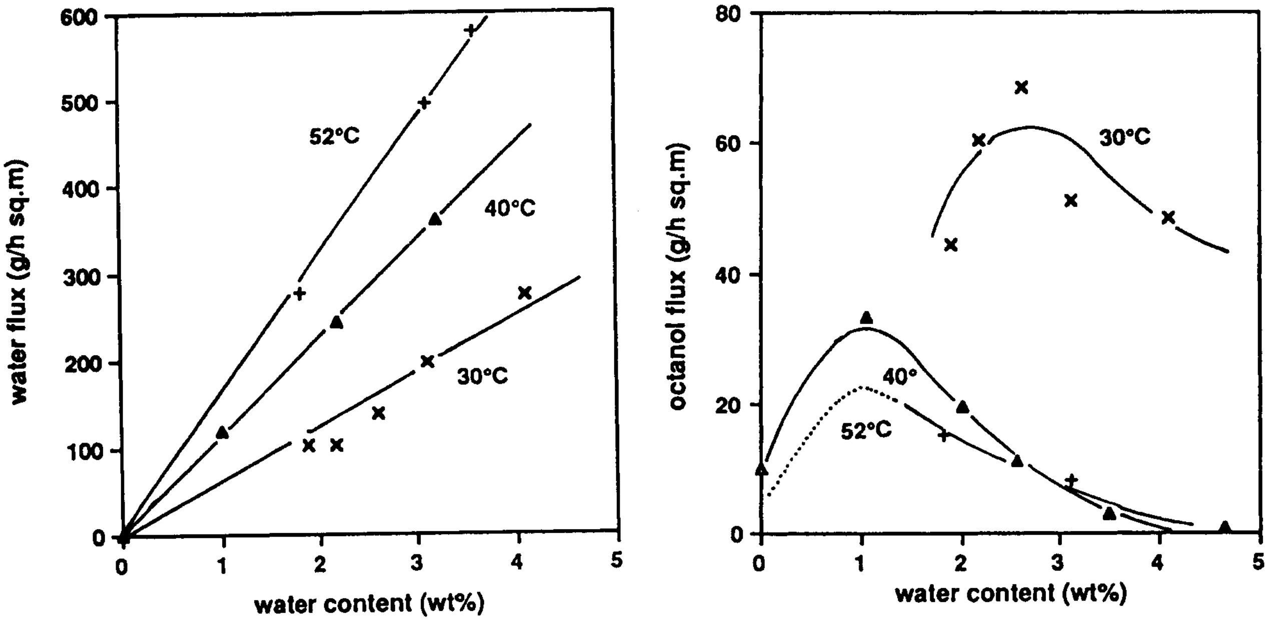

FIG. 12. Variation of octanol fluxes (right) and water fluxes (left) under negligible concentration polarization as a function of the water content in the feed at different temperatures. Stirring speed: 1700 rpm. Membrane thickness: 7 μm.

if the concentration polarization mainly controls the mass transfer, the temperature polarization should occur to a certain extent insofar as there is heat consumption in the membrane, i.e., a pervaporation flux. However, the effect of temperature polarization may not be discerned from that of the concentration polarization when the controlling parameter is only the stirring speed. This should be the case for the water flux since both concentration and temperature polarizations lead to a decrease in the observed water flux. The exceptional decrease in the intrinsic octanol flux with increasing temperatures allowed us to deduce such temperature polarization. Unfortunately, thermostatic control of the membrane, which would enable us to study the concentration polarization alone, is very difficult to implement in our pervaporation cell. Of course, the discrepancy between the observed and calculated octanol fluxes leads to a discrepancy between the experimental and calculated values of the permeate water content: it is lower than the one predicted by the model of concentration polarization alone (Fig. 13).

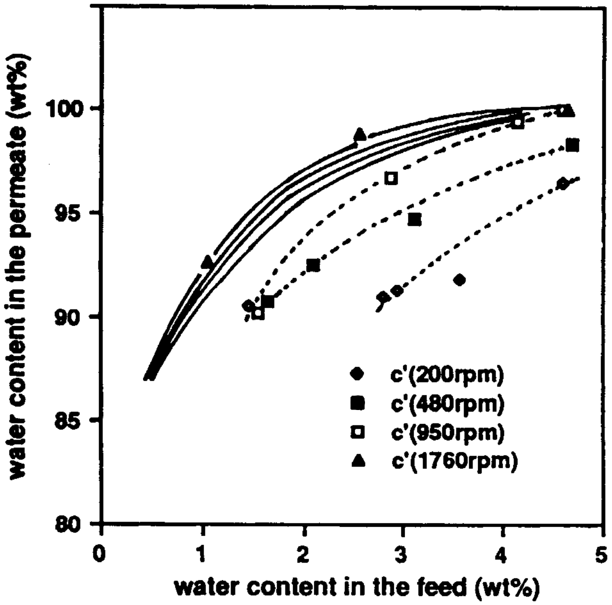

FIG. 13. Permeate water content versus water content in the feed for different stirring speeds in the pervaporation of water–octanol mixtures through a 15-μm thick CA membrane at 40°C. Solid lines correspond to computed results in the case of concentration polarization alone.

PREDICTION OF THE INFLUENCE OF DIFFERENT PARAMETERS ON THE APPARENT MEMBRANE PERFORMANCES

The resistances-in-series model, when it is applicable, is very convenient for the prediction of the behavior of a system in pervaporation. For instance, in the case of the extraction of organic solutes from dilute aqueous solutions by elastomer membranes, the flux of component B (i.e., water in this case) does not depend on the concentration of component A (i.e., organic solute), and the intrinsic permeability of the membrane to component A is constant.

The extent of concentration polarization, which can be defined as the ratio of the concentration of solute A at the membrane surface to that in the bulk, is derived from Eq. (16):

$$C_m^A/C_o^A = 1 - 1(1 + k_l/P) \tag{19}$$

It appears from Eq. (19) that the extent of polarization depends only on the ratio of mass transfer in the liquid to the intrinsic permeance of the membrane to component A, not on the feed concentration.

The concentration polarization ratio (C_m^A/C_o^A) is shown in Fig. 14 as a function of the ratio of the mass transfer coefficient in the liquid to the permeance of the membrane to the solute, k_l/P. The polarization ratio increases sharply first with the ratio k_l/P and reaches a value of 0.8 at a value of k_l/P of about 4. Beyond this point, the polarization ratio increases more and more slowly as k_l/P increases. As an increase in k_l/P for a given membrane (given P) requires a higher pumping energy, it might not be attractive, from an economic point of view, to reduce the concentration polarization beyond a certain value of k_l/P by increasing the fluid velocity. The gain in the overall performances become smaller and smaller when the mass transfer in the liquid k_l increases, but the energy cost to obtain such an increase in k_l is higher and higher [since k_l increases as the fluid velocity is raised to the power 0.8 in turbulent flows (*2*)]. Conversely, for given hydrodynamic conditions, an improvement in membrane permeance, e.g., by using thinner membranes, might not bring about the expected gain, especially if the polarization was already significant.

The enrichment coefficient decreases with an increase in the solute content:

$$\beta = \rho_p/[C_o^A + J_B(1/k_l + 1/P)] \tag{20}$$

It also depends on the extent of concentration polarization via the second

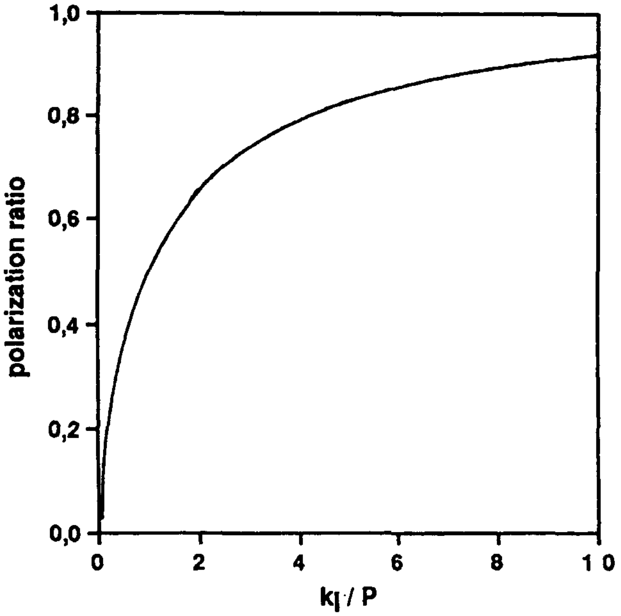

FIG. 14. Concentration polarization ratio (C_m^A/C_o^A) versus ratio of the mass transfer coefficient in the liquid to the permeance of the membrane to the solute (k_l/P). The master curve is valid for all concentrations insofar as the resistance model is valid.

term in the denominator. The departure from selectivity in the absence of polarization can be derived from Eq. (14):

$$\beta = 1/(1/\beta_o + J_B/k_{l\rho}P) \tag{21}$$

where the enrichment coefficient β_o in the absence of polarization ($1/k_l = 0$) is

$$\beta_o = \rho_p/(C_o^A + J_B\rho) \tag{22}$$

At a given concentration, the departure from ideal selectivity is larger when the mass transfer in the liquid phase is smaller. Figure 15 gives the variation of the selectivity as a function of the mass transfer coefficient in the liquid for different values of membrane permeance and feed concentration. When the flux of the solvents and of the membrane permeance increase while their ratio remains constant, the range of k_l in which the concentration polarization is effective is widened (Curves 1 and 4 compared with Curve 2). Under the same transport conditions in the membrane and

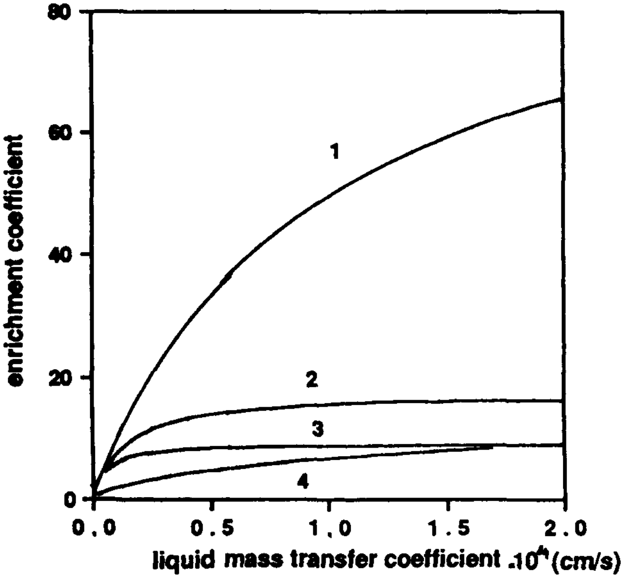

FIG. 15. Selectivity coefficient β as a function of mass transfer coefficient in the liquid phase for different cases:

Case 1: $J_B = 10^{-6}$ cm/s; $P_m = 2 \times 10^{-4}$ cm/s; $w_o^A = 0.005$
Case 2: $J_B = 10^{-6}$ cm/s; $P_m = 2 \times 10^{-5}$ cm/s; $w_o^A = 0.005$
$J = 10^{-6}$ cm/s; $P_m = 2 \times 10^{-4}$ cm/s; $w_o^A = 0.05$
Case 3: $J_B = 10^{-6}$ cm/s; $P = 2 \times 10^{-5}$ cm/s; $w_o^A = 0.05$
Case 4: $J_B = 10^{-5}$ cm/s; $P = 2 \times 10^{-4}$ cm/s; $w_o^A = 0.005$

in the external phase, the range of the mass transfer coefficient in the liquid extends more to higher values when the solute concentration decreases (Curve 1 compared with Curve 3).

The influence of concentration polarization on the total flux can be derived from the flux of the solute and that of the solvent. Insofar as the solvent flux (J_B) is constant, the total flux varies with the mass transfer coefficients and concentration exactly in the same way as the solute flux, i.e., it increases linearly with the solute concentration, with the slope given by the reciprocal of the sum of the membrane resistance and the liquid film resistance (Eq. 8). In the case of dependence of the solvent flux (J_B) on the composition of the mixture at the membrane upstream face, J_B must be calculated from this composition as computed by using Eq. (16) and the expression for the dependence of J_B on the composition. The selectivity can be easily derived from the component fluxes by using its definition.

The resistances-in-series model, when it is applicable, is a useful tool for guiding the choice of the best membranes and operating conditions, especially in the case of dilute solutions.

SYMBOLS

a	coefficient of the liquid mass transfer–stirring speed correlation
b	exponent of the liquid mass transfer–stirring speed correlation
C	mass concentration of the specified specie (superscript)
J	flux of a component (specified by the superscript)
k	mass transfer coefficient
P	permeance (permeability coefficient of the membrane as a whole) of the membrane to the solute
P'	intrinsic permeability of the membrane material to the solute
S	partition coefficient of the solute in the solution–membrane system
w	weight fraction of a component in the liquid

Greek

δ	membrane thickness
ρ	specific mass

Superscript

A	refers to the solute (which is the preferentially permeating component)
B	refers to the solvent (which is the slow component in the pervaporation)

Subscript

l	refers to the upstream liquid phase adjacent to the membrane
m	refers to the membrane
o	refers to the bulk liquid phase
p	refers to the permeate

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