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Diffusion of acetic acid and water through poly(vinylalcohol) membranes. Coupling effects

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Permeation fluxes of water and acetic acid from water–acetic acid mixtures were independently monitored as a function of time in differential permeation with dual detection. Two successive permeation waves were detected for water permeation and only one for acetic acid permeation in the transient regime. The onset of the second permeation wave for water coincides with that of acetic acid permeate whatever the condition. The time delay for the appearance of these waves decreases with increasing temperature and water content in the binary mixtures. The mean diffusion coefficient for different permeation waves and their activation energy were calculated from the permeation rates in the transient regime. The results strongly indicated a coupling of acetic acid flux with the second step of water permeation which probably results from the permeation of water–acetic acid aggregates.

(Keywords: diffusion; coupling; poly(vinyl alcohol) membranes)

INTRODUCTION

Diffusion of low molecular species in polymers is a fundamental process involved in the analyses of the permeation or the kinetics of sorption of these species in synthetic or natural polymeric materials. The understanding of the diffusion of permeants in polymers is also very important for the design of polymer materials for membrane processes. In the case of pervaporation of liquid mixtures (especially mixtures of water and protic organic solvents), the situation is generally complex, due to strong interactions of permeant molecules between themselves and with different segments of the membrane polymer materials. The complex behaviours may arise, e.g. from the swelling of the polymer network and its consecutive plasticization effects, or from aggregations of permeant species inside the membrane. These behaviours can then affect component permeation rates and hence the membrane performance. By adequate models, the mutual influence of the permeants in their course of permeation, usually called coupling effects, can be extracted from experimental pervaporation results by model fitting. Such an approach was illustrated by Brun *et al.*[1,2] in a paper in which the diffusion coupling effect was represented by concentration coefficients in the so-called 'exponential six-coefficients model'. The coupling effect and the plasticization effect of the transport of the components of a binary mixture could then be appreciated from the values of four coefficients in the exponential expressions. However, these coefficients were obtained by fitting of equations with several adjustable parameters so that it is not easy to assess their true meaning.

There are very few works concerning direct measurements of the diffusion coefficient of liquid mixtures in polymers. Watson and Payne[3] reported values of diffusion coefficients of different organic solvents in aqueous solutions through silicone rubber films and showed a certain concentration dependence of the diffusion coefficient. Coupling effects were neglected in the study. Although coupling effects may be negligible for the case of some aqueous solutions of organic solvents and silicone membranes, it might not be true for other systems: if there were strong interactions between permeants molecules, and with the membrane materials, coupling effect would occur. Such a coupling effect was reported for the water–ethanol–silicone system[4].

Differential permeation is a convenient method for diffusion coefficient determination; the advantages of this method in the determination of the diffusion coefficient of gases were discussed by Felder[5]. Nguyen *et al.*[6] showed that, in the cases of pervaporation of liquids and liquid mixtures, this method is an interesting tool not only for the determination of diffusion coefficients

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of solvents through flat and tubular membranes, but also for the study of phenomena involved in polymer–liquid or liquid mixture systems. In the present work, the differential permeation technique was used to study the diffusion of water and acetic acid from their binary liquid mixtures through poly(vinylalcohol) films of different acetyl contents. In this method, the upstream face of the membrane is suddenly put into contact with the liquid mixture to be studied, and by means of two specific detectors, the permeation rates of the two components are simultaneously monitored in time. From the diffusion transient regimes, i.e. the kinetics of the permeation rate changes, values of difusion coefficients may be computed. Furthermore, the number of diffusion 'waves' of the components[7] and the times at which they occur can give useful information on the mechanism of permeation of liquid mixtures.

The membrane–liquid mixture systems chosen in this study comprised water–acetic acid mixtures and poly(vinylalcohol) membranes. Dehydration of acetic acid is an important application for which pervaporation is an interesting process. In previous papers[8,9], we showed that poly(vinylalcohol) derivatives are potential candidates for the selective layer of pervaporation membranes. Although this work aims at studying the coupling effect in the diffusion of solvents from binary mixtures in dense membranes, the results obtained may help in designing appropriate pervaporation membranes for organic acid dehydration.

EXPERIMENTAL

Materials

Poly(vinylalcohol) (PVA) of different degrees of hydrolysis were provided by Aldrich Corp. They were indicated by a suffix number which represents the molar percentage of vinyl acetate monomer in the polymer: PVA_0, PVA_5 and PVA_{12} denoted samples containing 0%, 5% and 12% of vinylacetate, respectively.

Membrane preparation

Dense membranes were prepared by first casting aqueous polymer solutions on an appropriate plate by means of a 'Gardner blade', then evaporating the liquid film to dryness at 60°C. Films of ca. 40 μm thick were obtained in this way from solutions containing 7–10 wt % PVA.

Determination of membrane crystallinity

The crystallinity of the membrane was determined by means of a Fourier Transform Infrared spectroscope, Bruker IFS-85. The sample studied was pressed on the prism of an attenuated total reflectance device and the spectra were recorded at 2 cm^{-1} resolution from the Fourier transform of 128 scans. The crystallinity was calculated from the crystalline sensitive band at 1142 cm^{-1} [10] using equation (1):

$$\text{Per cent crystallinity} = 92(A_{1142}/A_{1425}) - 18 \qquad (1)$$

where A_{1142} and A_{1425} are respectively the absorbances at 1142 and 1425 cm^{-1}. In the absence of a standardization, the values obtained are used rather as indexes for a structure classification than true crystallinities. The density of the film, measured in a density column, also gives a qualitative idea of the crystallinity: the higher the polymer crystallinity, the more compact the film structure and the higher the density.

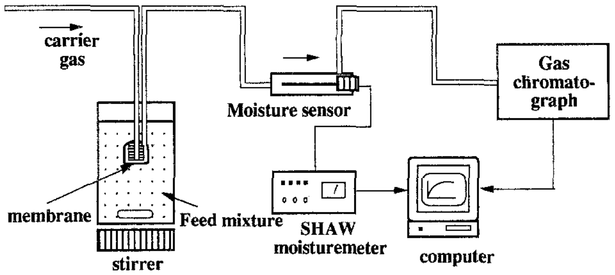

Figure 1 Schematic representation of the experimental device for differential permeation with a dual-detector

Pervaporation experiments

The pervaporation apparatus has been described elsewhere[8]. Briefly, it consists of a pervaporation cell with a membrane surface area of 20 cm^2 and a glass apparatus equipped with traps to condense the permeate removed from the membrane by a vacuum pump. The pervaporation experiments were performed at constant temperature and under a good vacuum (pressure less than 0.5 Torr). The vapours were condensed in traps cooled by liquid nitrogen. The weight of vapours obtained over a fixed period of time was used for the calculation of the permeation flux, J. A gas chromatograph, equipped with a thermal conductivity detector, was used to determine the permeate composition.

Dual-detection differential permeation

The cell and the experimental set-up are shown in *Figure 1*. The membrane and cell were first dried in vacuum and mounted under dry sweeping gas, then was dipped into the liquid tank. The effective surface area of the membrane in the cell is ca. 1 cm^2. Water and organic permeation fluxes were monitored independently by means of a Shaw moisture meter (Bradford, UK) and Flame Ionization Detector (Intersmat, France) connected in series. The sensor used for the moisture-meter gives a linear response for dew points ranging from −80°C to −20°C. The measured values were converted into water concentration using the known relationship between the water concentration and the dew point. In the case of dilute solutions of organics which are extracted by the membrane, the volume of the liquid should be high enough to ensure constant concentration of organics during the experiment. A source of errors derives from spurious time delays due to holdup times, residence and mixing times in chambers adjacent to the membrane. In order to minimize these times, the volume of different parts on the effluent line was minimized and attention was focused on parts which can promote mixing. Due to a minimum space required for the moisture sensor, the volume on the downstream line was relatively large (ca. 3 cm^3). A time delay can be easily taken into account by introducing it as a parameter in the equation for curve fitting. It allows us to check if there is any delay in the diffusion process.

Special care had also to be taken to avoid any leak by diffusion through sealing materials, connectors or tubings. The sweeping gas flow rate was adjusted according to the permeability and the membrane area to ensure low vapour pressures in the effluent gas. Typically, it was in the range of 30–50 $\mathrm{cm^2\,min^{-1}}$.

Calculation of diffusion coefficient

When the assumption of constant diffusion coefficient is valid, the diffusion coefficient can be calculated either by using values of flux and time at a singular point of the flux *versus* time dependence, e.g. the point corresponding to half of the steady state flux[3,6] or by fitting the flux *versus* time curve by equation (2)[7]:

$$J_i(t) = 1 + 2\sum_{n=1}^{\infty}(-1)^n \exp(-n^2\pi^2 D_i(t-\delta t_i)/l^2) \qquad (2)$$

where D_i is the diffusion coefficient, J_i is the dimensionless flux (the ratio of the flux at time t to the steady-state flux of the component i), δt_i is the time shift (if any) in the permeation kinetics, and l is the membrane thickness.

In this work, we used the latter method, which makes it possible to calculate the diffusion coefficient even when there is a considerable delay in the permeation process. As analytic solutions were generally not available for the case of concentration-dependent diffusion coefficient, we preferred to fit the data in the largest range possible. Generally departures from the data were observed at very low times (due to experimental errors) and to the end of permeation waves, where polymer swelling occurred.

When two successive permeation waves occur for a component, the total permeation flux at any instant is assumed to be the sum of the fluxes of the two individual permeation steps, each of them has its own diffusion characteristics as given by equation (3):

$$J_{\mathrm{exp}}(t) = J_1(t) + J_2(t) \qquad (3)$$

where $J_1(t)$ and $J_2(t)$ are the dimensionless fluxes of the components in the two steps. The values of D and δt were computed from experimental permeation fluxes at different times by using the Rosenbrock fitting algorithm[10]. The following symbols will be used: D_a for the diffusion coefficient of acetic acid, D^{I} and D^{II} for those corresponding to the first wave and the second wave of water permeation, respectively.

RESULTS AND DISCUSSION

Evidence of different phenomena in transient regime

Chronologically, the experiment which led us to study in detail the diffusion mechanism of solvents in a mixture was that carried out with the $\mathrm{PVA_{12}}$ membrane (made of PVA containing 12 mol % vinyl acetate moieties) and the water–acetic acid mixture containing 10 wt % of water at 30°C. The results are worth showing here as the two water permeation waves can be clearly seen for water permeation (*Figure 2a*), and the single organic permeation wave appears later than those of water (*Figure 2b*). When differential permeation was performed on the same membrane but with pure (dry) acetic acid, an extremely low permeation rate was observed (two orders of magnitude smaller). The fact that pure acetic acid did not permeate through the membrane, whereas it did in the presence of 10 wt % water means that the permeation of acetic acid is significant only when it is coupled with that of water. The stationary water permeation rate at the end of the first wave was one order of magnitude smaller than that after the second wave.

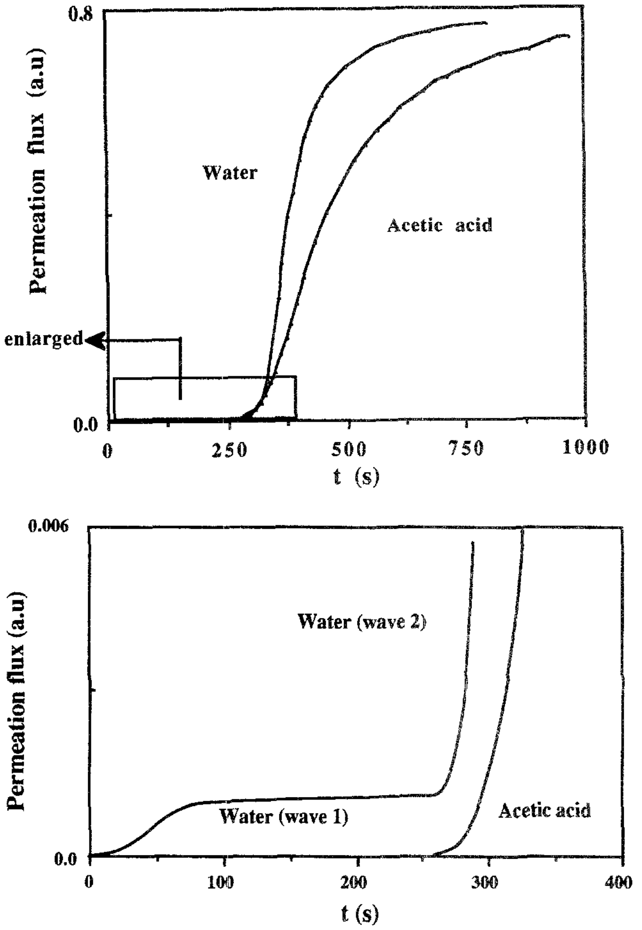

Figure 2 Water and acetic acid fluxes *versus* time in permeation of water–acetic mixture of 10 wt % water content through $\mathrm{PVA_{12}}$ membrane at 30°C: (a) curves for the entire time range; (b) enlargement of fluxes for small times

The values of the diffusion coefficient can only be computed from the transient kinetics with equation (2) when its underlying assumptions are valid. Hauser and McLaren[11] found that the diffusion coefficient of water in PVA derived from permeability and sorption coefficients (with the assumption of constant coefficients) increases with the water activity. In the present cases of water and acetic acid permeation through PVA, one can suspect that such a concentration-dependent diffusivity would occur and alter the transient permeation pattern. Transient permeation computation to extract the concentration-dependent diffusion parameters is nevertheless difficult and requires adequate software and a powerful computer, even when the right expression for the concentration-dependence is known *a priori*. We wanted to know what approximation we would make if equation (2) were applied to the transient flux which results from a diffusion process with a concentration-dependent coefficient. To do this, first we generated numerically transient permeation fluxes by using the generally admitted law in which the diffusion coefficient increases exponentially with the local permeant concentration. The generated transient permeation curve has a similar sigmoidal shape and a similar time delay to the experimental ones (*Figure 3*). Then we fitted the transient permeation fluxes with equation (2) to obtain a diffusion coefficient which must be a kind of mean diffusion

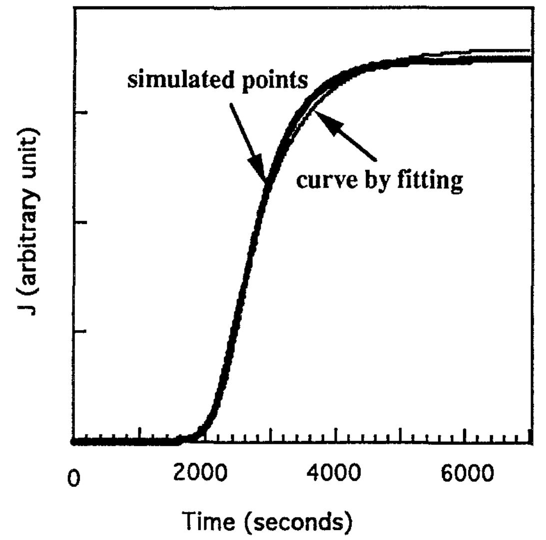

Figure 3 Fitting curve of the permeation points generated numerically from the following concentration-dependent diffusion coefficient: $D^* = 1 \times 10^{-10} \exp(4C)$ and $C_f = 1$; membrane thickness: 35 μm. With equation (2) in which the diffusion coefficient D_c is considered to be constant, and a delay time δt is included, the D_c value found by least-square fitting was: 1.6×10^{-9} cm^2 s^{-1} with $\delta t = -1600$ s.

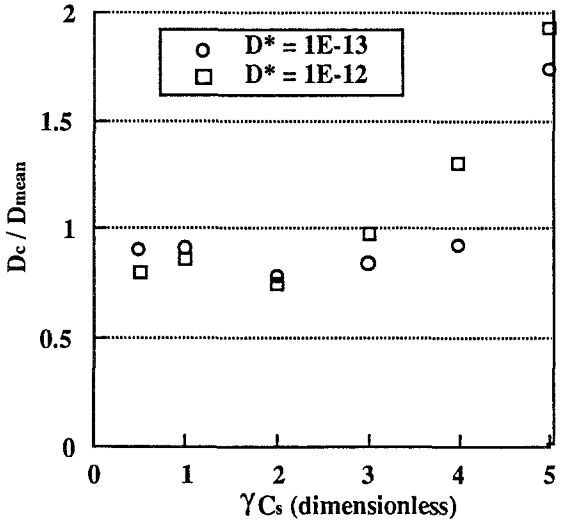

Figure 4 Variations of the $D_c/\bar{D}$ ratio as a function of the dimensionless plasticization coefficient of the diffusion concentration-dependence law $D = D^* \exp(\gamma C)$; Crank's mean diffusion coefficient is given by equation (5)

coefficient. The fitting quality, shown by *Figure 3*, was surprisingly good. As the fit involves a considerable time lag (1600 s), the main effect of the concentration dependence is to introduce a time delay. The obtained values of 'mean' diffusion coefficient, D_c, are compared with the mean diffusion coefficient, $\bar{D}$ (*Figure 4*) calculated from the Crank's definition of mean diffusion coefficient[12] and the exponential dependence of the diffusion coefficient on penetrant concentration:

$$\bar{D} = \frac{1}{C_f - C_i} \int_{C_i}^{C_f} D(c) \mathrm{d}C \qquad (4)$$

where C_i and D_f are the solvent concentrations in the membrane surface in the initial and the equilibrium states, respectively. With $C_i = 0$ and $D = D^* \exp(\gamma C)$, γ being the plasticization coefficient, integration of equation (4) gives:

$$\bar{D} = \frac{D^*}{\gamma C_f}(\exp(\gamma C_f) - 1). \qquad (5)$$

The results for various values of γC_f (*Figure 4*) show that under moderate plasticization (values of the argument of the exponential function lower than 4), the 'mean' diffusion coefficient, D_c, determined from curve fitting with equation (1) does not deviate more than 25% from the Crank's mean diffusion coefficient $\bar{D}$.

There was also the question of whether PVA, a glassy polymer in the dry state, exhibited the behaviour named 'case II' in the transient solvent penetration, as did several glassy polymer–solvent systems[13]. We did not observe moving boundaries in the diffusion of the water–acetic acid mixture in the membrane studied as have been observed in 'case II' sorption. This may be because the swelling of the material is not high enough to make the swollen part distinguishable from the dry part. The modelling of a 'case II' solvent diffusion requires many parameters lumped in a complex way[13–16] so that the use of these models for fitting purposes is practically impossible. Considering the problems arising from more sophisticated models, we have calculated only the 'mean' diffusion coefficient determined from curve fitting with equation (2) as an estimate of the mean permeant diffusivity for comparison purposes. For convenience, we will call this 'mean' diffusion coefficient 'the diffusion coefficient'.

The values of the diffusion coefficient corresponding to the different permeation waves were computed from the permeation curves; at 30°C, they are 3.7×10^{-8} for D_a (acid acetic), 3.4×10^{-8} D^I (water, first wave), and 7.1×10^{-9} cm^2 s^{-1} for D^{II} (water, second wave). Anomalous delays which were not observed in normal Fickian diffusion[5,6] were noticed for the onset of the diffusion waves; they were ca. 10 and 230 s for water diffusion waves, and 260 s for acetic acid diffusion through a 35 μm-thick membrane.

It appears that water permeates successively in two steps with significant difference between the values of the diffusion coefficient. As the composition of the liquid mixture in contact with the membrane surface remained constant, the occurrence of a two-step mechanism could be explained by either a diffusion by two separate pathways for water[17], or a late diffusion step in the polymer network which was modified by a first diffusion step (e.g. polymer chain relaxation)[13,16,18]. It should be noted that due to the presence, in the polymer film, of both permeant species in the second water wave and in the acetic acid wave, the diffusion coefficient of each permeant would be a function of both acetic acid and water concentrations. However, a mathematical problem must first be faced for such an extra-complication.

Influence of temperature on diffusion coefficient. Evidence of coupling of water and acetic acid permeations

Although the evidence of a two-step permeation was obtained with PVA_{12}, this polymer was not used for further studies due to its lack of resistance at higher temperatures. Transient permeation experiments were

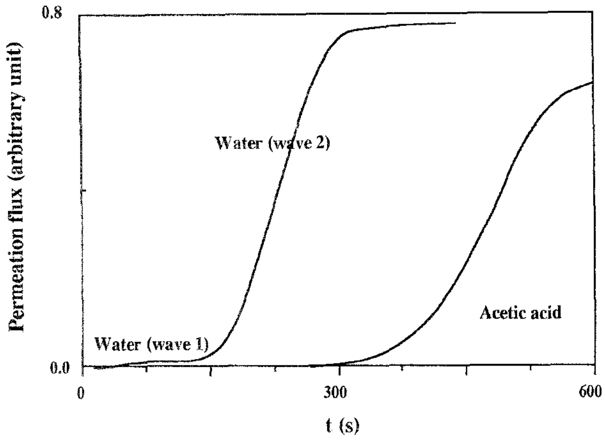

Figure 5 Acetic acid fluxes *versus* time in permeation of water–acetic mixture of 10 wt % water content through PVA_5 membrane. Differential permeation at 40°C

Table 1 Values of diffusion coefficients (cm^2/s) of acetic acid (D_a) and water (D^I for the first wave, D^{II} for the second wave) in differential permeation of water–acetic acid mixture of 10 wt % water at different temperatures. Membranes: PVA_0 and PVA^5

	PVA_0			PVA_5		
T (°C)	$D^{I*}10^8$	$D^{II*}10^8$	$D_a^*10^9$	$D^{I*}10^8$	$D^{II*}10^8$	$D_a^*10^9$
25					0.063	0.27
27		0.12	0.91			
30			1.2	0.89	0.14	2.4
40		0.58	5.4	2.9	1.3	4.0
50	2.7	1.4	9.2	6.2	7.8	17
60	4.1	3.9	19	11	8.4	25

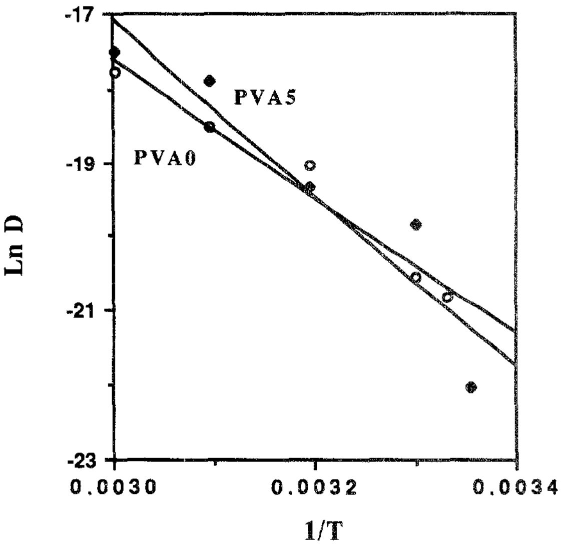

Figure 6 Arrhenius plot of diffusion coefficients of acetic acid through PVA_0 and PVA_5 membranes and for the water–acetic mixture containing 10 wt % water

Table 2 Activation energy for the permeation of water and acetic acid from a mixture containing 10 wt % through PVA_0 and PVA_5 membranes

	Water		
Membrane	Wave I (kcal mol^{-1})	Wave II (kcal mol^{-1})	Acetic acid (kcal mol^{-1})
PVA_0	9	20.7	18.6
PVA_5	16.7	30.1	23.4

then performed on PVA_0 and PVA_5 membranes at different temperatures for the mixture containing 10 wt % water. Typical permeation flux changes with time for water and acetic acid are shown in *Figure 5*. Both membranes exhibit similar transient patterns of water and acetic acid permeations as those obtained with the PVA_{12} membrane (*Figures 2* and *5*), though with different kinetics: the lower the acetyl content, the more the transient fluxes were shifted to larger times.

From the permeation fluxes in the transient regime, the values of the diffusion coefficient were computed and are given in *Table 1*. It can be seen that the first and the second waves of water permeation have comparable diffusion coefficient values. The values of water diffusion coefficients are always higher than the acetic acid ones at the same temperature. This is qualitatively consistent with their respective molar volumes (18 cm^3 mol^{-1} for water molecules and 60 cm^3 mol^{-1} for acetic acid): the bigger the size of the permeant, the lower their mobility in the membrane.

The diffusivity of both acetic acid and water increases with vinylacetate content of PVA membranes (*Table 1*, and values given above for the PVA_{12} membrane). Such an increase can be explained by a decrease in the crystallinity of the membrane, from 28% for PVA_0, to 23% for PVA_5 and 5% for PVA_{12} membrane. Indeed, it has been known that changes in the crystallinity degree affect many properties of polymer materials[19–22], particularly permeation properties: for instance, in the presence of a larger number of crystallites, the diffusion path of a solvent molecule in the polymer increases due to a greater tortuosity of the path. Although correlations between the diffusivity and the crystallinity degree exist[19], we do not have enough data to check their validity.

The variation of the diffusion coefficient as a function of temperature is generally analysed in terms of an Arrhenius-like relationship (*Figure 6*). The activation energy was determined from the Arrhenius plots (i.e. the plots of the logarithm of the diffusion coefficient *versus* the reciprocal of the Kelvin temperature). *Table 2* shows that the values of the activation energy of the two steps of water diffusion in both PVA_0 and PVA_5 membranes are quite different. The values of the activation energy for the first permeation step are about half of those for the second step; those for acetic acid are close to those for the second wave of water diffusion. Furthermore, the value of the time delay for the acid permeation wave coincided with that of the second wave of water permeation whatever the temperature considered, the membrane used or the water content (*Table 3*); it should be noted that the delay time for the first wave of water permeation was negligible compared with that of the second wave. These results suggest that the diffusion transport of acetic acid is 'coupled' with that of the second step of water permeation. This flux coupling (in terms of permeant transports through membranes) is consistent with the observed increase in acetic acid flux with the water flux in the second step, when the acetic acid content in the mixture, i.e. the driving force for acid permeation, decreases.

Table 3 Time delays for the acetic acid permeation and for the second wave of water permeation in differential permeation of water–acetic acid mixtures through PVA_0 and PVA_5 membranes in different conditions

Water content and temperature	PVA_0 Acetic acid time delays (min)	PVA_0 Water (II) time delays (min)	PVA_5 Acetic acid time delays (min)	PVA_5 Water (II) time delays (min)
10 wt % 25°C	–	–	45	45
10 wt % 27°C	134	134	–	–
10 wt % 30°C	–	–	18	18
10 wt % 40°C	18.8	16.5	6	5
10 wt % 50°C	5.7	5.5	2.2	2.2
10 wt % 60°C	3.8	2.6	1	0.9
5 wt % 30°C	–	–	128	128
15 wt % 30°C	–	–	14.2	14.0
20 wt % 30°C	–	–	10.8	10.6
25 wt % 30°C	–	–	4.5	4.5

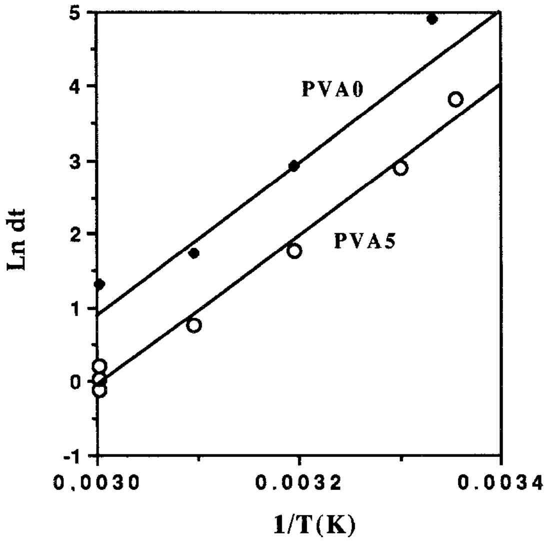

Figure 7 Arrhenius plot of time delays of the onset of the acetic acid permeation waves (or the 2nd wave of water permeation) for PVA_0 and PVA_5 membranes and for the water–acetic mixture containing 10 wt % water

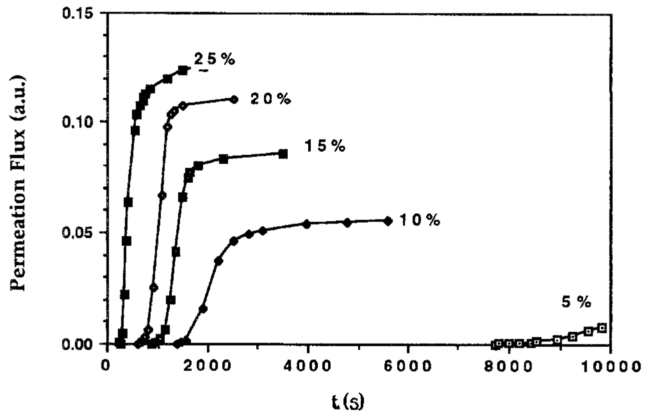

Figure 8 Acetic acid fluxes from water–acetic mixtures of different water contents *versus* time in the differential permeation of water–acetic mixtures through a 40 μm-thick PVA_5 membrane at 30°C

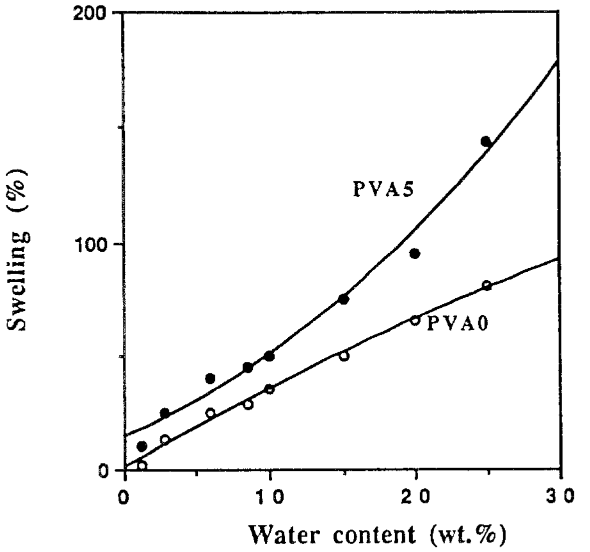

Figure 9 Swelling of membranes at different water contents in water–acetic acid mixtures at 30°C

The determination of the exact water diffusion mechanism in the transient regime required further studies, especially those on the structure and the physico-chemical properties of the membranes progressively penetrated by water molecules. Based on reported works, we assume that the different states of water (i.e. polymer-bound and aggregated water molecules) formed in the water penetration process[23,24] caused the singular water permeation behaviour. However, polymer structure changes can explain the appearance of the second water permeation wave as well. The parallel acetic acid permeation with the second-step water permeation can then be explained by either a change in membrane properties or the streaming of the organic compound by water clusters. Both explanations appear to be consistent with the above-mentioned absence of acetic acid flux when there is no water in the feed liquid.

The value of the time delay for acetic acid (and for the second water permeation wave) depends largely on the permeation temperature. The lower the temperature, the larger the delay. This parameter has not been studied so far, therefore no model is available. The variation of the time delay with the temperature can be accounted for by an Arrhenius-like relationship (*Figure 7*):

$$(1/\delta t) = (1/\delta t_0)\exp(-A/RT) \qquad (6)$$

The values of the coefficient A are +22.5 and 20.5 kcal mol^{-1} for the PVA_0 and PVA_5 membranes respectively. In the present state, this model is totally empirical. However, as the delay time is due to the concentration dependence, the similarities in the activation energies for the time delay and the diffusion coefficient would imply that the plasticization term does not change very much with temperature. It must be noted that γ can be regarded as characterizing the ability of a penetrant to 'plasticize' a polymer, i.e. to increase the polymer segment mobility and therefore the penetrant diffusion coefficient. The weak dependence of γ on temperature can be explained by the fact that the activation of the diffusion, which arises from local fluctuations in the system free-volume, would not change very much with the temperature as the flexibility and the statistical configuration of PVA chains remain unchanged.

Table 4 Values of diffusion coefficient and steady-state flux of acetic acid in mixtures of different water contents through PVA_5 membrane at 30°C. The flux of the mixture containing 10 wt % water was taken as the reference flux

Water content (wt %)	Relative acetic acid fluxes in PVA_5 at 30°C	$D_a \cdot 10^9$ ($cm^2 s^{-1}$)
5	0.39	1.4
10	1.0	2.3
15	1.5	3.1
20	1.8	5.2
25	2.0	8.7

Although the physical meaning of the parameter is not quite clear, we tentatively explain the higher value of the time delay for PVA_0 membrane compared with that for PVA_5 membrane by the presence, in the former membrane, of a larger number of crystallites. The crystallites reduce the mobility of the polymer chains, hence increase the energy barrier for the diffusion of water–acetic acid aggregates. The much higher value of time delay at lower temperature would be explained by the slower dynamics of chains, and by a lower number of permeant molecules having enough energy for an effective diffusion movement.

Influence of water content

Permeation fluxes of acetic acid from mixtures of different water contents through the PVA_5 membrane were plotted as a function of time in *Figure 8*. Large differences in the delay of the permeation onset can be observed, especially for the mixture containing 5 wt % water. The higher the water content, the shorter the time delay. This behaviour can be explained by a better 'plasticization' of the polymer chains, i.e. faster chain movements, by water molecules at higher water content due to higher solvent sorption. *Figure 9* shows effectively a better swelling of PVA_5 membrane at sorption equilibrium in mixtures containing more water. Such an increase in sorption can be explained by a stronger affinity of PVA for water than for acetic acid.

Table 4 gives the values of the diffusion coefficient and the permeation flux of acetic acid in mixtures with different water contents. In fact, relative heights of the steady-state FID signals, which were proportional to the permeation flux are given in *Table 4* since a calibration of the FID detector in terms of absolute flux is very difficult. The value of the steady signal obtained with the mixture containing 10 wt % water was taken as the reference value of the flux. It can be observed that both the diffusion coefficient and the relative acetic acid flux increase with the water content. If we take into account the decrease in the driving force for acetic acid permeation with increasing water content in the binary mixture, the flux increase indicates again a coupling of the acetic acid permeation with the water permeation. Indeed, when the water content increases, the driving force for its permeation increases, leading to an increase in water flux; the latter flux carries with it acetic acid molecules, causing an increase in the acid flux even when the acid content in the liquid mixture decreases. The increase in the diffusivity can be explained by the plasticization effect.

Vacuum pervaporation fluxes

Steady state vacuum pervaporation experiments were carried out on the same PVA membranes. Figure 10 shows the changes in the water and acetic acid fluxes at steady state (as calculated from the measured total fluxes and permeate composition) with the feed water content in the studied composition range. It can be seen that both the water flux and the acetic acid fluxes increased with the water content. The water flux increased faster than that predicted by a linear relationship; such behaviour has often been observed for the variation of the fast permeant with its content in the liquid mixture[1,2,25–26]; it may be attributed to an increased plasticization of the polymer material. The magnitude of the increase in acetic acid flux becomes smaller and smaller as the water content increases due to the decrease in the acetic acid activity (*Figure 10*).

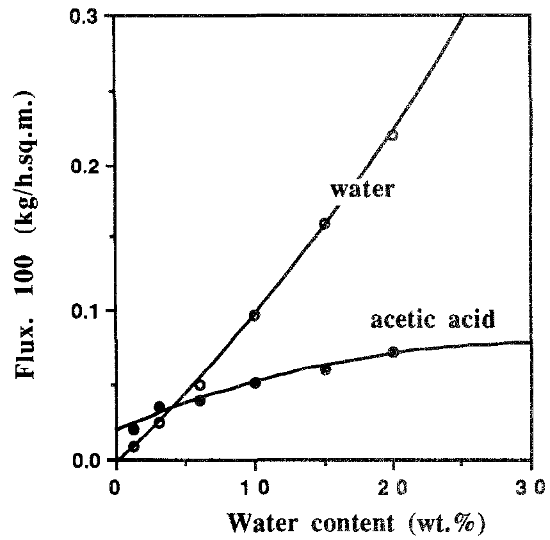

Figure 10 Steady state water and acetic acid fluxes *versus* feed water content in the classical vacuum pervaporation of water–acetic mixtures through PVA_5 membrane at 40°C

CONCLUSIONS

Transport coupling between acetic acid and water flux was evidenced by direct monitoring of individual fluxes of the solvent components in time by using the differential permeation method. Such experimental evidence would not have been possible without the exploration of the time-dependence of the transient fluxes. The use of the differential permeation method with a dual detector enabled us to show the occurrence of an early permeation step of water with low activation energy for the diffusion process. The acetic acid permeation occurs in parallel with the water delayed-permeation step, which both had similar diffusion activation energies. The delay time for the acetic acid and second-step water permeations decreased sharply with increasing temperature and increasing water-content in the mixture, in agreement with the transport coupling mechanism.

REFERENCES

1 Brun, J. P., Larchet, C., Merlet, R. and Bulvestre, G. *J. Membrane Sci.* 1985, **23**, 257

2 Brun, J. P., Larchet, C., Merlet, R. and Bulvestre, G. and Auclair, B. *J. Membrane Sci.* 1985, **25**, 55

3 Watson, J. M. and Payne, P. A. *J. Membrane Sci.* 1990, **49,** 171

4 Radovanovitch, P., Thiel, S. W. and Hwang, S. T. *J. Membrane Sci.* 1990, **48,** 55

5 Felder, R. M. *J. Membrane Sci.* 1978, **3,** 15

6 Nguyen, Q. T., Gref, R., Clément, R. and Lenda, H. *Colloid. Polym. Sci.* 1993, **271,** 1134

7 Gref, R., Nguyen, Q. T. and Clément, R. *Colloid. Polym. Sci.* 1993, **271,** 1143

8 Nguyen, Q. T., Essamri, A., Clément, R. and Neel, J. *Makromol. Chem.* 1987, **188,** 1973

9 Nguyen, Q. T., Essamri, A., Ping, Z. H., Neel, J. and Brueschke, H. 'Proceedings of fifth International Conference on Pervaporation Processes in the Chemical Industry', Bakish Materials Corp., Englewood, New Jersey, 1991, p. 67

10 Rosenbrock, H. H. and Storey, S. 'Computational Techniques for Chemical Engineers', Pergamon Press, New York, 1970

11 Hauser, P. M. and McLaren, A. D. *Ind. Eng. Chem.* 1948, **40,** 112

12 Crank, J. 'Mathematics of Diffusion', Oxford University Press, Oxford, 1975, p. 240

13 Windle, A. H. in 'Polymer Permeability' (Ed. J. Comyn), Elsevier, London, 1985, p. 75

14 Fu, T. Z. and Durning, C. J. *AIChE J.* 1993, **39,** 1030

15 Petropoulos, J. H. *J. Polym. Sci., Polym. Phys. Edn.* 1984, **22,** 183

16 Astarita, G. and Sarti, G. C. *Polym. Eng. Sci.* 1978, **18,** 388

17 Gref, R., Nguyen, Q. T. and Clement, R. *Colloid. Polym. Sci.* 1993, **271,** 1143

18 Berens, A. R. and Hopfenberg, H. B. *Polymer* 1978, **19,** 489

19 Kenney, J. F. and Willcockson, G. W. *J. Polym. Sci. A1* 1966, **4,** 679

20 Parker, R. B., Jr *J. Polym. Sci.* 1959, **41,** 53

21 Michaels, A. S. *Ind. Eng. Chem. Prod. Res. Dev.* 1962, **1,** 14

22 Korsmeyer, R. M. and Peppas, N. A. *J. Membrane Sci.* 1981, **9,** 211

23 Higuchi, A. and Ijima, T. *Polymer* 1985, **26,** 1207

24 Gref, R., Nguyen, Q. T., Rault, J. and Neel, J. *Eur. Polym. J.* 1992, **28,** 1015

25 Will, B., and Lichtenthaler, R. N. *J. Membrane Sci.* 1992, **68,** 127

26 Gref, R., Nguyen, Q. T., Schaetzel, P. and Neel, J. *J. Appl. Polym. Sci.* 1993, **49,** 209