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Clustering of solvents in membranes and its influence on membrane transport properties

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Abstract

Solvent clustering in membranes, if it occurs, could modify the sorption and diffusion behaviors of polymer membranes and therefore their transport properties. Solvent cluster formations in hydrophilic poly(vinyl alcohol) (PVA), in hydrophobic poly(dimethylsiloxane) (PDMS) and intermediate poly(vinyl acetate) (PVAc) membranes were studied by infrared spectroscopy, differential scanning calorimetry, X-ray scattering techniques, and by visual observations. A water saturated PVAc membrane contains non-freezable (bound) and liquid-like water molecules in equivalent amounts (ca. 1.6 wt%); membrane infrared studies during the sorption process indicated that water penetrates first in the membrane as monomeric molecules which aggregate later to form clusters. In PVA membranes, water molecules can exist under three states, i.e. non-freezable, freezable bound and liquid-like states, depending on the water content in the membrane. The cluster formation seems to affect the membrane selectivity towards water and the water and ethanol diffusivities in PVA membranes. In PDMS membranes, solvent clusters were evidenced by infrared spectroscopy and visual observations. The clustering of alcohols in PDMS makes the sorption behavior of these solvents in the membrane deviate from the Flory-type behavior observed for other solvents: the sorbed amount increases drastically with the surrounding-solvent activity in the high activity range, but the solvent diffusivity decreases.

Keywords: Clusters; Water; Alcohols; Membranes; Transport properties

1. Introduction

The transport of solvents through dense membranes is generally analysed with the solution-diffusion mechanism [1], which assumes a dispersion of the solvent molecules in the polymer under a unique state, e.g. individual molecules. However, such an assumption may not be valid in many cases. For instance, it is well known that water molecules may be present in a polymer in different states. In hydrophilic polymers such as poly(vinyl alcohol) [2], at least three states of water were detected. In hydrophobic membranes such as poly(dimethylsiloxane) (PDMS), Matsuura et al. [3,4] from the melting point detection in differential scanning calorimetry, suggested that 2-propanol was present in the membrane in both the bulk and bound states. Nevertheless, the alcohol amounts involved in the sorption were much higher (up to 60 wt% swelling for 2-propanol [3,4] than those reported by other authors for different alcohols [5–7] Similarly, the detected melting point of "sorbed" water in PDMS was made

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with samples containing a water amount [3] much higher than the PDMS-saturated water amounts reported in the literature [5,6]. Although variations in the sorbed water amount could be observed with PDMS samples of different origins, i.e. prepared in different ways, it seems questionable that such a high level of water sorption, 0.077 g water/g dry PDMS [3], could be reached in such a highly hydrophobic polymer. It is probable that the freezable bulk water or bulk propanol (i.e. clusters) detected in DSC in those cases was simply the surface phase similar to the solvent phase expelled from the membrane upon cooling observed by Pineri et al. [8] for another system. However, we are not suggesting that water molecules cannot aggregate with each other to form such a bulk water phase in PDMS. Due to possible experimental artifacts, we feel that the formation of water or alcohol clusters in membranes, either in hydrophilic or hydrophobic polymer membranes, needs to be carefully examined from both the experimental and fundamental view points before discussing its influence on the membrane properties.

2. Experimental

2.1. Infra-red spectroscopy

Two procedures were used with the attenuated total reflectance device (ATR). In the first one, the membrane sample immersed in the liquid medium to be studied was taken out of the conditioning liquid at finite intervals, wiped with paper tissue, and mounted in the ATR device for measurements. In the second one, a dried membrane was mounted in the ATR with one face in contact with a solvent reservoir and the other with the ATR prism. FTIR spectra were recorded with a Bruker IFS25 instrument at different times to characterize the structure of solvent molecules which reached the membrane face in contact with the ATR prism by diffusion from the reservoir.

2.2. Materials

PDMS materials of different dimensions were prepared by crosslinking vinyl terminated PDMS chains (Rhône Poulenc, RTV 141A) with cyclic tetrahydrosiloxane (Rhône Poulenc, RTV 141B) at 100°C in Teflon moulds (for blocks) or on polyethyleneglycolterephthalate (PET) films (for films). Unreacted species were washed out from the samples by acetone. Crystal clear samples were obtained.

Poly(vinyl acetate) films were obtained by casting an ethanol solution of the polymer on a glass plate; the solvent was next evaporated in an oven. Poly(vinyl alcohol) (PVA) membranes of different natures (100, 95 or 88% hydrolysis degrees) were obtained from aqueous solutions of the appropriate polymer by liquid dope casting on PET films in a similar procedure.

In order to avoid moisture sorption, especially for PVA membranes, the samples were vacuum dried and stored over phosphorus pentoxide.

2.3. X-ray scattering

A PVA sample of known sorption extents was quickly brought down in a special device to a low temperature. The X-ray ice scattering patterns were recorded at constant sample temperature with the Rigaku apparatus.

2.4. Sorption equilibria

The sorption extents at equilibrium were measured by weighing the polymer samples conditioned in liquids maintained at a constant temperature in sealed bottles. The measurements, which consisted of weighing the dry and swollen samples after elimination of sample surface solvent by blotting, were easy in the case of PVA membranes. For PDMS, due to its low water sorption, polymer blocks of ca. 30 g were used to obtain correct measurements. The water activity in the liquids was controlled by using solutions of lithium chloride at different concentrations. The detailed procedure was reported elsewhere [6].

2.5. Differential permeation

The technique which was used for the determination of the mean diffusion coefficient was detailed elsewhere [9,10]. Briefly, it consists of monitoring the transient permeation rate signals issued from a moisture meter and a flame ionization detector when a dry membrane is suddenly put in contact with the liquid mixture on the feed side while an inert gas sweeps the other side to carry the permeate to the detectors.

3. Results and discussion

3.1. Water clustering in poly(vinyl acetate)

Although poly(vinyl acetate) (PVAc) is not yet used as a dense separation layer in industrial membranes, its amorphous nature and its mild hydrophobicity made it a good candidate for the study of sorbed water clustering. When a PVAc film saturated with water is studied in DSC, an ice melting peak (in positive temperature scanning), or a water crystallization peak (in negative temperature scanning), is detected at ca. 0°C (Fig. 1). This strongly suggests the presence of water clusters whose size is large enough to behave similarly as bulk liquid water whose molecules are known to form clusters; their structure is shown schematically in Fig. 2. The amount of clustered water in PVAc as calculated from the ratio of the total energy of water crystallization to the enthalpy of pure water crystallization at 0°C corresponds to nearly half of the total amount of sorbed water, i.e. 1.6 wt%. Since no other crystallization (or melting) peak was observed in DSC experiments, we assume that the remaining water amount is in the bound, non-freezable, state. If the bound-water amount is expressed as the number of water molecules per vinyl acetate unit in the material, there is on an average 7 water molecules for every hundred vinyl acetate units. It appears that the hydrophobic chain environment of the acetate group prevents the polar carbonyl function to form efficient hydrogen-bonds with water. In a liquid medium, an ethyl acetate molecule, the molecular analog of a vinyl acetate unit in PVAc, is solvated at phase equilibrium by 0.14 water molecules, i.e. double the quantity of water per polar site.

In spite of the small total amount of water in cluster form (1.6 wt%), a 300 μm thick film turns from crystal clear to paper-white upon water saturation (Fig. 3). The white aspect obtained with the originally transparent materials indicates marked internal inhomogeneity leading to a refractive index gradient in the water-PVA system. Considering the small water content, the dispersed phase must consists of microscopic "droplets" of water in the solid polymer material. The droplet size would be of the order of magnitude of visible light wavelengths (400-800 nm) to scatter light. In such large clusters, water must be in a liquid-like environment and therefore must crystallize at the normal water crystallization temperature.

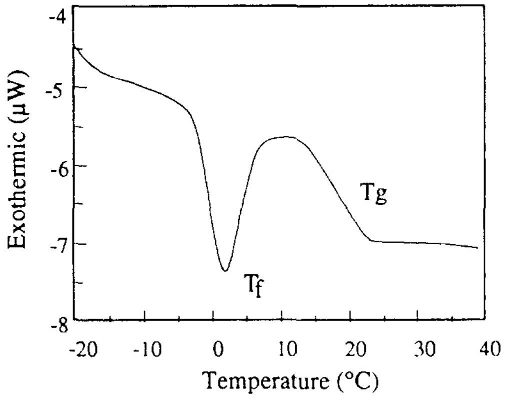

Fig. 1. DSC Thermograms of water saturated poly(vinyl acetate) membrane. Swelling degree: 3.2 wt%, heating rate 10°C/mn.

The above-mentioned results do not give any information on the state of water during water sorption in the polymer. Successive infrared spectra recorded with a 650 μm-thick PVAc film, mounted in an ATR device, when the sample is taken out form the liquid water bath at different contact times, show that the states of water change with time, as water progressively penetrates more and more into the polymer (Fig. 4). At the beginning of the sorption process, water seems to penetrate into the film mainly in the monomeric state as one can see in the early time spectra from the large peak at 3620 cm^{-1} and the smaller one at 3530 cm^{-1}. These frequencies would correspond to antisymmetric and symmetric stretching vibrations of O-H bonds of monomeric water [11], i.e. when water molecules are not bound to each other. As more water molecules are sorbed with time, the broad band in the 3200-3500 cm^{-1} range appears and increases rapidly with water content. In this broad band, two shoulders at 3450 and 3260 cm^{-1} can be observed; the 3450 cm^{-1} one grows faster with time than the other one. Their presence at higher water concentration in the poly-

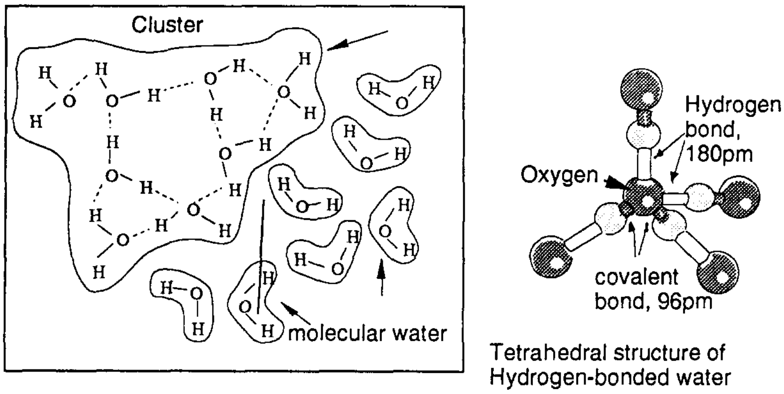

Fig. 2. Schematic representations of water clusters in liquid water and tetrahedral structure of water molecule with its maximum number of hydrogen bonds.

mer can be interpreted in terms of water association into hydrogen-bonded species. As the larger the OH stretching frequency decrease, the stronger the hydrogen bond, we assume that the low frequency band (at 3260 cm^{-1}) corresponds to the strongest hydrogen bonds such as those involved in multimers, while the 3450 cm^{-1} band could be assigned to the water dimer [11].

The clearly visible band at 3260 cm^{-1} not observed in liquid water (which has only one very broad band centered at 3400 cm^{-1}) suggests that the water-water complexes have more defined H-bond structures than those in liquid water.

3.2. Water in poly(vinyl alcohol) (PVA)

PVA polymers are hydrolysis products of PVAc. PVA properties depend largely on the residual acetyl content. We will focus our discussion on the completely hydrolysed PVA in this paper. It is the most hydrophilic PVA and therefore the most used in the manufacture of pervaporation dehydration membranes. In such hydrophilic materials, it is well known that different states of sorbed water can co-exist. In PVA, up to three states of water were detected [2,10]. DSC thermograms show that, depending on the total sorbed amount, only one or two water states are found (Fig. 5). At low water content (19 wt% swelling), only the PVA glass transition (T_g), was detected. The absence of water melting (and crystallization) DSC peaks indicates that the sorbed water is in the non-freezable state. At intermediate water contents, a crystallization peak, followed by a water melting peak, can be observed in the heating process after the quench of the sample at -100°C, while no crystallization peak is observed in the cooling process (Fig. 5). The highly swollen membrane shows only one crystallization peak upon cooling in DSC, and two melting peaks upon heating from -100°C.

A more detailed study of differently swollen PVA membranes under various cooling/heating procedures led us to conclude that the crystallization of

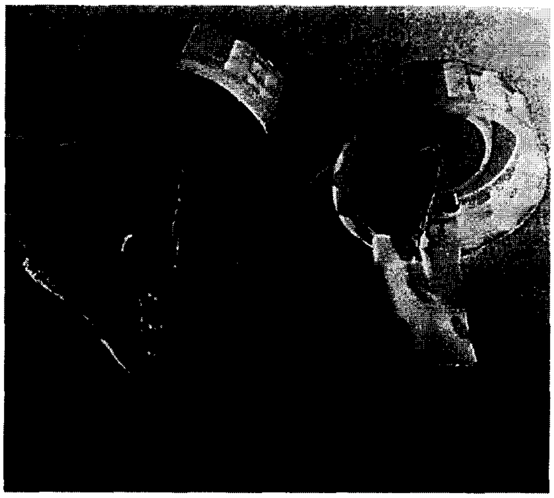

Fig. 3. Photographs of a dry PVAc film (left) and a water swollen PVAc film (right). Crystal-clear film on the left: dry film cluster. Paper-white film on the right: film with water clusters; the film thinner part (top right corner) appears more translucent due to partial evaporation during sample preparation for photography.

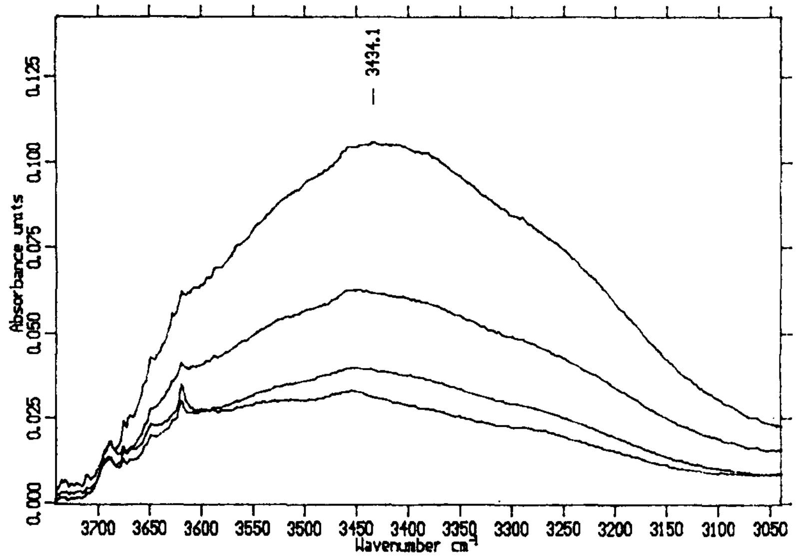

Fig. 4. IR spectra of a PVAc film in transmission mode at different immersion times in water at 25°C. Increasing IR absorbances correspond to increasing times.

water inside PVA membranes involves two steps [12]. The ice nucleus formation requires a sufficiently low temperature compared with the crystallization temperature (for the present cases, -100°C is a low enough temperature). The crystal growth must be fast compared with the temperature scanning for a phase transition peak to be observed. When a swollen membrane is cooled down in the present case, the water molecules which are under the interaction field of hydrophilic sites (hydroxyl groups) through the first layer of non-freezable bound water have their crystallization temperature depressed and would not have enough time to form nuclei and subsequently grow into ice crystal in any appreciable amount during certain cooling processes.

The procedure which involves a heating process

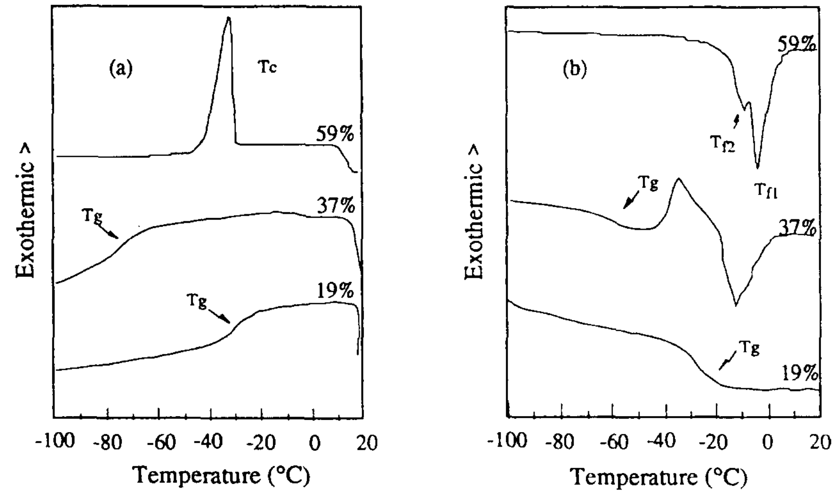

Fig. 5. DSC thermograms of PVA films of different swelling degrees (in wt% on DSC curves). In cooling mode (left) and in reheating mode after quenching at −100°C (right). Temperature change rate: 10°C/min.

after a quench at low temperature to allow the nucleation process to take place appears to us more appropriate for the study of water states by DSC. The fraction of freezable water which did not crystallize under conditions of stable crystal formation in the cooling step, will crystallize in the heating step from low temperatures; its amount can be calculated from the exothermic peak area. The water crystal will melt at a temperature lower than the normal melting point of free ice (ca. 0°C) if it is under the state of "freezable bound water" and will melt at the normal melting point if it is under the state of "liquid-like water" [13]. Provided that the two steps of crystallization of the freezable water are allowed to proceed, the melting peaks as well as the melting energy evolved during heating were reproducibly obtained in DSC. This fact suggests that the observed melting peaks corresponds to populations of water molecules whose thermodynamic/dynamic properties in the membrane are defined.

FTIR data obtained with PVA membranes of different water contents make complete the DSC ones: IR spectroscopy gives information on groups in direct interactions, while DSC does not. Due to the overlapping of OH bands from PVA with those from water, only a shift of the broad stretching band maximum from 3275 to 3370 cm^{-1} when the swelling degree increases to a large extent. Substraction of spectra of swollen membranes to the dry membrane spectrum gives rise to two peaks, assigned to water OH stretching vibrations, which are centered at 3280 and 3400 cm^{-1} (Fig. 6). As the membrane water content increases, the two peaks increases but not in the same proportion. The preponderant peak at low water content (3280 cm^{-1}) which corresponds to strongly hydrogen-bound water grows more slowly with increasing water contents than the high frequency peak (Fig. 6); the latter which corresponds to less powerful H-bonds is centered at the same frequency as that of liquid water. These results indicate that at low water contents water molecules are strongly bound to PVA hydroxyl sites. As the water content increases, a second population of less strongly bound water molecules becomes larger and larger due to the saturation of polymer hydrophilic sites; the subsequently sorbed water molecules are then less affected by the hydrophilic sites and tend to have similar hydrogen-bonds as those in liquid water. As expected, IR spectroscopy did not enable us to observe freezable bound water and liquid-like water separately. The detection of two distinct water-related bands whose frequencies do not change significantly with the water content is of major interest: this means that water molecules at room temperature exist in the material at least under two forms characterized by their respective specific environment.

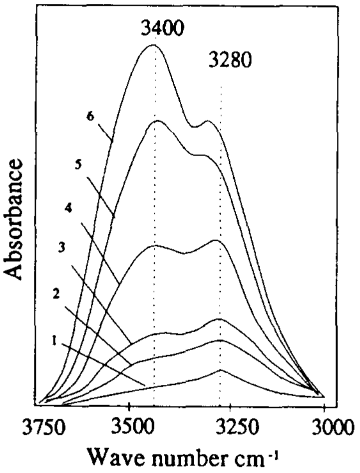

Fig. 6. IR spectra in ATR mode of 100% hydrolysed PVA membranes of different swelling degrees (1: 4.2, 2: 6.3, 3: 10.2, 4: 19, 5: 40, 6: 59% by weight). The spectra were obtained by subtraction of that of the swollen membrane from that of the dry membrane.

Wide angle X-ray scattering experiments performed on a sample first swollen in water at different sub-zero temperature confirm the existence of two types of freezable water, one corresponding to water crystals scattering at 23° and the other to those scattering at 25° (Fig. 7). Referring to the scattering pattern of pure ice at -30°C in which only one peak at 23° is detected, we assigned the 23° peak to the liquid-like water in PVA, and the other peak to freezable bound water. The area of the 25° peak is first constant when the membrane conditioning temperature increases, then decreases to zero at -2°C while that of the 23° peak is still large. Such features are qualitatively consistent with the interpretation based on DSC data, i.e. there exist two distinct types of frozen water with different melting points.

Direct evidence of clusters in the swollen PVA membrane at room temperature by visual opacity

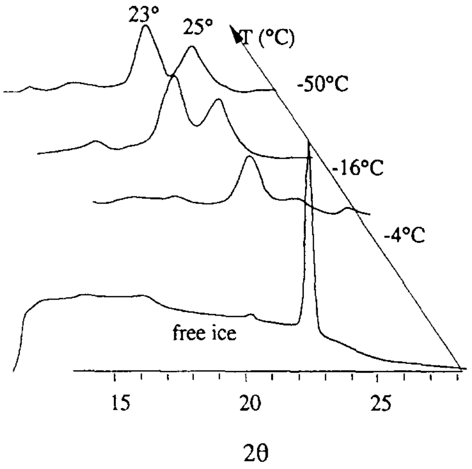

Fig. 7. Wide angle X-ray scattering patterns of PVA membranes equilibrated with water at 30°C and examined at different sub-zero temperatures. The X-ray pattern of pure water ice is given for comparison.

observation was not possible with the fully hydrolysed PVA sample. However, the fact that opacity aspect was observed in water-swollen membranes made of PVA of higher acetyl contents (5 and 12 mol% acetyl) crosslinked by glutaraldehyde (Fig. 8) suggests that the non-appearance of opacity under visible light may be due to cluster size which is smaller than the light wavelengths. Presumably, the size of water clusters is more limited by semi-crystalline regions which are more numerous in the fully hydrolysed PVA.

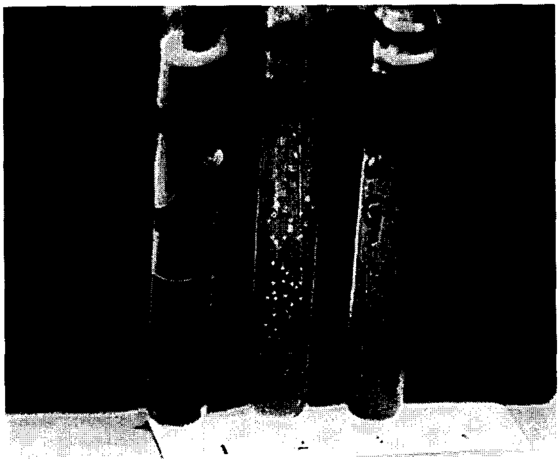

Fig. 8. Photographs of crosslinked (with 3 wt% glutaraldehyde) PVA of different hydrolysis degrees equilibrated in water. Left-side test tube: transparent sample of PVA of 100% hydrolysis degree. Middle test tube: translucent sample of PVA of 95% hydrolysis degree. Right-side test tube: quasi-opaque sample of PVA of 88% hydrolysis degree.

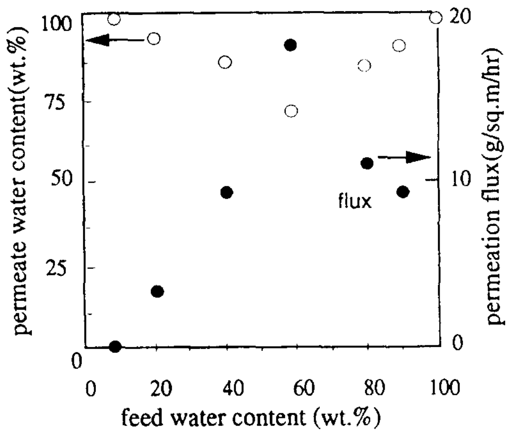

Fig. 9. Permeate water content versus feed water content in the pervaporation of water–ethanol mixtures at 30°C through a fully hydrolysed PVA membrane.

The membrane was used for the pervaporation of water-ethanol mixtures. A change in the membrane behavior seems to occur at ca. 10 wt% water in the feed mixture (Fig. 9): the permeate water content decreases from this water content and the permeation flux starts to increase significantly. The study of such ternary systems (water-ethanol-PVA) with the mentioned techniques is very difficult due to the very low ethanol melting point, and the large number of species issued from cross-interactions between the three components and their aggregates. We speculate that the decrease in selectivity as well as the increase in the flux was caused by the formation of solvent cluster when the water content reaches a threshold water content in ethanol. The change in the mean diffusion coefficient with the feed composition, measured by differential permeation, also indicate a change in the membrane behavior, i.e. an increase in both water and ethanol diffusivity with the water content at ca. 10 wt% water (Fig. 10). Solvent clusters seem therefore to favor the diffusion of both species.

3.3. Water-polydimethylsiloxane (PDMS)

The water sorption in PDMS was very weak (less than 0.2 wt% at equilibrium in pure water). Due to

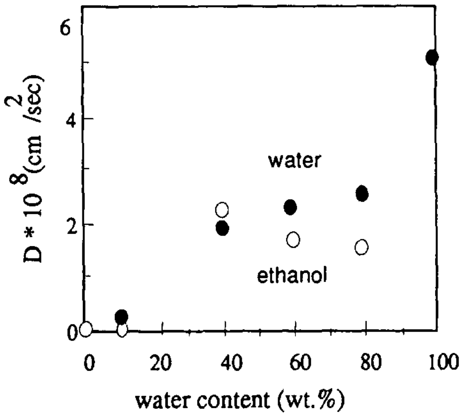

Fig. 10. Variation of mean diffusion coefficients (determined from differential permeation) of water (●) and ethanol (○) as a function of feed water content in the gas sweeping pervaporation at 30°C.

the low water level in PDMS, we failed to detect ice formation in the DSC study or water hydrogen bonding by IR spectroscopy. We tried to evidence the influence of an eventual water clustering on the variation of the sorption level as a function of water activity. The water sorption was determined by weighing 30 g. PDMS blocks equilibrated with a water bath whose activity in reduced by dissolving different amounts of Lithium Chloride. The small surface area-to-volume ratio of these large blocks ensures minimal error due to residual amount of surface solvent after blotting. The obtained sorption data are compared with Barrie and Machin's data [14] in Fig. 11. Good agreement between the two data sets is observed; our slightly higher sorption extents at low activities may be explained by the comparatively larger solution amount retained on the sample surface due to the higher viscosity of the more concentrated salt solutions. The sorption date cannot be accounted for by Flory-lattice model which holds for several PDMS-apolar solvent systems [5,15]: the sorption isotherm should be a straight line, according to the Flory model, for systems with low sorption like the water-PDMS one. The strong increase in the water sorption at high activity indicates water clustering inside the membrane. Polymer chain relaxation induced by water sorption or bond rupture seems to be unlikely in this case, as PDMS is a rubbery material and has no easily hydrolysable bonds in its chemical structure.

In spite of the low sorption level, clusters were made visible in PDMS by using 5 to 10 mm thick sample. Fig. 12 shows a clear opacity in thick PDMS sample equilibrated in water while a similar PDMS sample remains crystal clear in acetone, despite a much higher solvent content in PDMS in the latter case. Similar to the PVAc case, the transition from the opaque (cluster filled) polymer to a clear (dry or solvent swollen, but cluster-free) polymer was reversible. For instance, when the acetone-saturated PDMS sample is extracted with water, the sample ends up with the opaque aspect in pure water (Fig. 12). It appears to us that water, in spite of its very low average concentration in PDMS, tends to form liquid-like clusters. A rapid calculation shows that at the water concentration level in PDMS of 0.0018 cm^3/cm^3 of polymer, if all water molecules are present in uniform clusters of 500 nm size, 27 billion clusters will be randomly distributed in a one-centimeter PDMS cube. Such cluster density would lead to enough light scattering to turn opaque a transparent sample, as in the case shown in Fig. 12.

3.4. Alcohols in PDMS

Alcohols have also the ability to form multiple hydrogen-bonds through their hydroxyl groups and therefore to form clusters. However, there is so far no evidence of alcohols clusters in polymers, proba-

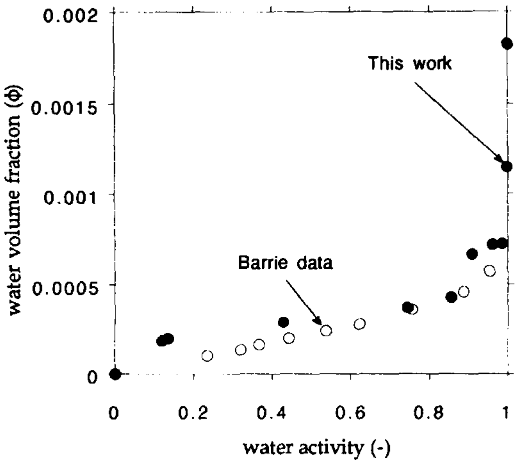

Fig. 11. Water sorption levels versus water activity in the external phase in equilibrium at 40°C with PDMS. Barrie and Machin data (○) and our data (●).

bly due to difficulties raised by small cluster size and number. We applied the same experimental techniques as before to PDMS-alcohol systems in an attempt to evidence alcohol clusters in polymers. DSC was not a suitable technique as the used DSC instruments cannot give reliable thermograms in the range of very low temperatures in which experiments should be carried out to detect small clusters of low melting point solvents.

Again, we tried to evidence alcohol clustering via its influence on the sorption isotherms in PDMS. Alcohol sorption isotherms have similar shapes as water sorption isotherm: the sorption levels are low at low activities but they increase sharply as the activity approaches unit value. Fig. 13 shows the ethanol and propanol sorption data and the calculated Flory isotherms when the interaction parameter was determined from the sorption equilibrium with pure liquid alcohols (unit activity). Although the alcohol sorption isotherms can be fitted with the Koningsveld-Kleinjtens equation in which the interaction parameter is a function of the permeation volume fraction [5], the use of three adjustable parameters in this equation makes difficult any physico-chemical interpretation. Nevertheless, the failure of the Flory lattice model to account for the alcohol sorption in

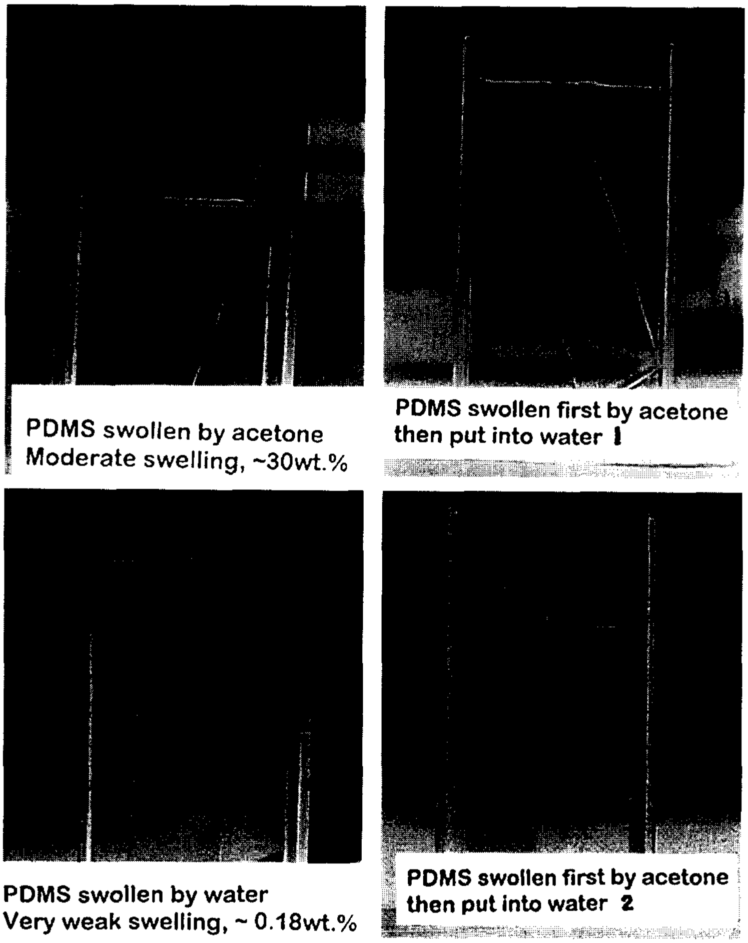

Fig. 12. Photographs of a thick PDMS sample at equilibrium in water. The crystal clear sample is still crystal clear after its swelling in acetone (top left). The acetone-swollen sample remains clear first when it is put into water (top right), but turns translucent after complete leaching of water by washing (bottom right). The originally crystal clear sample becomes opaque when it is equilibrated in water (for 3 weeks), in spite of its very weak swelling (bottom left).

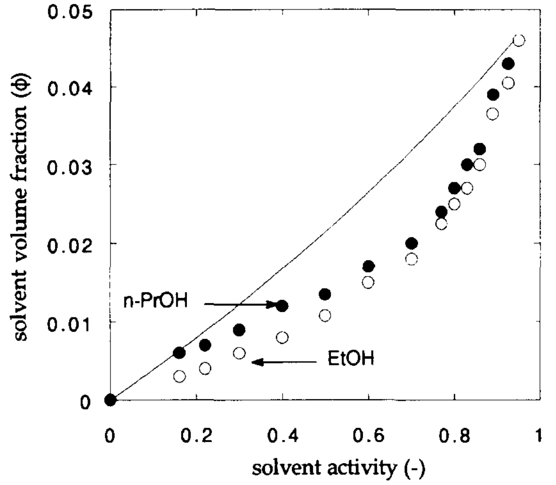

Fig. 13. Ethanol and 1-propanol volume fractions versus the alcohol activity in the vapor in equilibrium with PDMS at 80°C. Experimental points computed from those reported in [6]. Calculated curves by using the Flory model.

PDMS, while it holds well for non-polar solvent sorption in the same material [5], led us to conclude that one of the Flory's assumption, that of a random distribution of sorbed molecules under the effect of the same "mean interaction field" is no longer valid when solvent clustering occurs. A new model, the ENSIC (engaged species induced clustering) model, was derived to account for the dual possibility of solvent molecules to form solvent clusters and to interact with polymer sites. We showed that this simple, two-parameter model accounts correctly for the sorption behavior of a variety of species in diverse materials [16].

No opacity was observed in alcohol-saturated PDMS, even when thick PDMS samples were used. However, it should be noted that visible light scattering will not be observed when clusters are present but too small to scatter light. In order to observe visible light scattering, the clusters need to be enlarged. To do this, we added water to ethanol. The ethanol-saturated PDMS samples became opaque when 25 wt% water is added to the liquid ethanol. As water alone sorbs very little in PDMS due to the high hydrophobicity of the latter but has strong affinity to ethanol, one can expect that the added water goes preferentially into the small ethanol clusters and makes them large enough to scatter visible light.

When small amounts of ethanol were present in water, the opacity was observed in thinner samples than the one with which opacity was obtained with pure water. The higher the ethanol contents, the more opaque the polymer sample (Fig. 14). This observation suggests that ethanol molecules accentuate solvent clustering in PDMS.

FTIR spectroscopy results confirm undoubtedly the presence of ethanol and 1-propanol clusters in PDMS. When alcohol molecules are in the monomeric monomolecular state, e.g. when the alcohol is diluted in carbon tetrachloride, one major peak is observed at 3630 cm^{-1} (Figs. 15 and 16). When more alcohol is added to the non polar CCl_4 medium used as a reference system, the alcohol molecules tend to form clusters by intermolecular hydrogen bonding (peaks at 3350 cm^{-1}) (Fig. 15). In pure liquid, only one peak centered at 3320 cm^{-1} is found in alcohol spectra. Alcohol in PDMS gives rise to a broad band centered at the same frequency as clustered alcohol in CCl_4, i.e. 3350 cm^{-1}, without observable peak for monomeric alcohols at 3630 cm^{-1} (Figs. 15 and 16).

Influence of alcohol clustering on membrane transport properties.

In a previous study, we showed the water as well as alcohol permeation fluxes increased linearly with its activity on the upstream face, the downstream face being kept at practically nil vapor pressure [6]. When the solution-diffusion permeation model is applied to this case with the usual assumptions of an

Fig. 14. Photographs of PDMS samples equilibrated with ethanol aqueous solutions. The sample opacity increases from the left side to the right side, when the ethanol content (wt% ethanol content marked on the bottle) increases.

exponential dependence of the diffusion coefficient on the permeant concentration and fast sorption kinetics compared with the diffusion kinetics, a diffusion coefficient which decreases with the local solvent concentration was found. The overall mobility of the alcohol permeant appears then to be increasingly reduced with the increase in alcohol activity, i.e. with the mean cluster size [6].

3.5. General discussion

The results obtained with different polymer materials indicated that water can aggregate into clusters inside polymer membranes, even when they are known as hydrophilic membranes and are very efficient membranes for water extraction from organic media. The solvent aggregation in membranes under conditions similar to pervaporation/vapor permeation ones was undoubtedly shown with the help of IR spectroscopy experiments and direct visual observations, both carried out at room temperature. Therefore, interpretation problems like the ones which could be raised in DSC studies can be avoided. The latter studies had the advantage of giving amounts of water in different states. A close examination of the results reveals different situations depending on the nature of the polymer material and the sorption level.

In very hydrophobic polymers like PDMS, the sorption level is very low and water molecules readily form clusters in the rubbery material.

In less hydrophobic polymers like PVAc which sorb moderately water, part of sorbed molecules is bound to polar sites and becomes non freezable and the other part is liquid-like water.

In hydrophilic polymers like PVA which can sorb large water amounts, the states of sorbed water change with the sorption level. At low sorption, the sorbed species are bound to hydrophilic sites under the non-freezable state until all accessible sites are saturated. The subsequent sorbed molecules are then more loosely bound to the hydrated sites but they are still sufficiently perturbed by the sites so that their crystallization is more difficult. At high sorption level, the added molecules will experience negligible influence of the hydrophilic sites and behaves as bulk water.

Organic solvents like alcohols can also form clusters in materials which dislike such protic solvents.

A rationale of the solvent clustering in polymer membranes can be made from physico-chemical considerations of the solvent-polymer systems. From the thermodynamic viewpoint, clustering must lead to more stable systems. The clustering of solvent molecules reduces the interface area between solvent

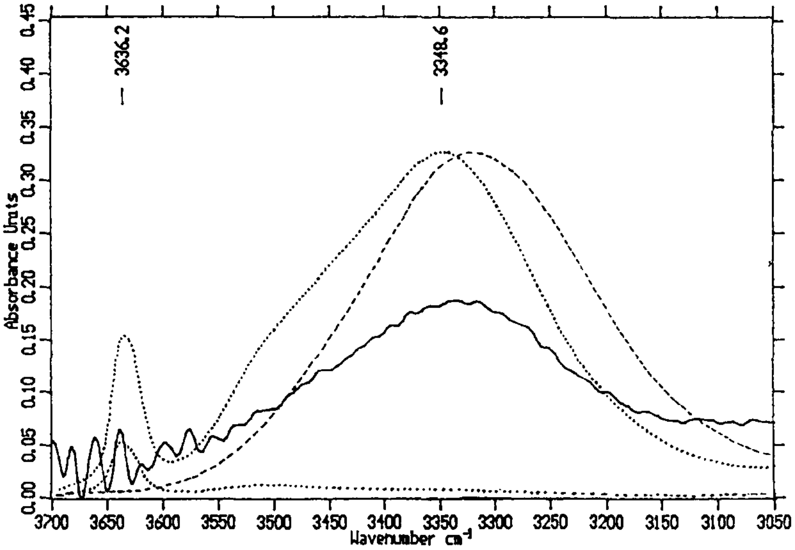

Fig. 15. IR spectra of 1-propanol diluted in CCl_4 (0.3 and 1.8 wt%, dotted lines) liquid propanol in ATR mode (dashed line) and propanol at saturation in PDMS.

molecules and polymer groups. It tends to happen to solvent species which "dislike" some groups in the material, but "like" each other; in this case, their aggregation satisfies their interaction potential (negative enthalpy change) while allowing a certain degree of random distribution (of clusters) and therefore an entropic gain (positive entropy change). Formation of clusters distributed over the entire material volume gives then rise to a more stable state than that of completely dispersed solvent molecules.

It should be noted that such a situation is not predicted in "mean field" approach, e.g. in the Flory approach. As only a mean interaction between the solvent and the polymer is considered, the less attractive the interaction, the fewer the solvent molecules (randomly) distributed in the polymer material. In contrast with this, clustering results first from strong interactions between solvent molecules compared with those between the polymer sites and solvent molecules and secondly from the entropic gain obtainable through the higher "disorder" in the system due to solvent distribution. It can occur in liquid media (e.g. the reported propanol/CCl_4 case) as well as in polymer media. The cluster size is not only determined by the balance between the solvent-solvent, polymer-solvent interactions and interfacial energy on one hand and the entropic gain from the dispersion on the other hand, but also on elastic energy. This is the work involved in cluster growth to overcome the elastic constraints set by the polymer network. The elastic resistance increases with the cluster size; chemical or physical cross-link points would strongly restrict the cluster growth when the biggest size allowable by the crosslink-blocked chains is reached. Some theoretical approaches have been attempted to evaluate this type of contributions [17].

From the above fundamental considerations, most observed features can be rationalized. Water cluster size would be more limited in fully hydrolysed PVA than in partially hydrolysed PVA or in amorphous PVAc due to the presence of numerous crystallites; this explains the non-observation of opacity in the first polymer, the fair opacity in the second polymers, and the high opacity in the last polymer which is also the most hydrophobic material. Stronger interaction field from hydroxyl sites made possible the formation of perturbed freezable bound water clusters in PVA but not in PVAc, whose polar sites are less hydrophilic. The existence of similar freezable-bound water clusters in ionomer membranes [18] is probably due to the strong interaction field from

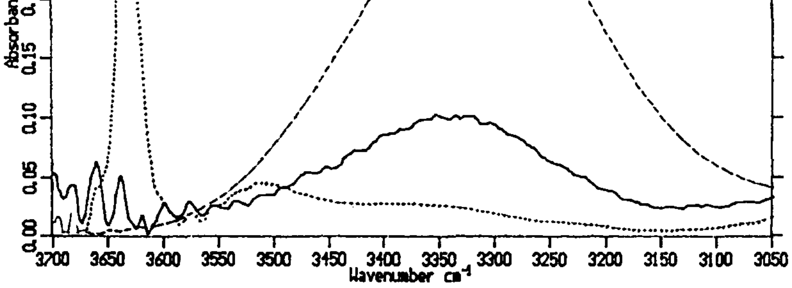

Fig. 16. IR spectra of ethanol diluted in CCl_4 (0.22 wt%, dotted line) liquid ethanol in ATR mode (dashed line) and ethanol at saturation in PDMS (solid line).

ionic sites. At the other end, the completely hydrophobic PDMS must have only bulk water clusters, despite the very low sorption level. Schematically, the higher the hydrophobicity, the lower the water sorption level and the stronger the water clustering tendency. In agreement with this, we showed that for alcohols, the stronger the hydrogen-bound ability, the stronger their tendency to form clusters, i.e. the larger the increase in the mean cluster size at activites close to 1 [6]. The assumption of alcohol cluster formation made previously is then confirmed by the present work. It should be noted that the cluster formation may be induced by "nuclei" (like impurities [19]) in the polymer material. However, the presence of impurities would not be a pre-requisite for the formation of clusters. Conversely, clusters can be formed in the absence of impurities in the material. Indeed, the same membrane sample behaved differently depending on the solvent medium with which it is in contact: it turned opaque in water but remains crystal clear in aprotic solvents, like acetone, chloroform or toluene.

The key point concerns the influence of cluster formation and characteristics on the membrane permeation properties. This is a very complex problem if we consider both the thermodynamic and the kinetic aspects. In steady-state permeation, there is a gradient in the permeant content in the membrane section. If we assume that there is a local equilibrium between different states of the permeant as generally admitted, then the equilibria between species as a function of their overall concentration need to be known. Further, the permeation flux of a species is determined by the mobility of the species in different states, as well as their population. The problem becomes even more complex with permeant mixtures. For instance, the two-parameter ENSIC model proposed for the sorption equilibrium of one penetrant in a homogenous polymer will require six parameters to describe a two-penetrant sorption with cross-interactions.

So far, we have tried to know how the clustering phenomenon may affect the permeant sorption and the diffusion. The preliminary results indicate two possible effects due to the presence of the cluster. One effect is the decrease in the mean diffusion coefficient which results in a much smaller flux at high permeant activities than that expected from constant diffusivity. Such an effect was observed in pure alcohol permeation [6]. The other effect is an increase in the mean diffusion coefficient with increasing activities, probably due to an increase in polymer segmental mobility. Indeed, a plasticization effect of water on the glassy PVA (or PVAc) was evidenced in DSC. For PVAc, the glass transition temperature (T_g) was shifted ca. 10°C downward, from ca. 30°C for dry PVAc (Fig. 1). The T_g can be much depressed when more water is sorbed. In the example shown in Fig. 5, PVA T_g decreases from 80°C (dry PVA) to -25°C at 19% water sorption and -60°C at 37% water sorption.

In conclusion, clustering of penetrant molecules in a dense polymer membrane is not limited to water and hydrophobic membranes. As we showed that alcohol clustering can occur in a PDMS membrane, as well as water clustering in hydrophilic membranes, the phenomenon may be general. It would occur whenever penetrant molecules exhibit strong affinity with each other (in comparison with penetrant-polymer affinity), and the polymer network elasticity allows local volume expansion. When it happens, both sorption, diffusion and permeation properties would be affected. However, much more work is required to elucidate its effect on membrane properties.

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