Pervaporation of water–ethanol mixtures with polyacrylate-grafted polyethylene acid (PE-g-AA) membranes
Physico-chemical analysis of the transport mechanism

Z.H. Ping a,∗, Q.T. Nguyen b, S.M. Chen a, Y.D. Ding a

a Department of Macromolecular Science, LMEP, Fudan University, Shanghai 200433, PR China
b Laboratoire “Polymères, Biopolymères, Membranes”, UMR 6522, CNRS-Université de Rouen, 76821 Mont-Saint-Aignan Cedex, France

Received 21 January 2001; accepted 1 May 2001

Abstract
Polyacrylate-grafted polyethylene (PE-g-AA) membranes were studied in pervaporation. The membrane performances are improved by an increase in the acrylic grafting ratio. The water and ethanol sorption and diffusion properties in the membrane loaded with different counter-ions, as well as the interactions between the solvent and the membrane ion pairs, were measured. The results show that the ion pairs are preferentially solvated by water, and the water content in the liquid mixture at which the ion pair is dissociated is much smaller for the potassium membrane than for the lithium membrane. The easier dissociation of the K carboxylate ion pair in the water–ethanol mixture explains the increase in the permeability according to the sequence Li+ < Na+ < K+. The apparent contradiction between the sulfonate and the carboxylate membranes with regards to the alkaline cation sequence according to which the permeability changes is explained by the difference in the ionization ability of the sulfonate and carboxylate ion pairs. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polyacrylate-grafted polyethylene; Membrane separation; Water; Ethanol; Interaction energy

1. Introduction
In the past decade, much progress has been made in the understanding and the description of solvent sorption and transport processes in pervaporation using the solution-diffusion model [1–3]. However, there have been much less research devoted to the relationships between the membrane chemical and physical structures and the pervaporation properties. This can be explained by the fact that the molecular mechanism of permeation of solvent mixtures is very complex due to the continuous change in the interactions between different chemical groups of the membrane materials and the solvent molecules coming from the liquid mixture.

Roizard et al. [4] and Jonquieres et al. [5] reported relationships between the chemical structures and the pervaporation properties of membranes made of polymers whose chemical structures were progressively changed. Without such a control of the membrane structures, it seems that the establishment of the molecular mechanism of pervaporation is very difficult. Moreover, the relationships are only valid for specific membrane material–solvents systems.

Dehydration by pervaporation has become an important industrial application of pervaporation. Two types of hydrophilic membranes have been used, poly(vinyl alcohol)-based membranes, and ionic
membranes. The latter perform well in the dehydration of organic solvents, they also show features which are interesting from the fundamental viewpoint, their pervaporation performances can be altered by loading the same membrane with different counterions [6]. Among the ionic membranes, polyacrylate membranes seem to be the most interesting due to their high flux and selectivity towards water in water-alcohol mixtures. Composite pervaporation membranes with a dense layer made by deposition of a polyacrylic acid layer onto a porous support was once manufactured by Kalsep Ltd. (UK). Nevertheless, these membranes would cause some problems in industrial operations, since polyacrylates can be dissolved by water and water rich-organic mixtures. Thus, the active layer can be attacked in accidental water overshoots in the feed stream. Such a drawback can be avoided by preparing films, which can be obtained by irradiation-induced grafting of polyacrylates onto semi-crystalline polymer films, such as polyethylene, polypropylene, polytetrafluoroethylene, or their copolymer films. These films provide a good mechanical support for the chemically grafted active polymers for pervaporation [7,8]. The nature and the grafting ratio can be easily monitored in the irradiation-induced grafting method [8].

The pervaporation properties of different ionomer membranes were already reported by several authors [8–10]. The first part of the present paper deals with the preparation of different membranes with polyacrylate grafts and the study of the transport of water and ethanol in pervaporation through the membranes. In order to establish structure-property relationships, we focus our attention in the second part on the structure and properties of water molecules in the specific environment of the acrylate-grafted membranes. Different techniques (infrared spectroscopy, calorimetry, microgravimetry, differential permeation) were used for this purpose.

2. Experimental

2.1. Materials

The standard polyacrylate-grafted polyethylene (PE-g-AA) membrane was kindly provided by Morgan Ltd. Its total ion-exchange capacity was ca. 3 eq/kg and its acrylic grafting ratio was about 50%. The grafting ratio is defined as the ratio of the weight of grafted chains to that of the initial film. The dry thickness of this membrane in Na\(^+\) acrylate form was 35 μm.

The other grafted membranes were prepared by post-grafting of acrylic acid onto pre-irradiated PE, FEP and Tefzel films. FEP is the common name of tetrafluoroethylene-hexafluoropropene copolymer. Tefzel is the trade name of tetrafluoroethylene-ethylene copolymer. The pre-irradiated films were prepared by irradiating the base-film in air with an electron beam in different conditions (different energies and electron impact densities on the film). The irradiation in air leads to the formation of hydroperoxide or peroxide on the polymer chains [11]. Although there may be a decrease in the number of peroxide sites formed in the semi-crystalline films, the pre-irradiated films can be stored over several weeks without loosing significantly their grafting ability. The grafting was performed according to known procedures [12]. Typically, the pre-irradiated film is put in a reactor containing a degassed solution of monomer (e.g. acrylic acid) and the graft polymerization is carried out under a nitrogen atmosphere with the Fenton system (ferrous sulfate and hydrogen peroxide) as the polymerization initiator. Depending on pre-irradiated film nature, the monomer concentration, the reaction temperature and time, films of different grafting ratio were obtained.

2.2. Sample preparation

To obtain the acid form of a PE-g-AA membrane sample, the sample is treated with HCl solution, then thoroughly washed with distilled water. The alkaline acrylate membranes were prepared by titration of the membrane in acid form with an appropriate alkaline aqueous solution, followed by the washing and vacuum drying steps.

The dried membrane samples were stored in a desiccator over 4A molecular sieve until their use.

2.3. Sorption enthalpy determination

The sorption heat measurements were carried out with the help of Dr. Escoubes (Macromolecular Materials Lab, CNRS-Claude Bernard University, Lyon, France) using a calorimeter coupled with a
The membrane sample was first thoroughly dried under high vacuum (10^{-5} torr), until a constant weight was observed in the microbalance. The membrane weight gains \( \Delta M \) at different activities \( P/P_0 \) of ethanol or water vapor were next recorded and used to determine the membrane water sorption isotherm. The total heat quantity released by the vapor sorption at each increment of vapor pressure was parallely measured. The molar sorption enthalpy, which is negative, is calculated by bringing back the energy to the number of moles of vapor absorbed for the vapor pressure increment. The precision of such a molar sorption enthalpy determination is ca. \( \pm 10\% \). The rather poor precision is due to a low quantity a low rate of heat released, and the cumulative errors of weight and heat determination.

2.4. Conductivity measurement

The electrical conductivity of solutions of dry alkaline-metal acetates in anhydrous ethanol (dried with 4A molecular sieve) of different compositions was measured with a conventional conductimeter (Metrohm, Switzerland) at a frequency of 2 kHz. The electrode used in this study appeared to be quite stable in pure ethanol and the same calibration constant was found after the measurements. The equivalent conductivity was calculated according to the following equation:

\[
\Lambda = 1000 \times Kc^{-1}
\]

where \( K \) is the conductivity (S cm\(^{-1} \)) measured at the concentration \( c \) (equiv l\(^{-1} \)) and \( \Lambda \) measured in (S equiv cm\(^{-1} \) l\(^{-1} \)).

The relative ionization degree of the salt at a concentration \( c \) was taken as \( \Lambda/\Lambda_0 \), where \( \Lambda_0 \) is the limit equivalent conductivity obtained by extrapolation to a nil concentration of the plot of \( \Lambda \) versus \( c^{0.5} \). 

2.5. Diffusion coefficient determination

The diffusion coefficients of water and ethanol were determined by differential permeation. The principle of the technique was reported in a previous paper [13]. Briefly, the experimental set-up consists of a stirred tank containing the feed liquid, a precise moisture sensor (Shaw Ltd., UK) an flame ionization detector (FID) and a personal computer equipped with an analog-signal acquisition board. Such a set-up allowed us to monitor in time simultaneously the transient permeation rates of both water and the organic compound, when a sweeping-gas permeation cell equipped with the membrane sample is put into the feed liquid. In the present study, the feed liquid is the water-ethanol mixture of 10 wt.% water content kept at 25°C.

The average diffusion coefficient of a solvent through the membrane was obtained by the best fitting of the transient flux curve with the Barrer equation

\[
\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n + 1)^2\pi^2} \exp \left[-\frac{D(2n + 1)^2\pi^2 t}{4L^2}\right]
\]

2.6. IR measurements

The membrane sample was first equilibrated with the atmosphere in a sealed vial at a constant humidity degree over a salt solution whose activity is known from the literature. FTIR spectra were recorded on a Bruker IFS25 spectrophotometer. The equilibrated sample was quickly mounted in a dry confined atmosphere onto a ZnSe crystal of an attenuated total reflectance (ATR) device. For a study of the influence of the sorption of a water-ethanol mixture on the IR spectrum, the membrane sample was first conditioned in the liquid mixture until the sorption equilibrium is reached, and the sample was carefully blotted with paper tissue before mounting. A sheet of elastomer was firmly pressed on the back of the film in the ATR device during the experiment to prevent the solvent loss by evaporation. The incident beam angle was maintained at 45°. At least 256 scans were performed for each measurement. The resolution in wavelength was 2 cm\(^{-1} \). For a convenient presentation, all the obtained spectra were brought back to the same level by using the 1425 cm\(^{-1} \) band (CH\(_2\) vibration band) as the reference band. As no quantitative analysis is intended, this procedure has no influence on our interpretation.

2.7. Determination of pervaporation characteristics

A classical vacuum-pervaporation set-up was used. The flux was obtained from the permeate weight, and
the permeate composition was determined by gas chromatography.

3. Results and discussion

3.1. Flux and selectivity of the standard membrane loaded with different counter-ions

The influence of the alkaline counter-ions on the membrane characteristics was reported in a previous paper [10]. The interesting feature reported was the absence of the trade-off between selectivity and permeability that is usually observed with membranes made of different materials. Increasing selectivity and permeability were obtained with the following sequence of alkaline counter-ions, \( \text{Li}^+ < \text{Na}^+ < \text{K}^+ \).

It should be noted that the sequence for the selectivity of ionic membranes bearing sulfonate groups to the same mixture is the reverse of that for the permeability, which is \( \text{Li}^+ > \text{Na}^+ > \text{K}^+ \) [6,9,14]. The change in the sulfonate membrane characteristics with the counter-ion nature was well interpreted on the basis of the change in the ion pair hydration. For the carboxylate membranes, the interpretation has not yet been founded on experimental facts.

In the present work, we extend the study of the pervaporation characteristics to the membrane loaded with organic quaternary-ammonium ions. Fig. 1a and b show similar patterns for the organic cations as those for alkaline cations reported in [11]. The flux sequence is the same as the selectivity for the organic cations, i.e. Me\(\text{NH}_3^+ < \text{Me}_2\text{NH}_2^+ < \text{Me}_3\text{NH}^+ < \text{Me}_4\text{N} \). In this representation, Me stands for the methyl group, and the positive charge on the nitrogen atoms is omitted for simplicity. Yoshida and Miura [15] reported the reverse sequence for the permeability of the Nafion membrane whose sulfonic acid groups were neutralized by the same organic quaternary-ammonium ions. They proposed that the variation in the permeability with the counter-ion nature is related to the size of the hydrated quaternary-ammonium ions.

We observe again no trade-off between selectivity and permeability. The absence of trade-off between selectivity and permeability is thus a characteristic feature of membranes bearing carboxylate groups. It is worth noticing that the above sequence is that of basicity of the conjugated bases of the organic counter-ions [16]. One can infer from these sequences that the stronger the conjugated base of the organic counter-ion, the greater the flux and the selectivity of the membrane loaded with the counter-ion. It seems that the basicity of the conjugated base of the counter-ion is the key parameter which determines the pervaporation characteristics of the weak acid.
membrane, whatever the nature of the counter-ion, the stronger the basicity, the larger the carboxylate-salt ionization, and the better the membrane.

3.2. Conductivity study of the model ion pairs in pure ethanol

The ionization degree of the membrane carboxylate groups in ethanol can not be directly measured with the methods designed for aqueous media. We measured the ionization degree in ethanol for acetate salts, which are used as model compounds for the membrane carboxylate groups. It was found that the ionization of acetate in pure ethanol is very low even at nil concentration, because the conductivity of above salts in water is 10 times higher than in pure ethanol. For the convenience of calculation, we calculated the relative ionization degree of the salts to compare the ionization ability of two salts in pure ethanol.

Fig. 2 shows that the relative ionization degree in ethanol is higher for the potassium salt than for the lithium one. This result confirms the interpretation of the better flux and selectivity based on the larger ionization degree of potassium carboxylate compared with that of the lithium one, which was inferred from the results obtained with the organic counter-ions.

![Fig. 2. Relative Ionization degree of potassium and lithium acetates vs. square root of the salt concentration in pure ethanol.](image)

3.3. Water and ethanol diffusion and sorption properties of the membranes loaded with different alkaline metal ions

The standard membrane loaded with K⁺ shows higher water sorption than the Li⁺ one in the 0–1 activity range (Fig. 3). The ethanol sorption in both the K⁺ and Li⁺ membranes is much smaller than
that of water sorption, the amount of solvent sorbed at the 0.9 activity value is 50 times larger for water than for pure ethanol (Fig. 3). These data indicate the much larger affinity of the membranes to water than to ethanol. The greater ability of the K\(^+\) loaded membrane to absorb water compared with Li\(^+\) one is also consistent with the higher permeability of the former in pervaporation.

Fig. 4a and b show the variations, as a function of the reciprocal Kelvin temperature, of the diffusion coefficient of water and ethanol in the membranes loaded with different alkaline metal ions. The water diffusion coefficients in all membranes are higher for water than for ethanol and increase with temperature according to an Arrhenius-like relationship (Fig. 4). The values of the diffusion activation energy are higher for ethanol than for water (Table 1). They vary with the nature of the counter-ion according to the sequence Li\(^+\) > Na\(^+\) > K\(^+\). These data are consistent with the variation in flux and selectivity previously reported [10]. The very low values of the activation energy for water and ethanol diffusion in the K\(^+\) loaded membrane compared with the Li\(^+\) and Na\(^+\) loaded membranes (Table 1) are surprising. We suggest that the number of ionized carboxylate groups in the K\(^+\) loaded membrane is large enough so that the solvated ionic groups are in close contact on the diffusion pathway, making the site-to-site diffusion jumps very easy (i.e. no significant polymer chain movement required).

### 3.4. Influence of the PE-g-AA grafting ratio

Table 2 shows that the increase in the grafting ratio leads to an increase in the selectivity. The flux data are difficult to interpret, they vary significantly with the irradiation (and grafting) conditions, even when the membranes have similar grafting ratios (Table 2). Such behaviors are observed for the membrane series based

### Table 1

<table>
<thead>
<tr>
<th>Membrane counter-ion</th>
<th>Water diffusion activation energy (kcal mol(^{-1}))</th>
<th>Ethanol diffusion activation energy (kcal mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^+)</td>
<td>27.6</td>
<td>39.3</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>26.3</td>
<td>30.9</td>
</tr>
<tr>
<td>K(^+)</td>
<td>5.9</td>
<td>8.4</td>
</tr>
</tbody>
</table>
Table 2

<table>
<thead>
<tr>
<th>Base-films differently irradiated</th>
<th>Grafting ratio (%)</th>
<th>Permeation flux (kg h⁻¹ m⁻²)</th>
<th>Permeate water content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE 50</td>
<td>0.15</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>PE 100</td>
<td>0.14</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>PE 110</td>
<td>0.52</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>PE 130</td>
<td>0.66</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>PE 160</td>
<td>1.5</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>PE 440</td>
<td>0.38</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>Tefzel 70</td>
<td>0.46</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>Tefzel 100</td>
<td>0.46</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>Tefzel 140</td>
<td>0.28</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>Tefzel 230</td>
<td>0.40</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>FEP 40</td>
<td>0.76</td>
<td>31</td>
<td></td>
</tr>
</tbody>
</table>

The peculiar behavior of FEP membranes can be explained by its elastomer nature (non-crystalline) which makes the grafting ratio limited, and the membrane swelling large. It should be noted that the flux data in Table 2 were normalized to a membrane thickness of 35 μm. The membranes having a grafting ratio >100% were generally fragile in their swollen state and thicker starting PE films had to be used.

The improvement in the membrane performances with the grafting ratio suggests that the graft phase plays the key role in the solvent permeation. However, a precise relationship between the membrane structure and their performances cannot be drawn. This is due to the fact that even when the nature of the graft and the starting film are the same, the fine structure of the obtained membranes may differ significantly in terms of graft average length and density, and in terms of crosslinking degrees of both the base film and the graft phase. The crosslinking of the graft phase and that of the base polymer are caused by the coupling reaction between two macro-radicals, the former in the grafting step and the latter in the pre-irradiation step. The permeation flux depends greatly on the membrane swelling, i.e. on the crosslink density and distribution. Unfortunately, the latter parameters are very difficult to measure. We speculate that a high flux is observed in the case of low crosslinking of the membrane.

3.5. IR study of the solvation of the membrane ion pairs

The ion-solvent interactions are the parameters that control the ionomer membrane selectivity. IR spectroscopy was successfully used for the elucidation of the interactions between solvents and the ion pair of membranes bearing sulfonate groups [17–19]. With regards to the ion-solvent interactions, the main difference between a sulfonate membrane and a carboxylate one is the dissociation (ionization) ability of the ion pairs. The latter depends on both the ion pair nature and the polarity of the solvent medium.

The ion pair of an alkaline metal ion and a carboxylate anion has a lower dissociation ability than that with a sulfonate ion due to the weak-acid nature of the carboxylic acid. Both the ion pair and the dissociated ions have the ability to attract solvent molecules, but the dissociated ions always have larger solvation ability than the corresponding ion pair. However, the situation is much more complex when an ionomer membrane is put in a solvent mixture due to the preferential interaction between the components. Water is generally the preferred solvent for ions and ion pairs. The subsequent molecules attracted by the ions or ion pairs can be either water or the organic solvent.

3.6. Alkaline metal ion interactions with COO⁻ of the membrane in the dry state and in pure solvents

The constant frequency of the asymmetric band for the PE-g-AA membrane loaded with different alkaline
metal ions in the dry and solvated states (Table 3) indicates that the alkaline ion is symmetrically bound to carboxylate ion according to the formula

$$\left(\text{C}_n\text{O}^\nu\right)^{\text{M}^+}$$

The symmetric COO\(^{-}\) band wave number increases when the alkaline metal size decreases, i.e. when the electrostatic field of the metal ion increases. This also means that the electrostatic interactions increase when the counter-ion is changed in the series from K\(^+\) to Li\(^+\).

After sorption equilibrium with pure water, the COO\(^{-}\) symmetric band is shifted towards the same wave number (1406 cm\(^{-1}\)), while they are not significantly changed after equilibrium with pure ethanol. This behavior suggests that whatever the alkaline metal ion, the ion pair is completely dissociated in water, while it is not significantly affected by ethanol. The very low sorption of pure ethanol observed for these films would be the cause of the absence of influence of pure ethanol.

### 3.7. Solvation of alkaline metal carboxylate by water–ethanol mixtures of different compositions

The IR study was focused on the concentration range of the greatest interest in solvent dehydration, i.e. in the 0–20 wt.% water content in ethanol. As the change in the COO\(^{-}\) symmetric band frequency is obscured by the band at 1417 cm\(^{-1}\) due to ethanol CH\(_3\) group absorbance, we report here only the data on the COO\(^{-}\) asymmetric band.

The COOK asymmetric band centered at 1559 cm\(^{-1}\) in pure ethanol starts to have a shoulder at 1552 cm\(^{-1}\) when the water content in ethanol is as low as 2 wt.% (Fig. 5b). The intensity of the band at 1552 cm\(^{-1}\) increases as the water content increases to become stronger than that of the original band at 6 wt.% water in ethanol (Fig. 5b). The COOLi asymmetric band maximum does not change until the water content reaches 20 wt.% (Fig. 5a). The observed changes can be attributed to the hydration of the carboxylate groups. The observation of the change in intensities for the two COOK bands with the water content suggests that in the membrane, there are two changing populations of carboxylate groups, one with dissociated, hydrated groups, the other in the non-dissociated state.

We propose a new parameter to characterize the sensitiveness of the alkaline metal carboxylate to hydration in water–ethanol mixtures. The parameter, which can be called the inversion content, is defined as the water content at which the asymmetric vibration band of dissociated and hydrated COO\(^{-}\) prevails over the non-dissociated one, when the membranes are equilibrated with water–ethanol mixtures of different compositions.

Table 4 shows that the inversion content increases when the counter-ion changes from K\(^+\) to Li\(^+\), i.e. the COOK ion pairs undergoes ionization in the liquid mixture much more easily than the COOLi one. The increase in the selectivity to water in pervaporation when the counter-ion changes from Li\(^+\) to K\(^+\)

### Table 3

Characteristic wave numbers of the COO\(^{-}\) asymmetric and symmetric stretching vibration bands for the PE-g-AA ‘M\(^+\)’ membranes in the dry state, in pure ethanol, and in pure water

<table>
<thead>
<tr>
<th>Cation M(^+)</th>
<th>Asymmetric COO(^{-}) (cm(^{-1}))</th>
<th>Symmetric COO(^{-}) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry</td>
<td>Solvated by EtOH</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>1558</td>
<td>1559</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>1554</td>
<td>1559</td>
</tr>
<tr>
<td>K(^+)</td>
<td>1558</td>
<td>1559</td>
</tr>
</tbody>
</table>

### Table 4

Inversion content for the PE-g-AA ‘M\(^+\)’ membranes (water content at which the asymmetric vibration band of dissociated and hydrated COO\(^{-}\) prevails over the non-dissociated one in the sorption equilibrium with water–ethanol mixtures of different compositions)

<table>
<thead>
<tr>
<th>Carboxylate counter-ion</th>
<th>Li(^+)</th>
<th>Na(^+)</th>
<th>K(^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inversion content (wt.%)</td>
<td>20</td>
<td>10</td>
<td>6</td>
</tr>
</tbody>
</table>
thus corresponds with the increase in the preferential hydration of the ionic sites.

The increase in the intensity of the water deformation band according to the sequence \( \text{Li}^+ < \text{Na}^+ < \text{K}^+ \) (Fig. 6), when the membranes are in equilibrium with the same liquid mixture, indicates an increase in the sorbed water amount according to the same sequence. It also explains the same increase in the permeation flux (on the basis of the solution-diffusion model).

3.8. Thermodynamic properties of the solvents absorbed by the membranes loaded with different alkaline metal ions

Fig. 7 shows the variations of the heat of solvation of the potassium and the lithium loaded membranes by pure water and pure ethanol at 20°C as a function of the sorption extent. Here, the heat of solvation is the heat generated per mole of effectively sorbed solvent. The differences in the heat of solvation of the potassium and lithium loaded membranes are not quite significant if we take into account the precision of the heat determination from the independent gravimetric and calorimetric measurements.

In spite of the large differences in the amounts of sorbed water and ethanol for the same solvent activity (Figs. 3 and 7), the heats of solvation of the membranes per mole of sorbed water and ethanol are the same (Table 5). However, these behaviors are understandable, as each molecule of effectively sorbed solvent, whether it is water or ethanol, results from the same interaction, that between an OH group and
Fig. 7. Variations of the heat of solvation of K$^+$ and Li$^+$ loaded PE-g-AA membranes by water (a) and ethanol (b) at 20°C as a function of the sorption extent.

Fig. 7 also shows the value of the heat corresponding to the absorption of a water molecule in the second hydration layer. It is obtained from the second energy level after the transition in the heat generated by a mole of sorbed water from a high to a low value, when the sorption extent increases (Fig. 7). There is no second solvation layer for ethanol due to its limited sorption extent (Fig. 7). The difference in the values of the heat of hydration in the two layers (ca. 29.3 kJ/mol) represents the difference in interaction energy between a water molecule directed bound to the ionic site and that between a water molecule bound to a site via a directly bound water molecule. Note that the second-layer hydration energy, ca. 33.4–7.6 kJ/mol (Table 5), corresponds well to the energy of a strong hydrogen-bond, e.g. that between two favorably-oriented water molecules.

Table 5 also shows the value of the heat corresponding to the absorption of a water molecule in the second hydration layer. It is obtained from the second energy level after the transition in the heat generated by a mole of sorbed water from a high to a low value, when the sorption extent increases (Fig. 7). There is no second solvation layer for ethanol due to its limited sorption extent (Fig. 7). The difference in the values of the heat of hydration in the two layers (ca. 29.3 kJ/mol) represents the difference in interaction energy between a water molecule directed bound to the ionic site and that between a water molecule bound to a site via a directly bound water molecule. Note that the second-layer hydration energy, ca. 33.4–7.6 kJ/mol (Table 5), corresponds well to the energy of a strong hydrogen-bond, e.g. that between two favorably-oriented water molecules.

Table 5

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Counter-ions</th>
<th>Water</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K$^+$</td>
<td>Li$^+$</td>
<td>K$^+$</td>
</tr>
<tr>
<td>Solvation energy (1st layer) (kJ mol$^{-1}$)</td>
<td>62.7-75.2</td>
<td>58.5-66.8</td>
<td>62.7-47</td>
</tr>
<tr>
<td>Maximum $P/P_0$ value</td>
<td>0.5</td>
<td>0.75</td>
<td>&gt;0.75</td>
</tr>
<tr>
<td>Sorption extent at saturation limit (wt.%)</td>
<td>13</td>
<td>15</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Solvation energy (2nd layer) (kJ mol$^{-1}$)</td>
<td>33.4</td>
<td>37.6</td>
<td>33.4</td>
</tr>
<tr>
<td>Maximum $P/P_0$ value</td>
<td>&gt;0.5</td>
<td>&gt;0.75</td>
<td>&gt;0.5</td>
</tr>
<tr>
<td>Sorption range (wt.%)</td>
<td>12-55</td>
<td>15-45</td>
<td>12-55</td>
</tr>
</tbody>
</table>

The sorption extent at which the first hydration layer is saturated is ca. 14 wt.%. This saturation limit for the first hydration layer corresponds to ca. two water molecules per ion pair on the average for both the lithium and potassium counter ions. The sorption of a water molecule in the second layer occurs at a water activity which are much higher for the Lithium loaded membrane than for the potassium one (Table 5). This observation is consistent with the above-reported one.
3.9. On the difference in the behaviors of sulfonate and carboxylate membranes

It is interesting to compare the behavior of the PE-g-AA membrane loaded with different counter-ions to that of sulfonate membranes [14]. The main point to discuss about is the reverse sequence of loaded counter-ions for the permeation flux change, while it is the same for the selectivity. We postulate that for both membrane series, the transport of water and ethanol mainly occurs through the zones surrounding the ion pairs according to a solution-diffusion mechanism. For both series, the selectivity to water of the membranes is governed by the relative interaction power between the fixed anions, the counter-ion, and water. The selectivity sequence, \( \text{Li}^+ < \text{Na}^+ < \text{K}^+ \), is explained by the decrease in the fixed anion-alkaline cation attraction due to the increase in the cation size. Such a decrease in the anion-cation attraction makes the hydration and the dissociation of the ion pair easier according to this sequence. All the data obtained with both series were consistent with this interpretation.

With regards to the permeation flux, the reverse sequence (\( \text{Li}^+ > \text{Na}^+ > \text{K}^+ \)) observed for the sulfonate membrane was explained by the increase in the hydration number of the cation from \( \text{K}^+ \) to \( \text{Na}^+ \) and \( \text{Li}^+ \) [15,17–19]. As the sulfonate-alcaline ion pairs are easily dissociated, the feed mixture is in contact with dissociated ions from practically all the sites in the sulfonate membranes. The difference in total water content in the membrane (selectivity to water) is thus mainly due to the hydration of the cations, which follows the order \( \text{Li}^+ > \text{Na}^+ > \text{K}^+ \).

In fact, the increase in flux results from the increase in the amount of water (and ethanol) dissolved in the membrane [1]. As more water molecules are dissolved by the potassium PE-g-AA membrane than by the sodium or lithium one, the flux increases according to the \( \text{Li}^+ < \text{Na}^+ < \text{K}^+ \) sequence.

The main property which makes the difference in the flux sequence for the two series is the ionizability of the fixed anion. The conjugated sulfonic acid is much stronger than the carboxylic acid. As a result, sulfonate ion pairs are much more readily dissociated than carboxylate ones. According to Hara et al. [20] sulfonates are completely dissociated in hydrophilic media, so that the permeation transport through dissociated-ion zones in the sulfonate membranes, where the hydration of the alkaline ions prevails. We showed that the dissociation of carboxylate ion pairs is limited in water-ethanol mixtures. For a mixture with fixed composition, potassium carboxylate is more dissociated than Li- and Na-carboxylates, i.e. the proportion of dissociated ions will be the highest with \( \text{K}^+ \) (the lowest with \( \text{Li}^+ \)), leading to the highest total water sorption, thus the highest permeation flux, for the potassium membrane. This is also consistent with the intrinsic property of the bare alkaline ion: the smaller the bare cation, the greater its interaction with the fixed carboxylate, and the lower its hydration ability. Due to its limited dissociation in ethanol-rich media, the Li-carboxylate is not able to reach its maximum hydration number, contrary to the Li-sulfonate.

The situation is more complex when the fine structure of the membrane is changed. Ethanol molecules can penetrate into the region where there are already sorbed water, driven by the chemical potential difference. As the penetration of ethanol molecules will give rise to the film volume expansion, the sorption extent will also be controlled by the elastic resistance of the film to volume expansion. One can therefore, adjust the crosslinking extent to get the best compromise between permeability and selectivity for the target separation.

4. Conclusion

In the pervaporation of water-ethanol mixtures, the PE-g-AA membranes showed a different behavior from that of the Nafion sulfonate membrane. While the pervaporation selectivity of the PE-g-AA membranes changes with the nature of the fixed-charge counter-ion in a similar way as that for the sulfonate membrane (\( \text{Li}^+ > \text{Na}^+ > \text{K}^+ \)), the membrane permeation flux varies according to the reverse sequence. The data obtained from different physico-chemical studies allowed us to explain this behavior by an easier dissociation of the \( \text{K}^+ \) carboxylate ion pair in the water-ethanol mixture than that of the other counter-ions. All the sulfonate ion pairs are easily dissociated in the water-ethanol mixture, so that the Nafion membrane permeability increases with the absorbed water amount, with the hydration number of the cation.
The important role of the ion pair number also explains the improvement of the performances of the PE-g-AA membranes when the acrylic grafting ratio increases. However, the situation appears to be more complex when the fine structure of the membrane is changed. When the swelling of the membrane in the water–ethanol mixture is high enough due to the grafting ratio increase, ethanol molecules can penetrate into the region where there are already sorbed water, driven by the chemical potential difference. High performance membranes could be obtained by adjusting the crosslinking extent to get the best compromise between the permeability and selectivity characteristics for the target separation.

Acknowledgements

We would like to thank Mrs. Bozzi and Escoubes for their assistance and for fruitful discussion. Project 29774003 supported by National Natural Science Foundation of China and Key Laboratory of Molecular Engineering of Polymer of Ministry of Education of China.

References