Transport Properties of Poly(vinyl alcohol) Membranes of Different Degrees of Crystallinity. I. Pervaporation Results

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SYNOPSIS

Dense poly(vinyl alcohol) (PVA) membranes of different crystallinities were prepared and studied in pervaporation of water–ethanol mixtures. High selectivities to water were obtained with all types of membranes. Permeation fluxes increase exponentially with the water content in the liquid mixture. At a given water content, the membrane permeability decreases drastically when its crystallinity increases. When the pervaporation temperature increases, the permeation flux increases according to the Arrheniuslike law, with a permeation activation energy that depends strongly on the crystallinity of the membrane. A permeation model, in which the volume fraction of amorphous polymer intervenes in both the sorption and the diffusion laws, was proposed and validated by the experimental data. With the obtained values of the parameters, the permeation flux can be calculated for membranes of a given crystallinity at any temperature and composition of the water–alcohol mixture. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Pervaporation (PV) 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.

Poly(vinyl alcohol) (PVA) is known for its excellent film-forming properties. Currently, this polymer was chosen for the manufacture of the active layer of composite membranes for the dehydration of organic mixtures.[1] These membranes were extensively used in many industrial dehydration units. They generally showed excellent selectivities toward water in organic solvents, but with rather low permeabilities, especially when the organic solvents are short-chain alcohols.

Michaels[2] showed the importance of the crystallinity of polyethylene films in PV of hydrocarbon mixtures. The membranes underwent further crystallization when conditioned in the liquid mixture. Although PVA is known as a semicrystalline polymer, it seems that there were no detailed studies on the correlation between its crystallinity and its transport properties in PV.

The crystalline structure of PVA was discovered by Bunn in 1948.[3] As the crystalline regions in PVA are generally considered to be impermeable to solvents such as water,[4,5] the crystallites are then obstacles and the penetrant molecules have to pass round them. Therefore, the crystalline structure of the films (shape, size, and orientation of the crystallites) should have notable influence on the transport properties.

If the diffusive transport occurs only in the amorphous phase, selectivity will not be significantly affected by crystallinity, but the permeability will be expected to be the highest possible with a completely amorphous film. Under these conditions, manufacturing such a film would be of great interest in PV.

It seems very difficult to prevent crystallization without altering the permeation selectivity and permeability. The introduction of side groups more bulky than H or OH as acetyl groups in the PVA chains perturbs the crystalline organization, but also alters the selectivity of the membranes.[6] The polar side groups interact with the penetrant molecules and modify their transport properties.

Polymer blending is another way to prevent crystallization, but important fractions of the other

polymer are required to obtain significant reduction of the crystallinity.[7] In this case, for the same reasons, the transport properties are notably affected. Cross-linking is perhaps the most effective way to prevent crystallization. However, competition between crystallization and cross-linking might occur if the cross-linking is carried out at high temperatures.[8]

As it seems difficult to completely avoid crystallization while maintaining the initial good properties of the PVA films in PV, it seems interesting to know to what extent the physical structure of the PVA membranes may affect their transport properties and how we could control it, by an appropriate film preparation.

The object of this work was to study the influence of the crystallinity of PVA membranes on the transport of water–alcohol mixtures in PV. The study was focused on fully hydrolyzed PVA, because of its stronger tendency to crystallize compared with other PVA in the acetylated series. It is also the most selective polymer in PV (in this series) with regard to the dehydration of alcohol–water mixtures.[9]

The system that we chose to study is a complex one: We deal with a heterogeneous membrane, composed of two solid phases (crystalline and amorphous), with very strong interactions among the three components (water, alcohol, and PVA). Nevertheless, even if a detailed description was not obtained, a quantitative empirical correlation between the crystalline structure and the transport properties would greatly contribute to a better understanding of the effect of the physical structure of a membrane on its PV properties.

THEORETICAL ASPECTS

It is generally admitted that the transport through a PV membrane involves a sorption step at the membrane upstream face, followed by a diffusion through the dense film and a desorption into the vacuum. Under a high vacuum on the downstream side of the film, the desorption is considered to be a fast step. Furthermore, if we assume that there is negligible concentration polarization, i.e., no transport limitation in the liquid phase in contact with the membrane, and if the sorption kinetic is fast, the transport will be controlled by the diffusion in the membrane phase.

In a first approximation, the semicrystalline polymer may be described as a two-phase system, composed of two distinct domains (amorphous and

crystalline). This widely used model is known as the "two-phase" model (Fig. 1). From now on, we will call "crystallinity" the volumic fraction of crystallites in the polymer, as calculated by using this model, from the density of the samples.

The effects of the presence of crystallites result from at least two main features: First, they are considered to be impermeables to penetrating molecules, and, second, they should act as giant cross-linking regions:

(a) *The very low permeability of the crystallites* enables us to define a tortuosity coefficient "t" of the diffusion process, which would be a function of the volume fraction of crystallites (or crystallinity), of the shape and size of the crystallites, and of their orientation in the film. Moreover, the total sorption capacity of the polymer will be reduced, due to the very low sorption in the crystallites.

(b) *The physical cross-linking effect of the crystallites.* The crystalline regions act as giant cross-linking regions with respect to those chains that are partially embedded in several crystallites; the swelling and diffusion are reduced compared to those in the totally amorphous polymer. The restraint of cross-linking regions on the segmental mobility makes the diffusion process more difficult and dependent on the size and shape of the penetrant molecules. Thus, a blocking factor "b" reduces also the diffusivity in the polymer.
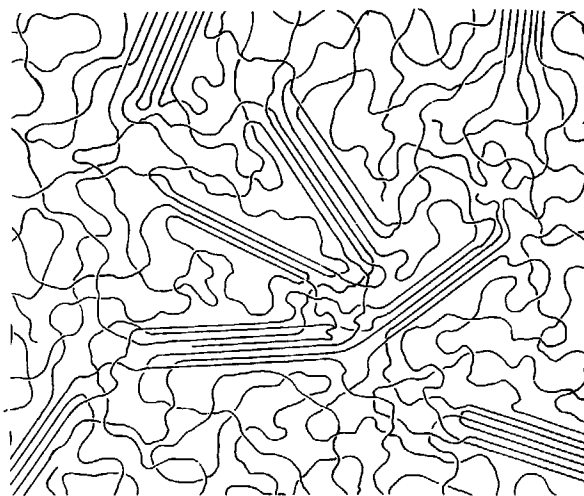

Figure 1   Schematic representation of the two-phase model for semicrystalline polymers. The organized regions, with parallel chains, are the crystallites.

The first step in PV (*sorption*) is assumed to be a thermodynamic property of the polymer with the surrounding upstream phase. Solubility in PVA films is considered to be proportional to the amorphous volume fraction "p_a"[10]:

$$c = c_a(p_a) \qquad (1)$$

where c and c_a are, respectively, the penetrant volume uptake in the semicrystalline polymer and in the entirely amorphous polymer. This simple expression does not account for the cross-linking effect; the solubility is considered to be unaffected by the cross-linking effect, except at very high degrees of cross-linking or only if the penetrant considerably swells the polymer.[11]

We assume now that sorption in the polymer follows a simple partition rule, i.e., the solvent molar content in the polymer is proportional to the water molar content in the liquid. This is at least true for the water–ethanol system, for which results reported in the literature show that, for water content in the liquid less than about 40%, the system, although strongly nonideal, works as if Henry's law was followed.[12,13]

During PV, because diffusion is the limiting step, we assume that thermodynamical equilibrium is achieved at the interface between the membrane and the liquid phase. The concentration of water at the face of the membrane in contact with the feed, "c_{m1}," which is equal to that measured in steady-state sorption experiments, would be

$$c_{m1} = Kc_1(p_a) \qquad (2)$$

where c_1 is the concentration of water in the feed mixture in contact with the membrane and K is a constant (called solubility coefficient), which depends on the temperature and on the nature of the liquid (for instance, different mixtures of water–alcohols).

Effect of Polymer Crystallinity on the Limiting Diffusivity

The second step in PV, *diffusion*, is a kinetic property of the polymer. To account for the simultaneous effects of the crystallites presented above, the intrinsic thermodynamic diffusion coefficient "D^*" of the penetrant in the polymer should be written as follows:

$$D^* = \frac{Da^*}{tb} \qquad (3)$$

where Da^* is the diffusion coefficient of the penetrant in the entirely amorphous polymer. The stars specify that the diffusivity consists of extrapolated values at zero concentration. This diffusivity is probably close to that in the "dry" part of the membrane (in contact with the vacuum), where desorption takes place.

Different theoretical analyses that take into account the influence of the volume fraction of the impermeable crystalline phase $(1 - p_a)$ on the tortuosity "t" lead to more or less complex correlations with the fraction of the amorphous polymer. More recent studies with unoriented polyethylene films showed that the tortuosity can be correlated to the amorphous fraction by a very simple power law[14]:

$$1/t = (p_a)^m \qquad (4)$$

where $m > 1$ is a power depending on the nature of the polymer used.

In our approach, we used the simplest relationship for the tortuosity and the blocking factor:

$$D^* = D_a^*(p_a)^m \qquad (5)$$

Values of m, reported in the literature and calculated using the expression (5), vary from about 0.3 for polyethylene to about 1 for poly(ethylene terephthalate).[15]

Water diffusivity in PVA was reported[12] to increase exponentially with the molar water content. This suggested us to use an empirical relationship that correlates the diffusion coefficient D to the local content of the penetrant in the polymer, c[16]:

$$D = D^* \exp(Gc) \qquad (6)$$

G, sometimes called the "plasticization coefficient,"[17] is a characteristic of the system at a given temperature. In the Fujita theory, G accounts for the effectiveness of the penetrating molecules to take advantage of the increase of the available free volume in the matrix for their diffusion; G is inversely proportional to the free volume of the polymer–penetrant system. In the case of semicrystalline polymers, G is the coefficient related to the amorphous phase, and if there are no microfractures near the crystallites, G should be constant whatever the crystallinity of the sample.

The relation (6) should be adequate for the water–PVA system, in which the penetrant and the polymer have similar chemical groups (hydroxyl). Long's statement was that in this case the fraction of penetrant–polymer contacts should be propor-

tional to the concentration c of the penetrant in the polymer or to the volume fraction it occupies in the polymer.[15]

Integration of Fick's law by using Long's relationship gives the following expression of the flux of water, "J":

$$J = \frac{D^*}{\delta G} [\exp(Gc_{m1}) - \exp(Gc_{m2})] \qquad (7)$$

where δ is the membrane thickness, and c_{m1} and c_{m2} are, respectively, the water content in the membrane, at its upstream and downstream interface. At very low downstream pressure in the downstream compartment, c_{m2} is practically nil and eq. (7) becomes

$$J = \frac{D^*}{\delta G} [\exp(Gc_{m1}) - 1] \qquad (8)$$

By combining eq. (8) with eq. (2), the last equation can be written as follows:

$$J = \frac{D^*}{\delta G} [\exp(GKp_ac_1) - 1] \qquad (9)$$

It should be noted that this model concerns the permeation of a *pure liquid:* It can be used for binary mixtures only if the two components permeate independently of each other, i.e., each component does not "perturb" the diffusion of the other component, or its local concentration, in the film. This hypothesis will be discussed with regard to the experimental results.

The validity of eq. (8) for pure component permeation was shown by studying the concentration profiles in the membrane in PV.[18,19] Few results and validated models are available with regard to the concentration profiles in the case of mixtures. In this case, deviations from the model might be due to the so-called coupling effect.

The "coupling" occurs first during sorption into the membrane, which no longer obeys Henry's partition equation, and should be accounted for by using a more fundamental and comprehensive approach such as the Flory–Huggins or Flory–Rehner theory.[20,21] The concentration of a component in the membrane, at the upstream face, can be calculated by solving the equations obtained by equating the activity of the component in the liquid to that in the membrane.

Second, there might be also a diffusion coupling, i.e., a streaming diffusion flux of one component due to the flux (or the driving force) of the other.[22] The transport model that takes into account these two coupling effects will be very complex, with many parameters to be determined. Thus, we will focus our attention on the limit case in which both component fluxes are uncoupled.

We correlate D^* to the volume fraction of the amorphous phase, p_a, by using eq. (5). The final relationship used to express the flux of water will be

$$J = P^*(p_a)^m [\exp(\gamma c_1 p_a) - 1]/G \qquad (10)$$

where P^* (equal to the ratio between Da^* and δ) is the intrinsic permeance in the amorphous part of the membrane and "γ" (equal to GK) is a constant independent of the crystallinity of the film.

According to eq. (10), the PV flux of an independently permeating component increases exponentially with the volume fraction of the amorphous phase and the molar content of this component in the liquid.

The influence of the temperature on the permeation rate is generally accounted for by an Arrheniuslike law[23,24]:

$$J = P^* [\exp(\gamma c_1 p_a) - 1]$$
$$\times \exp[-Ea/R(1/T - 1/T°)]/G \qquad (11)$$

where $T°$ is a reference temperature (in our case 300 K).

With expression (11), it would be possible to predict the flux obtained with a membrane of a given crystallinity as a function of the water content in the mixture and of the temperature of the experiment. Reciprocally, if the permeation of the molecules in the membrane proceed independently of each other, it would be possible, by measuring the flux obtained with a membrane, at a certain temperature, to deduce its crystallinity. Moreover, by measuring the overall flux, it would be possible to determine the eventual crystallinity changes occurring during very long lapses of time during PV, as a function of the liquid mixture in contact with the membrane or the temperature of the experiment.

EXPERIMENTAL

Membranes of Different Crystallinities

We used PVA powder from Janssen Chimica, with a molecular weight of 115,000 and less than 0.2% of acetyl content (as determined from NMR data).

Homogeneous solutions of 10% by weight polymer in water were obtained by first adding the powder in water at ambient temperature and then heating under reflux and moderate stirring the solution during 2 h. The cooled and degased solution was cast on a glass plate by a Gardner blade. Then, water was allowed to evaporate slowly, at room temperature. After 2 days, drying was completed under vacuum at 20°C. The films obtained in this way have a crystallinity of 25–27%, as determined by density, X-ray scattering, or IR spectroscopy. Crystallinity was further raised by an appropriate heat-treatment. Scanning electron microscopy ensured us that the internal structure of the films was a dense and compact one, showing no pores or distinct crystalline features.

Crystallinity Measurement

Crystallinity is defined[25] as the ratio of the volume occupied by the crystallites in the sample. Therefore, if the specific volumes of the two phases are known, the crystallinity can be calculated from the density of the material. The density of PVA films was obtained by adding dichloro-1,2-ethane ($d = 1.255$) to a membrane sample put in trichloro-1,1,1-ethane ($d = 1.35$), until the sample was maintained in equilibrium with the liquid mixture, i.e., it did not sink to the bottom or float on the surface. The solvents were chosen due to their value of density which encloses that of the PVA samples studied and their nonabsorption by the polymer. A pycnometer was used to measure the density of the liquid mixture, which equals that of the PVA sample. The crystallinity values obtained by density were checked by complementary techniques, as infrared spectroscopy

and X-ray scattering, which are described in detail elsewhere.[26]

Pervaporation Apparatus

The PVA films, supported by a filter paper, are clamped at the bottom of a cylindrical double-wall glass cell fitted with four baffles and a six-blade axial turbine. The hydrodynamic conditions in the cell, determined by the stirring speed,[27] were such that we could neglect the concentration polarization in the liquid mixture. The data obtained correspond then to the intrinsic transport properties of the considered films (see Fig. 2).

For the determination of the PV characteristics of each membrane, we used an automatic set up[28] (Fig. 1). Each 10 min, permeate samples of 0.6 mg are collected in a trap cooled by liquid air. The sample is then heated until total evaporation and then injected into a chromatograph equipped with a thermal conductivity detector. The injection and sampling valves are controlled by a computer to optimize the conditions of the experiments (in particular, the time needed to collect 0.6 mg of permeate in the trap). The sample is injected in the column using directly the carrier gas in the chromatograph. The chromatograph (GIRA) was equipped with a Porapak Q column whose size was optimized to obtain the shortest time for the analyses. This apparatus is very convenient for the determination of small permeate fluxes and also for checking the stability of the membranes. A careful calibration allowed us to determine the permeation flux for each component and, thus, the water content in the permeate.

The accuracy and the short time intervals needed for each flux determination enabled us to study the
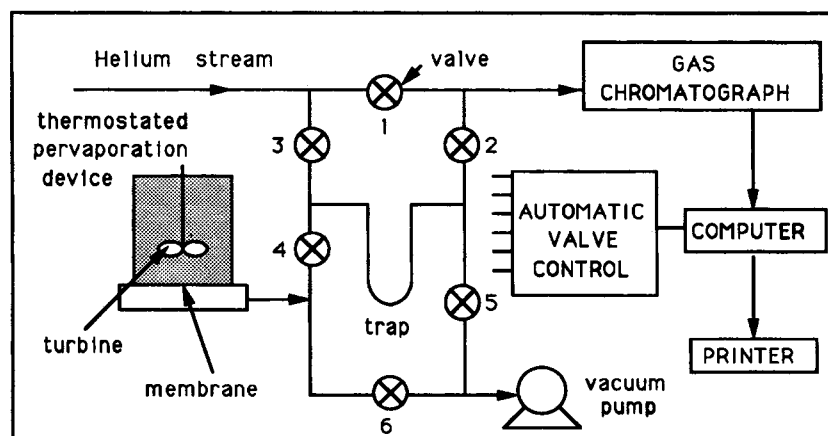

Figure 2 Automatic pervaporation apparatus.

crystalline films, without introducing notable crys-
tallinity changes during the experiments. Each ex-
perimental result was obtained after an equilibration
time of about 1 h between the membrane and the
liquid mixture. During this time, five or six flux val-
ues were given by the automatic setup. We ensured
that three successive flux values from the automatic
setup were identical, after changing the composition
of the liquid mixture.

The total time needed for the study of a mem-
brane was about 8 h; with a classical PV device,
several days or weeks would be needed for these ex-
periments, because the fluxes are very small at a low
water content in the feed.

A short time of contact between the membrane
and the liquid mixture is an important condition,
because additional crystallinity changes may occur
with time. Nevertheless, we detected an increase in
the crystallinity after PV experiments, but as it was
less than 5%, we will neglect it. A discussion of the
reasons of this crystallinity increase is discussed in
detail elsewhere.[26]

RESULTS AND DISCUSSION

Membranes of Different Crystallinities

To check our model, we wanted to study the largest
crystallinity domain as possible. Unfortunately, it
was not possible to obtain films of less than 25%
crystallinity by the usual evaporation techniques,
nor films of more than about 65%.[29] Thus, we made
films of 25% crystallinity, by the technique described
in the Experimental part, and then raised the crys-
tallinity as much as possible by heating these films
at appropriate temperatures in an oven under ni-
trogen stream.

Table I shows the final crystallinity (average val-
ues, for at least two films) obtained after heat treat-
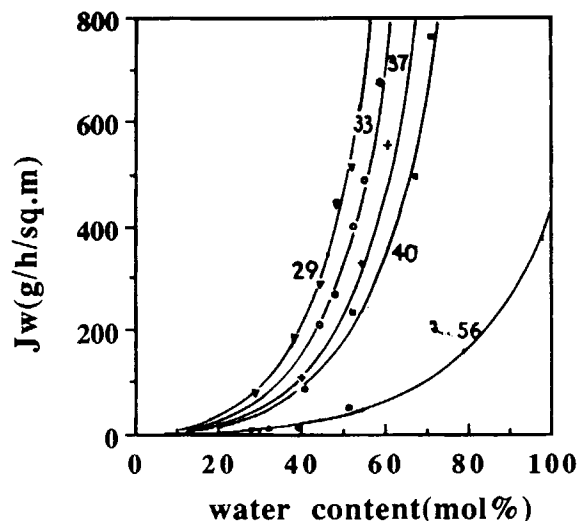ment of 25–27% crystalline films. It can be observed

Figure 3   Flux of water (Jw) through PVA films of dif-
ferent crystallinities, obtained by vacuum pervaporation
at 40°C of water–ethanol mixtures, as a function of the
water content (mol %) in the liquid (cw). Simultaneous
fitting of the experimental set of values obtained for four
different crystalline membranes (29, 33, 37, 40, and 56%)
by using eq. (10).

from this table that the progressive rearrangement
of the chains leading to a higher crystallinity is ac-
celerated by heating at temperatures above the glass
transition temperature, which is equal to 75°C
± 10°C, according to Pritchard.[30] Heating at lower
temperatures (70°C, 900 min) has a negligible effect
on crystallinity.

The samples used in PV had 25–56% crystallinity.
The films were 20–25 μm thick. Corrections taking
into account the film thickness were made, by con-
sidering that the fluxes were inversely proportional
to the thickness; all the fluxes were normalized to a
25 μm thickness.

Pervaporation Experiments

Pervaporation of Water–Ethanol Mixtures

Membranes of 27–56% crystallinity were compar-
atively tested in PV of mixtures of water and ethanol
under isothermal conditions.

The partial fluxes of both water and ethanol, in
steady-state conditions, are shown in Figures 3 and
4, as a function of the water content in the mixture
and for membranes of different crystallinities. In all
the cases studied, the higher was the crystallinity,
the lower was the permeability to both components.
This is an expected tendency, since the density of
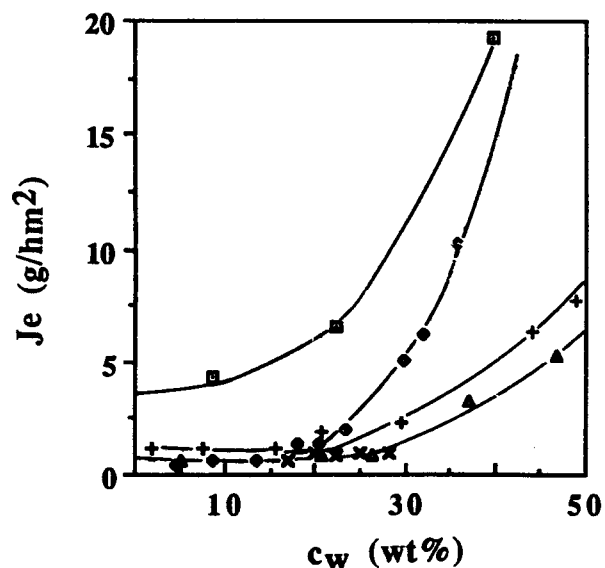the sample increases and, therefore, the total free

**Table I   Average Crystallinity Increase of PVA
Films of 25–27% Crystallinity after Heat
Treatment at 70, 130, and 150°C**

	Temperature (°C)					
	70	130			150	
Heating time (min)	900	10	30	120	780	25	155
Final crystallinity (%)	29	35	37	39	44	33	56

Figure 4 Flux of ethanol (Je) through PVA films of different crystallinities, obtained by vacuum pervaporation at 40°C of water–ethanol mixtures, as a function of the water content (wt %) in the liquid (cw). Crystallinity of the PVA films: (□) 27%; (◆) 33%; (▲) 37%; (+) 40%; (×) 56%.

volume accessible to the permeants decreases when the crystallinity increases.

The PVA membranes showed a remarkable selectivity toward water. This can be explained by the specific affinity of PVA to water, which favors the water sorption into the membrane. The alcohol flux, at 40°C, did not exceed 10 g/h m² (whatever the concentration of the liquid mixtures), whereas the water flux was sometimes as high as 1000 g/h m². At low water content, the fluxes are very low. Beyond a certain water content in the feed, there is an exponential increase in water flux (Fig. 3), attributed to the plasticization effect of water on PVA.

The selectivity, which is defined as the ratio between the water content in the permeate and the water content in the feed, is not significantly affected by the membrane crystallinity. Indeed, this would be the case if the transport of the permeant molecules took place only through the amorphous regions of the polymer and if there were no "third" phase in the polymer, i.e., distinct regions or microcracks between crystallites and amorphous regions.

The activity gradient of a species between the two sides of the membrane is considered to be the driving force for its permeation, if there is no diffusion coupling. The exponential increase in water flux with the water content is not in contradiction with this statement, but the increase in alcohol

flux (Fig. 5) when the water content increases, i.e., the activity of the alcohol decreases in the feed mixture, is.

Coupling between Water and Ethanol Fluxes

The similar variation of water and ethanol fluxes as a function of the feed water content (Figs. 3 and 4) suggests that a permeation coupling might occur during the sorption or/and the membrane transport
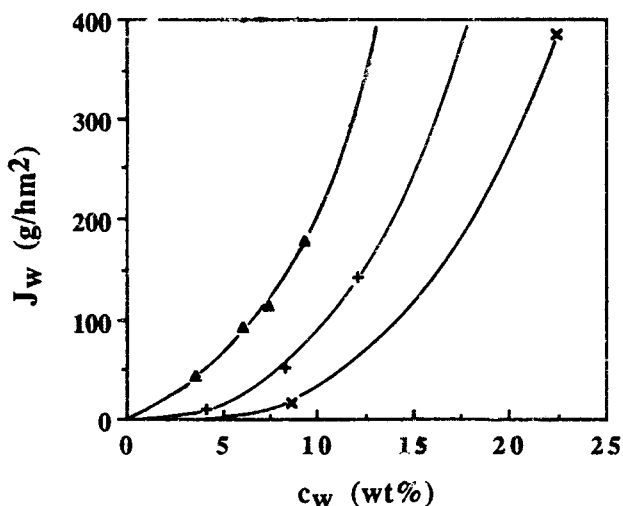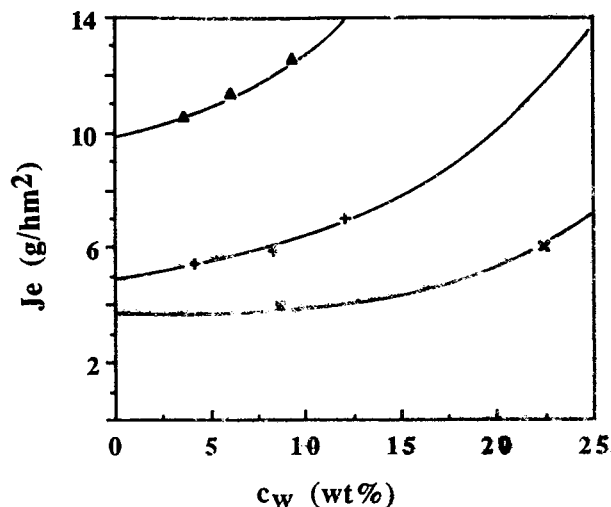

Figure 5 Water and ethanol partial fluxes (Jw and Je) obtained in pervaporation at (×) 42°C, (+) 63°C, and (▲) 77°C of water–ethanol mixtures through a 27% crystalline film, as a function of the water content (wt %) in the liquid (cw).

steps. Ethanol flux is very small at low water content in the liquid mixture in contact with the membrane. It will not increase with the water content, i.e., with the decrease in its own driving force, except when there is a coupling effect. It has been shown[12] that there is a "thermodynamical coupling" during sorption: Alcohol sorption in PVA membranes increases when water content in the liquid increases. Depending on the nature of the alcohol used, water sorption may also be enhanced by the presence of alcohol. The water solubility in PVA at any given water content was greater with isopropanol than with ethanol or methanol. This kind of coupling effect is difficult to take into account, since in systems in which there are strong interactions between the polymer and the components of the liquid mixture in contact with it, the interaction parameters (which are used in Flory–Huggin's equation for the calculation of the solvent sorption) are concentration-dependent. As the water fluxes through the studied membranes were much higher than were the ethanol fluxes, the influence of the ethanol fluxes on the water fluxes due to the coupling in the transport process is assumed to be negligible.

Calculation of the Pervaporation Parameters G and P*

In the first approach, eq. (8) was applied to membranes of different crystallinities. Good agreement was observed for the least-square fitting performed separately on each water flux–feed water content curve. The fact that a "two-parameter model" fits the results indicates that, whatever is the membrane structure, the flux of water (the preferentially permeated solvent for PVA membranes) increases exponentially with the water content in the feed mixture. This very simple model was indirectly checked by many groups[18,19,31,32] (by studying the concentration profile in the membrane) but only in the case of pure solvent permeation (academic case with no interest for practical purposes). Its successful use in our case means that the presence of ethanol, in a large concentration range, did not affect the water permeation (i.e., negligible coupling). However, we do not speculate that it is a general equation, applicable to any membrane–solvent mixture systems. In our opinion, it should be valid for systems in which the membrane is very selective to one component, especially in the sorption step. Similar observations were already made by one of us[33] for other systems in which the membrane was also very selective. This equation also fits the results obtained by different authors[34–36] in the limit case of highly selective membranes in the extraction of organic

solutes in dilute aqueous solutions: At low concentration, the expansion in the Taylor's series gives a flux of the preferentially permeated component proportional to its concentration in the feed medium. Hence, this simple phenomenological equation is quite convenient for the prediction of the flux of the preferentially permeated component, i.e., generally, the minor component, when the composition of the feed mixture is changed.

To better understand the influence of the crystallinity on the parameters of the transport equation, least-square fittings of the results obtained with water–ethanol mixtures and five membranes of crystallinities ranging from 29 to 56% were carried out by using eq. (10). An unique expression was obtained for the whole set of experimental data with good agreement (Fig. 3):

$$Jw = 20.6(p_a)^{2.2}[\exp(11.1c_1p_a) - 1] \quad (12)$$

The first factor of 20.6 represents the limit permeance (at zero permeant concentration) of the amorphous PVA to water (at the considered temperature), which is constant over the studied range of crystallinity. The value of the exponent (2.2) appears to be high compared with those in the literature for other systems.[15] However, it should be noted that the size of the crystalline regions is rather important in our case, due to the crystallites growth during the heat treatment of the samples.[26] The diffusive path is therefore longer and might explain the high value of the exponent.

The plasticization coefficient is not crystallinity-dependent. In agreement with the model, this means that the increase in the mobility of water in the film, due to the free-volume increase caused by the local amount of water in the polymer, occurs exclusively in the amorphous phase. This result confirms the model in which the crystallites act as impermeable fillers. However, it should be emphasized that the model can be applied to the permeation only if the penetrant does not modify the crystalline regions. In our case, it may no longer be valid at higher water content in the liquid phase, since changes in the crystalline regions may occur.[26]

Equation (12), which was obtained for 25 μm-thick membranes, can be extended to membranes of any thicknesses by postulating the inverse proportionality relationship between the permeance and the membrane thickness.

Some Comments on the Ethanol Flux

The ethanol fluxes were measured with reasonable accuracy, although they were very low compared

with the water flux. It appears that the membrane of 27% crystallinity shows the highest ethanol fluxes, whereas the membranes of higher crystallinity show practically the same ethanol flux in the feed water content range from 0 to 20 molar % (Fig. 3). The ethanol flux increases exponentially with the molar water content in the feed at water content higher than about 20 mol %. The flux increase is stronger for membranes of lower crystallinities, as in the case of water fluxes.

The comparison of the curves of water fluxes vs. feed water molar content (Fig. 3) and those of ethanol fluxes (Fig. 4) leads to the conclusion of important flux coupling effect (parallel behaviors) for ethanol transports. Since the PVA membranes exhibit much lower transport resistance to water than to ethanol, we can conclude that there is a streaming flux of ethanol by the water flux.

Influence of the Temperature on the Transport Properties

Whatever the temperature of the experiment, the curves of water and alcohol fluxes vs. feed water content have the same exponential shape, as can be seen in Figure 5.

By using eq. (11), we determined the apparent activation energy "E_a" in the 40 and 80°C range for films of different crystallinities. Very good agreement was obtained between the model and the experimental results. E_a values for membranes of different crystallinities that are the same for mixtures of different compositions are given in Table II.

We observe a very strong dependence between crystallinity and E_a. The apparent activation energy is composed of a sorption energy term and an activated diffusion term, the first term being generally neglected.[24,37] The activation energy is then a measure of the difficulty that a molecule experiences in its diffusion through the polymer. As we have already mentioned, the crystallites bring two cumulated effects: obstacles and giant cross-linking regions. It appeared that the higher is the crystallinity the more difficult is the passage of molecules through the

polymer matrix. With regard to the diffusion in the amorphous phase alone, the activation energy is somewhat the energy required to loosen the local network (separation of polymer segments) for an effective jump of the permeant molecule. Therefore, both the cross-linking and the obstacle effects contribute to the observed increase of the activation energy in films of higher crystallinity (Table II).

An interesting observation is that the plasticization coefficient γ, calculated with our model [eq. (8)], does not significantly vary with the temperature, since the interaction parameters should depend a priori on the temperature in our system, in which strong hydrogen bonds affect both sorption and diffusion processes.

It appears from our results that the water concentration in the feed, c_1, and the temperature, T, have similar effects on the water flux.

CONCLUSIONS

The proposed model for the permeation of water in PV of water–ethanol mixtures can be used to predict the permeation flux through PVA membranes of different crystallinities at any temperature and composition of the feed mixture. Such a model would be very useful in the calculation of the pervaporation process, in which the semicrystalline properties of the polymer membrane is taken into account.

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Table II   Activation Energy (E_a) for Permeation of Water from Water–Ethanol Mixtures as a Function of the Crystallinity of the PVA Membranes

	Crystallinity (%)		
	28	38.9	56
E_a (kcal/mol)	11.4	23.1	20.8

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