

# Gas-Sweeping Pervaporation: A Method for Studying the Transport of Solvent Mixtures in Polymers: Application to the Methanol–Propan-1-ol–Cellulose Triacetate System

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## SYNOPSIS

A new method using a batch gas-sweeping pervaporation was proposed for the measurement of different transport parameters of a polymer film to a solvent mixture. In addition to the total permeation flux and the selectivity of the film to the mixture, the diffusion coefficients and the permeation coefficients of the components can be determined. The method, which is based on new solutions of the second Fick law in which the upstream concentration is time-dependent, was applied to the transport of methanol-propan-1-ol mixtures through a cellulose triacetate membrane and their results were compared with those obtained in vacuum pervaporation. Both the methods give equivalent selectivity and permeation fluxes at all methanol contents. The diffusion coefficient of methanol, which was ca.  $10^{-7}$  cm<sup>2</sup>/s in cellulose triacetate when pure methanol was used, was found to be much smaller when methanol was mixed with propan-1-ol (ca.  $10^{-9}$  cm<sup>2</sup>/s). From the practical viewpoint, the cellulose triacetate membrane shows a high permeation flux with a rather good selectivity to methanol. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

In the study of the separation of liquid mixtures by polymer membranes, vacuum pervaporation is generally used. Vacuum pervaporation is a technique that consists of a partial and selective evaporation of a compound from a liquid mixture through a dense membrane that is in contact on one side with the liquid, while the other side is kept under high vacuum. This process needs a vacuum pump and a cold trapping of the permeate. The gas-sweeping pervaporation needs no vacuum but a constant sweeping gas flow in the downstream compartment.<sup>1</sup> Because of the dilution effect, it is difficult to trap perfectly the permeate, and the measurement is then not very precise. This may be a reason why, so far, the gas-sweeping process is not popular in studies of liquid mixture separation by membrane processes. If penetrant fluxes through a membrane can be obtained by other ways than by cold trapping, then

sweeping-gas pervaporation may be also useful for fundamental studies. In comparison with vacuum pervaporation, gas-sweeping pervaporation is more convenient, as the experimental equipment is less expensive, e.g., it needs no vacuum pump and pumping energy for its operation and it needs no cold trapping, i.e., expensive liquid nitrogen. Moreover, vacuum pervaporation has many limitations in the study of membrane transport properties since it is not always easy to change the operating conditions, e.g., in the downstream compartment. For instance, to study the influence of the downstream vapor pressure,<sup>2</sup> a controlled condensation<sup>2</sup> or a controlled inert gas leak is required.<sup>3</sup> Moreover, classical vacuum pervaporation gives only few transport and separation parameters (typically, the total flux and the selectivity) of the membrane. In gas-sweeping pervaporation, vapor pressures and temperature in the downstream compartment can be changed through the control of the sweeping gas.<sup>4</sup> Automatic on-line measurement in order to analyze the transient regime of solvent permeation is also difficult in vacuum pervaporation, whereas in sweeping-gas pervaporation, the permeate sample

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can be directly injected in the gas chromatograph and errors due to cold trapping and complete evaporation of the condensed permeate can be avoided.

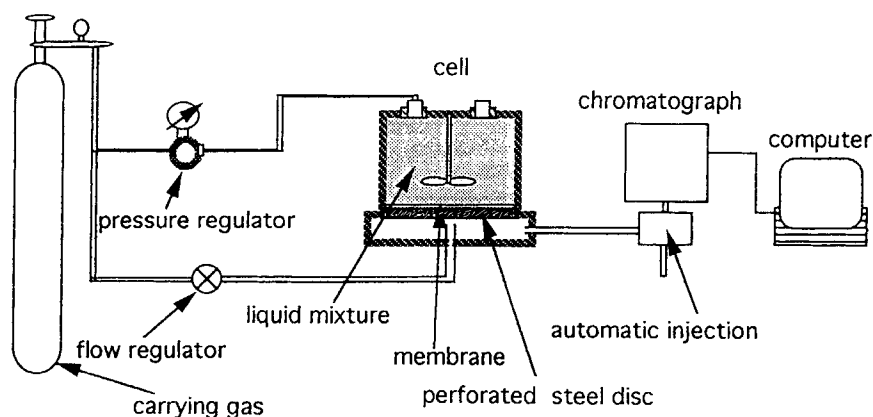
In previous articles, we showed that a quantitative analysis of the permeation fluxes in the transient regime, which results from a sudden contact of one face of a dry polymer film with a pure liquid or a liquid mixture, led to the diffusion coefficient of the penetrant.<sup>5,6</sup> Moreover, qualitative or semiquantitative analyses of this regime can give useful information on the transport mechanism.<sup>6</sup> The principle of such a method is used here, in the case of solvent mixtures, to make it possible to determine simultaneously the transport parameters and pervaporation characteristics of polymer films.

In this work, we propose a new set of equations derived from solutions of the second Fick's law and a new experimental arrangement of gas-sweeping pervaporation that can be used to determine fundamental parameters of the solvent transport. The setup could normally be used to study transient permeation parameters in any cases in which there is a change in penetrant composition on one face of the polymer material. Then, we apply the proposed method to the study of the separation of methanol (MeOH) and propan-1-ol (1-PrOH) mixtures through cellulose triacetate (CTA) membranes and compare the results with those obtained by vacuum pervaporation. Separation of the MeOH-1-PrOH mixture by vapor permeation and by vacuum pervaporation using PVA composite membrane have already been reported in the literature.<sup>7</sup> It appears that for a given membrane-solvent system vapor permeation is more selective but with lower fluxes than those observed in pervaporation.<sup>7</sup> However, there has been no comparison between gas-sweeping pervaporation and vacuum pervaporation. The proposed method allows one to evaluate some more

fundamental transport characteristics similar to those known in gas permeation, e.g., the diffusivities of components that simultaneously permeate a polymer film from mixtures of different compositions. Such data are generally difficult to obtain and only a few of them are available in the literature.

## BASIC EQUATIONS AND BOUNDARY CONDITIONS

This method for the study of solvent transport in polymers is based on new solutions of the second Fick law obtained under the condition of known time-dependence of the permeant concentration at the upstream face of a polymer film (which will be called the "membrane").<sup>8</sup> Let us consider a membrane with an area  $A$  and a thickness  $l$  that separates a permeation cell into an upstream (retentate) compartment and downstream (permeate) compartment. Furthermore, we assume the concentration of the components of the studied mixture to be zero in the latter compartment; this is practically obtained when the flow rate of sweeping gas is high enough in the compartment (Fig. 1). When a dry membrane is suddenly put into contact with the liquid mixture on its upstream face, first, a transient permeation flux of permeant (s) will result from the difference in the permeant concentrations at the membrane upstream and downstream faces. Then, the permeation reaches a quasi-stationary state in which the concentration profile is quasi-set. The value of the permeant concentration at the upstream face in this state corresponds to the *initial* state of the feed mixture. The diffusion coefficient of the permeant (s) can be calculated from these transient fluxes<sup>5,6</sup> in the *early* stage of the measurement. If the pervaporation process is allowed to continue for



**Figure 1** Schematic representation of the gas-sweeping pervaporation setup.

a much longer time, the concentration of the considered component in the *batch* feed mixture (i.e., in a closed cell) will slowly change with time due to selective transport of the components of the mixture. Such a composition drift will result in a change in the permeant concentration at the membrane upstream face, which, in turn, gives rise to a change in permeation fluxes in the *late* stage of the measurement.

To relate the variations of early and late transient fluxes with time to the operating parameters by means of mathematical expressions, we must assume that the process of diffusion in time can be described by the second Fick law with a constant mean diffusion coefficient. Indeed, the main difficulty in the use of a concentration-dependent diffusion coefficient (which is the general case) resides in the choice of an appropriate expression for the concentration-dependence, on the one hand, and in the difficulty to solve the second Fick law, even in the case of stationary boundary conditions, on the other hand. It should be noted that the validity of the assumption could be checked by examining the deviation of the fitting of the transient diffusion pattern with the corresponding solution obtained with a constant diffusivity.

Using a similar procedure as in a previous work,<sup>8</sup> we introduce a time-dependent concentration  $c(l, t)$  under the form of the following series:

$$c(t) = c_0 \sum_i a_i \exp(-\beta_i t) \quad (1)$$

where  $c_0$  is the concentration, at the upstream membrane surface, of the considered component at the beginning;  $a_i$  are constants satisfying the relationship  $\sum a_i = 1$ . The parameters  $\beta_i$  are positive if  $c(l, t)$ , the permeant concentration at the membrane upstream surface, decreases with time;  $\beta_i$  are negative if  $c(l, t)$  increases with time; and  $\beta_i = 0$  if  $c(l, t)$  is constant. The use of a series as shown in eq. (1) makes it possible to represent various forms of the time-dependent concentration  $c(l, t)$  and therefore to obtain a solution general enough, with regard to the concentration at the boundaries, to apply to various practical situations. The mathematical calculations cannot be detailed in the frame of this article. We will give here only the final equations corresponding to the specific case of batch pervaporation, the basic procedure being given in a previous article.<sup>8</sup> For a batch membrane operation, the change in the concentration in the external phase can be simply represented by eq. (1) with only the first term of the series:

$$c(t) = c_0 a \exp(-\beta t) \quad (2)$$

The component permeation flux at time  $t$  is then related to the diffusion coefficient  $D$  in the polymer material by (3)

$$J = Dc_0 \frac{a \sqrt{\frac{\beta}{D}}}{\sin\left(\sqrt{\frac{\beta}{D}} l\right)} \exp(-\beta t) \times -2 \frac{c_0 D^2}{1} \sum_k \frac{(-1)^k a \lambda_k^2}{(\beta - \lambda_k^2 D)} \exp(-\lambda_k^2 D t) \quad (3)$$

for  $\lambda_k = (k\pi)/l$ , where  $k = 1, 2, \dots, \infty$ .

The value of  $\beta$  can be determined from the permeation data in the late transient regime (see next paragraph). The diffusion coefficient  $D$  can be calculated from eq. (3) by numerical fitting of the experimental fluxes at different times. During the early stage of the measurement, if the amount of mixture put in the cell is much larger than the amount of permeant extracted through the membrane during the *diffusion* transient regime, the penetrant concentration at the upstream membrane surface remains practically constant, i.e.,  $\beta_i \rightarrow 0$ , and eq. (3) reduces to

$$\lim_{\beta \rightarrow 0} J = \frac{Dc_0}{l} \left( 1 + 2 \sum_k (-1)^k \exp(-\lambda_k^2 D t) \right) \quad (4)$$

This is the well-known equation used in the differential permeation method for the determination of the diffusion coefficient,<sup>5,6</sup> which is a special case of this method.

### Permeability Coefficient and Membrane Selectivity

If the amount of liquid put into the cell is not very small, the change in its composition will occur much later than in the early transient regime, since the total amounts permeated during the early transient regime (which is the integral of the flux over this time) is small. In the *late* stage of the measurement, the permeation flux [eq. (4)] reduces to

$$J_s = Dc_0 \frac{a \sqrt{\frac{\beta}{D}}}{\sin \sqrt{\frac{\beta}{D}} l} \quad (5)$$

One can then obtain the value of the parameter  $\beta$  from the slope of the plot of the logarithm of the experimental flux as a function of time:

$$\beta = - \frac{\partial \ln J_s}{\partial t} \quad (6)$$

The determination of  $\beta$  can be made without any calibration of the sensor for permeants, provided that the sensor signal is proportional to the flux. This is one advantage of the method.

In the further discussion, we will call the flux in the late transient regime,  $J_s$ , the quasi-steady state flux. By using the boundary conditions and the mass balance in the quasi-steady state regime, the permeability coefficient can also be calculated:

$$P = \frac{ml}{A} \beta \quad (7)$$

where  $m$  is the total initial mass of the feed mixture put in the cell and  $A$  the membrane surface area. In fact, the definition of the permeability coefficient is somewhat arbitrary, since this parameter, widely used in gas permeation, is rarely used in pervaporation. We define it as

$$P = DKC_f \quad (8)$$

since the flux in the quasi-steady state regime is given by eq. (9):

$$J_s = DKC_f \frac{W^r}{l} \quad (9)$$

where  $C_f$  is the total concentration of all components in the feed mixture,  $K$ , the partition coefficient of the permeant between the liquid phase and the membrane, and  $W^r$ , the weight fraction of the considered component in the feed liquid.

The selectivity  $\alpha$  of membrane for a mixture of two components  $i$  and  $j$  is defined by the following relationship:

$$\alpha = \frac{W_i^p / W_j^p}{W_i^r / W_j^r} \quad (10)$$

where  $W_i^p$  and  $W_j^p$  are, respectively, the weight fractions of the components  $i$  and  $j$  in the permeate, and  $W_i^r$  and  $W_j^r$ , the weight fractions of components  $i$  and  $j$  in the retentate. From eqs. (9) and (10), one can obtain

$$\alpha = \frac{P_i}{P_j} = (DK)_j \quad (11)$$

## EXPERIMENTAL

### Membranes

The membranes were prepared from 10 wt % solutions of cellulose triacetate (CTA) (Eastman Kodak) in dioxane by casting a liquid film on a glass plate and drying it in an oven at 50°C.

### Measurement Setups and Procedures

#### Gas-sweeping Pervaporation

The setup for gas-sweeping pervaporation is schematically shown in Figure 1. The membrane in the cell was supported by a perforated steel disc (aperture of the holes ca. 0.25 mm). Carrier gas flows from the center to the periphery of the disc. A finite mass of liquid solvent (typically, 30 g) preheated at the measurement temperature was put into a stirred cell that was previously held at constant temperature and under a continuous flow of carrier gas (nitrogen). The flow rate generally used was 1.1 cm<sup>3</sup>/s. Samples of ca. 0.1 cm<sup>3</sup> of the gas stream that exits the cell were periodically injected into a gas chromatograph equipped with a 2 m Porapak-Q column. Injections of retentate were also made during measurement. The pressures on both sides were usually atmospheric pressure, except in the study of the effect of pressures. The output signal from the flame ionization detector (FID) was digitized and recorded on a computer, and the peak areas were calculated. The component peak areas corresponding to samples withdrawn at different times were stored in a file and were retrieved later for the calculation of the transport parameters.

#### Differential Permeation

The differential permeation method was used for the determination of the diffusion coefficient of pure organic liquids; the setup and method have been already detailed elsewhere.<sup>5</sup> In this case, chromatographic separation is not needed. The membrane upstream face was suddenly put into contact with the pure liquid kept at constant temperature and under atmospheric pressure. The vapor was extracted on the downstream side into a nitrogen carrier gas, which flows through the FID for a continuous measurement of the permeation rate.<sup>5,6</sup> The diffusion coefficient was determined by fitting the transient fluxes by means of eq. (4). This method allows one to measure eventually the permeability coefficient if a calibration was made. Calibration of

the FID requires standard, calibrated sources of the vapors (MeOH, PrOH), which were not easy to obtain. Therefore, we used this technique only for the determination of the diffusion coefficient.

### Classical Vacuum Pervaporation

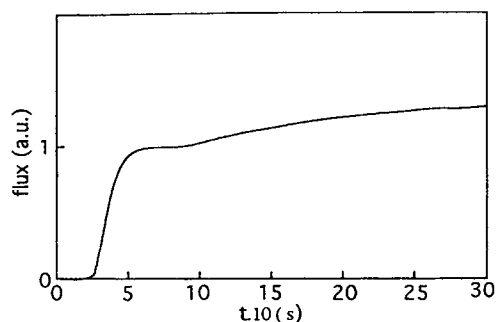
A volume of a liquid mixture of 100 cm<sup>3</sup> was put into a cell equipped with a heating jacket and a stirrer. The membrane was supported by a sintered disc and its surface area was ca. 20 cm<sup>2</sup>. On the permeate side, a vacuum of ca. 1 mbar was maintained throughout the experiment. The permeate extracted was condensed in liquid air for given time intervals. The total flux and permeation selectivity were determined from the mass of condensed permeates and from their compositions obtained by gas chromatographic analysis of thawed permeates.

## RESULTS AND DISCUSSION

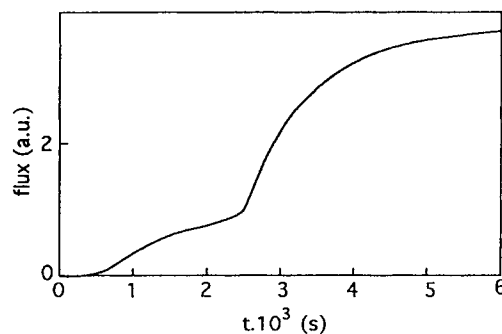
### Determination of Transport Parameters

First, the values of the diffusion coefficient of pure methanol and propanol through the CTA membrane were determined by differential permeation: They were obtained by fitting the variations of the transient flux of the solvent with time (Figs. 2 and 3) by means of eq. (4) and are shown in Table I. As a relaxation of the polymer chains in the membrane was observed in both pure solvents at the end of the transient diffusion regime (second "wave" in the curves of flux vs. time in Figs. 2 and 3), the fitting was carried out on the early part of the curve (corresponding to a true transient diffusion). The relaxation of polymer chains upon solvent permeation was already observed in several systems<sup>5,6</sup> and generally causes a swelling of the polymer material.

Figure 4 shows the typical time dependence of component permeation fluxes (surface area of chro-



**Figure 2** Time dependence of permeation flux of pure MeOH at 40°C in differential permeations.

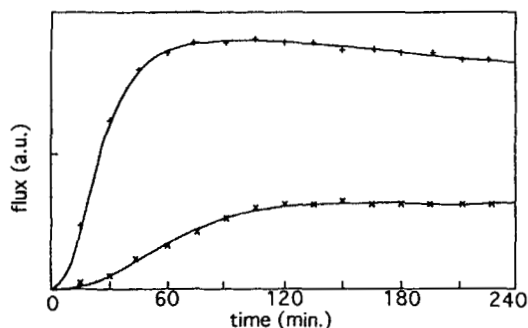


**Figure 3** Time dependence of permeation flux of pure PrOH at 40°C in differential permeations.

matographic peaks of the permeate components) of a mixture of methanol and propanol through the CTA membrane. They show the variation of experimental fluxes as a function of time when a fixed amount of a liquid mixture (methanol-propanol 20 : 80 mixture) is suddenly poured on the cellulose triacetate membrane in the gas-sweeping pervaporation cell. The first part of the curves, the *early* transient fluxes, corresponds to the transient diffusion regime consecutive to the instantaneous change in the concentration at the upstream face, when the dry membrane is put into contact with the mixtures; the second part represents the flux change with time that results from the composition change in the cell due to permeation through the membrane. A decay in the flux at long time is observed for methanol (Fig. 4): This solvent is preferentially and continuously extracted through the cellulose triacetate membrane so that its concentration in the mixture decreases with time. On the contrary, the low permeation rate of propanol through the membrane makes the change in the propanol content very weak and its steady-state permeation rate practically constant (Fig. 4). Therefore, the variations of fluxes with time for methanol are effectively resolved in two distinct parts: From the early-time part, the dif-

**Table I** Component Diffusion Coefficient Obtained at Different Compositions of Retentate Mixtures at 40°C

	$W_{\text{MeOH}}$					
	0.00	0.05	0.20	0.50	0.70	1.00
$D_{\text{MeOH}} \cdot 10^{10}$ (cm <sup>2</sup> /s)	—	7.2	8.2	6.7	6.7	1370
$D_{\text{PrOH}} \cdot 10^{10}$ (cm <sup>2</sup> /s)	4.0	2.6	4.2	2.1	3.9	—



**Figure 4** Typical time dependence of MeOH and PrOH permeation fluxes for the feed mixture of 20 wt % of MeOH in gas-sweeping pervaporation at 40°C.

fusion coefficients can be correctly determined; from the late-time part, the permeability coefficients and the selectivity of the membrane to the mixture can be calculated as follows:

The parameter  $\beta$  is determined from the slope of the plot of the logarithm of the surface area of chromatographic peaks of the considered component at quasi-steady state as a function of time (Fig. 5). This parameter can be determined with correct accuracy only for the fast component A, i.e., methanol. For the slow component B (i.e., 1-propanol in this case), the change in its peak area is too small for an accurate determination of parameter  $\beta$  from such a plot and another calculation method is used. First, the membrane permeation coefficient to methanol  $P_A$  is calculated from eq. (7) by using the  $\beta$  value obtained for methanol. Next, the membrane selectivity coefficient  $\alpha$ , defined by eq. (10), is calculated by using the following relationship derived directly from this equation by considering the linear relationships between the content of any component in the analyzed mixture and its peak surface area:

$$\alpha = \frac{S_A^p/S_B^p}{S_A^r/S_B^r} \quad (12)$$

where  $S_A^p$  and  $S_B^p$  are, respectively, the areas of chromatographic peaks of the components A and B in the permeate and  $S_A^r$  and  $S_B^r$  are, respectively, the areas of the chromatographic peak of the components A and B in the retentate.

Now, the permeation coefficient for the low component B (1-propanol)  $P_B$  can be calculated from the permeability of the fast component A (methanol) and membrane selectivity  $\alpha$ , by the following relationship [eq. (11)]:

$$P_B = P_A/\alpha \quad (13)$$

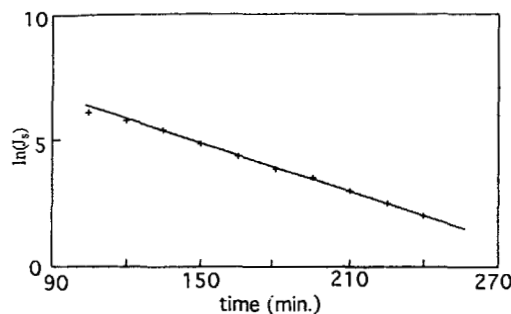
As one can see, it is not necessary to know the absolute values of fluxes for the estimation of the component permeability and membrane selectivity, i.e., no calibration is needed.

From eqs. (8) and (9), the permeation flux of a component is determined:

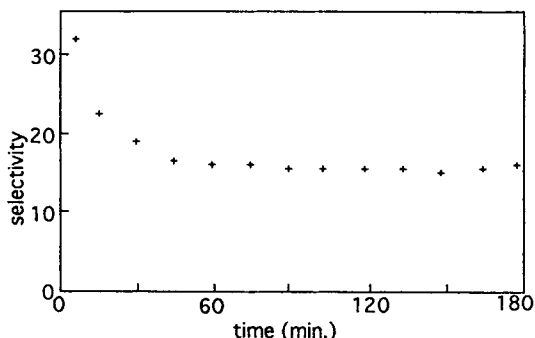
$$J_s = P \frac{W^r}{l} \quad (14)$$

where  $P$  is the permeation of the considered component, and  $W^r$ , its weight fraction in the retentate in the quasi-steady state. The diffusion coefficient of a component from a mixture can be obtained by fitting the experimental data of fluxes at different times with eq. (4).

This calculation procedure was applied to the gas-sweeping pervaporation results and yields the results shown in Table I and Figures 6–9. As usual, the component permeation fluxes are preferred to the permeabilities. Table I shows the values of the diffusion coefficients of methanol and 1-propanol at different methanol contents. There are rather large scatterings of the values of the diffusion coefficients, which can be explained by the fact that the number of experimental points is limited compared with that obtained in differential permeation.<sup>5</sup> The determination of the diffusion coefficient by this method is less feasible than that obtained in differential permeation in which a continuous signal is fed directly to the detector without chromatographic separation. Therefore, values of  $D$  obtained by the data should be regarded as indicative data rather than as reference data. The membrane permeability  $P$  is also an “apparent” permeability for which eq. (4) is valid. Only the membrane selectivity and the permeation fluxes are quantitative results. The number of experimental points, therefore the accuracy of the determination, can eventually be increased by mini-



**Figure 5** Time dependence of logarithm of quasi-steady state permeation flux of MeOH: determination of the value of the  $\beta$  parameter.



**Figure 6** Time dependence of membrane selectivity for the feed mixture containing 20 wt % of MeOH in gas-sweeping pervaporation at 40°C through a 20  $\mu\text{m}$ -thick CTA membrane.

mizing the time required for analyses, e.g., by using a shorter chromatographic column or two chromatographs fed alternatively or by analyzing with a mass spectrograph. However, the order of magnitude of the diffusion coefficient may be sufficient to give useful information for the understanding of the pervaporation process: The results from Table I indicate that the diffusion of methanol is much faster (two orders of magnitude) when methanol molecules come from the pure solvent than when they come from the mixture with propanol. Such a behavior was not observed for 1-propanol, whose diffusion coefficient remains constant when the solvent is mixed with methanol. A "coupling effect" was therefore evidenced for the diffusion in this system: Methanol molecules appear to be retarded by propanol molecules in their simultaneous diffusion through the CTA membrane. Such a phenomenon was already suggested in the transport of components in a mixture but never directly proven.<sup>9</sup> In the present case, the coupling can be explained by the interactions between the two chemically similar solvent species.

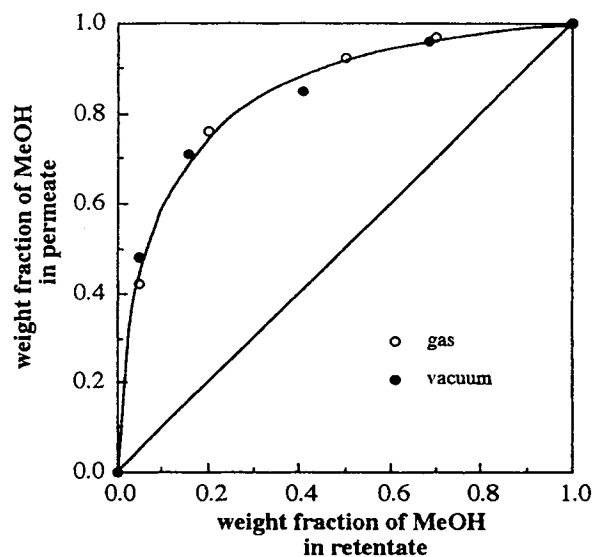
#### Change in the Selectivity with Time

Figure 6 shows a decrease in the selectivity with time for the mixture containing 20 wt % methanol. The decrease is large during the first 30 min, then it levels off. Such a decrease was found for all studied mixtures (20–80 wt % methanol). The change in the selectivity with time can be attributed to changes in the polymer properties due to penetrant-polymer interactions. When solvent molecules penetrate a polymer, they interact with polymers according to their physicochemical affinities to different chemical groups on polymer chains. Hydroxyl groups on both

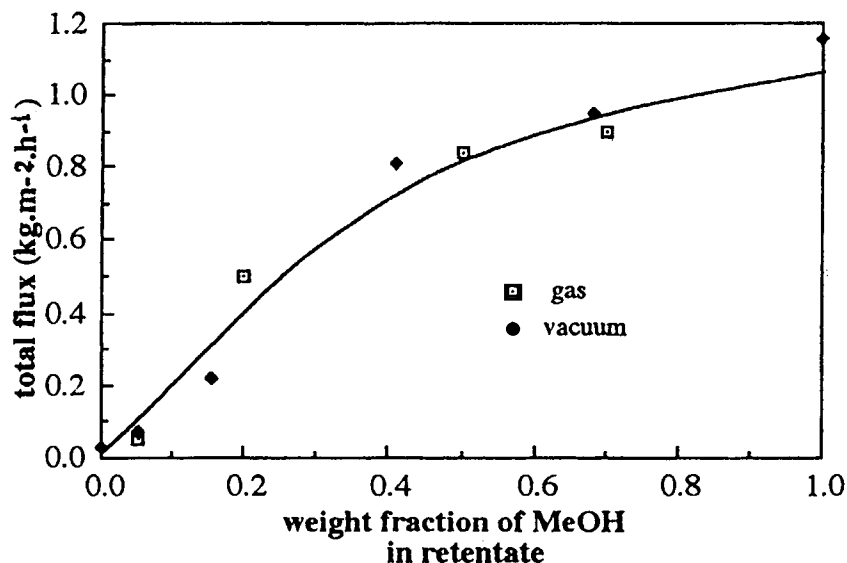
methanol and propanol molecules can interact with carbonyl groups on CTA chains by a hydrogen-bonding interaction. Hydrocarbon radicals ( $-\text{CH}_3$  and  $-\text{C}_3\text{H}_7$ ) in the alcohols can develop van der Waals interactions with hydrocarbon counterparts on CTA chains. An analysis in the frame of rational thermodynamics of the diffusion transient regime of pure alcohols through the CTA membrane<sup>10</sup> showed that for methanol, the interactions, probably in a hydrogen-bonded complex, dominate the process, whereas for propanol, the swelling, which led to a deformation of the polymer network of the polymer, dominates the process. From Figures 2 and 3, which show the permeation rates of methanol and propanol in differential permeation experiments, one can see the large swelling effect of propanol on the CTA membrane: After the diffusion, steady state was reached (Fig. 3, first wave) and the permeation rate increases to a larger extent (before leveling-off, Fig. 3, second waves) than in the case of methanol. The decrease in the selectivity with increasing time can be explained by the swelling due to propanol, in consistency with the rational thermodynamics.<sup>10</sup>

#### Comparison of Gas-sweeping Pervaporation with Vacuum Pervaporation

To make a comparison with vacuum pervaporation, the measurements in gas-sweeping pervaporation were carried out under conditions similar to those



**Figure 7** Methanol contents in permeate vs. methanol content in feed in vacuum and in gas-sweeping pervaporations for the same membrane and pervaporation temperature (40°C).

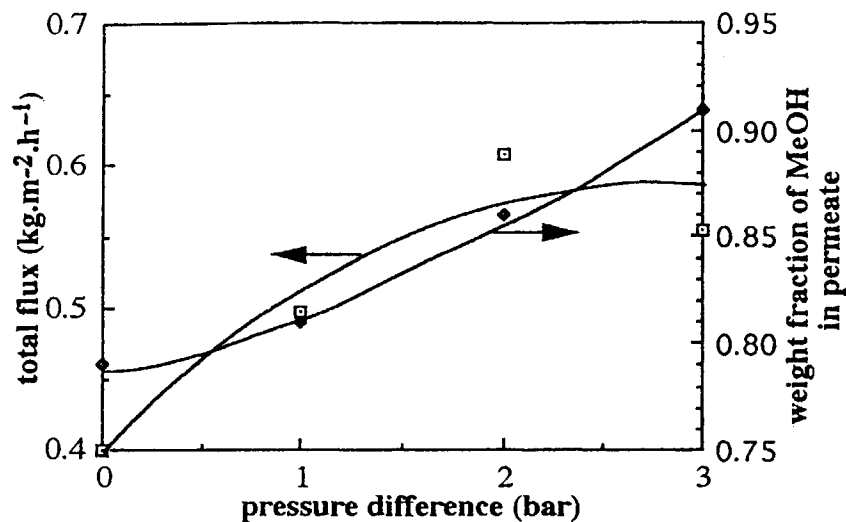


**Figure 8** Total permeation flux vs. methanol content in feed in vacuum and in gas-sweeping pervaporations for the same membrane and pervaporation temperature (40°C).

in vacuum pervaporation. The conditions were those in which the temperature is the same, the upstream pressure is atmospheric, and the flow rate of carrier gas is high enough to ensure as low as possible permeate concentration at the downstream membrane surface, but not too high to create the downstream overpressure against the upstream side. The plots of methanol content in the permeates (which represent the permeation selectivity) obtained in vacuum and in gas-sweeping pervaporations as a function of the feed methanol content (Fig. 7) are very close to each other. The same conclusion can be

made from the plots of permeation rates as a function of the feed composition (Fig. 8). Fundamentally, any differences in flux would stem from differences in vapor-phase activities right at the membrane surface on the downstream side. To be comparable with pervaporation under high vacuum, this vapor-phase activity should be negligible compared with the equivalent vapor pressure of the components on the upstream side.

As the membrane in our gas-sweeping setup is supported by a perforated disc with relatively large holes, we considered the boundary layer effect neg-



**Figure 9** Dependence of total permeation flux and selectivity on upstream pressure in gas-sweeping pervaporation. CTA membrane thickness:  $l = 20 \mu\text{m}$ ; pervaporation temperature: 40°C.



ligible on the downstream side. With this assumption in mind, a rapid evaluation of the validity of this condition can be done from the results obtained with the experiments. In all cases, the activity of methanol in the vapor in the downstream phase did not exceed 3% of that in the upstream compartment and can be considered to be negligible. The very close characteristics obtained in both techniques indicate that gas-sweeping pervaporation by means of the proposed experimental setup can be conveniently used for studying the membrane characteristics, provided that the sweeping gas flow rate is high enough to ensure a low permeant activity at the membrane downstream face.

When these results are compared with those obtained with the GFT composite membrane made of a thin PVA active layer<sup>7</sup> on a microporous support, it appears that the CTA membrane is much more selective than is the composite membrane in pervaporation and slightly less selective than the same membrane in vapor permeation.<sup>7</sup> For instance, at 20 wt % methanol in the mixture, the methanol contents in the permeate were, respectively, 32 wt % for pervaporation and 85 wt % in the case of the PVA composite membrane and 75 wt % in the case of the CTA membrane. Its permeability is much higher than that of the composite membrane in pervaporation and in vapor permeation, especially when the thickness (higher for CTA membrane) and the permeation temperature (lower for CTA membrane) are taken into account: At 20 wt % methanol in the feed, the total flux was 0.25 kg/h/m<sup>2</sup> for the composite membrane (whose active layer is ca. 5 μm thick) at 60°C in pervaporation and negligible flux in vapor permeation, whereas that for the 20 μm-thick CTA membrane was 0.39 kg/h/m<sup>2</sup> at 40°C. Thus, the CTA membrane compares favorably with the PVA composite membrane in the MeOH/1-PrOH separation.

### Upstream Pressure Effect

When the upstream total pressure increases, e.g., by applying an inert gas pressure, while the downstream pressure is kept equal to the atmospheric pressure, both membrane selectivity and permeability increase (Fig. 9). At a fixed temperature, according to the generally accepted pervaporation mechanism, the membrane characteristics will not change significantly with the upstream pressure<sup>1,9,11</sup> if the driving force for the permeation does not change very much with the upstream pressure due to the small value of the term  $v_i \Delta p$  (where  $v_i$  is the penetrant partial molar volume, and  $\Delta p$ , the difference in pressure

between two sides of the membrane). This must be true in our experiments due to the low vapor pressure on the downstream side. Therefore, these results cannot be explained in the frame of the classical mechanism. To explain this behavior, the rational thermodynamics may again be used.<sup>5</sup> In this framework, the membrane permeability depends also on the deformation tensor related to the mechanical deformation of the membrane,<sup>5</sup> i.e., on the change in membrane "structure" due to anisotropic mechanical deformation under the high upstream pressure in pervaporation. In fact, as the membrane was supported by a perforated metal disc, under the influence of high-pressure differences, a deformation of the polymer material occurs at the aperture of the perforated holes. However, the influence of the changes in the polymer network structure, e.g., stretching of the polymer chains or changes in segment-segment interactions, etc., is not easy to analyze in the present situation.

The influence of the flow conditions (flow patterns, gas velocity, etc.) can also be studied by changing the flow rate and the configuration of the downstream compartment. This will be the object of a further study.

### CONCLUSION

In comparison with vacuum pervaporation, the gas-sweeping pervaporation with on-line chromatographic analysis gave more information on transport and makes easier the study different permeation parameters.

The cellulose triacetate membrane showed a relative high flux to the methanol-propanol mixture with moderate selectivity to methanol. Both its selectivity and permeability were significantly higher than those of the industrial PVA-based membrane. The diffusion migration of methanol was shown to be slowed down in the presence of propanol. The upstream pressure can affect the membrane characteristics if a membrane (local) deformation occurs with increasing upstream pressures.

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