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Transport Properties of Ion-Exchange Membranes During Pervaporation of Water-Alcohol Mixtures

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Abstract: Pervaporation properties of PESS ion-exchange membranes in contact with water-aliphatic alcohol mixtures were obtained. PESS ion-exchange membranes were prepared by chemical modification of the interpenetrating polymer network system polyethylene-poly(styrene-co-divinylbenzene). PESS membranes were loaded with different alkali metal ions as counterions. The obtained data showed that properties of PESS membranes depended strongly on the kind of counterions, degree of cross-linking, and difference in the polarities between water and organic component of the binary mixture. Results obtained for PESS membranes were compared with data obtained for Nafion 117 ion-exchange membrane.

Keywords: Pervaporation, PESS ion-exchange membrane, Nafion 117 membrane, water-aliphatic alcohol mixtures

INTRODUCTION

Membrane separation technologies can offer energy savings, low-cost modular construction, high selectivity of separated materials, and processing of temperature-sensitive products (1). Membranes separate mixtures

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according to physical or chemical attributes of their components, such as molecular size, charge, or solubility (2). Liquid substances could be separated specifically from the main stream, either to save raw materials, to minimize the disposal of effluents or to recycle the by-products. Nowadays the separation of liquid mixtures can also be achieved by membrane pervaporation (3–5).

Pervaporation is recognized as a separation process in which a binary or multicomponent liquid mixture is separated by a partial vaporization through a dense lyophilized membrane (6). The feed mixture is in a direct contact with one side of the membrane whereas permeate is removed in a vapor state from the opposite side into a vacuum or sweeping gas (Fig. 1) and then condensed. The driving force for the mass transfer of permeants from the feed side to the permeate side of the membrane is a gradient in chemical potential, which is established by applying a difference in partial pressures of the permeants across the membrane. The difference in partial pressures can be created either by reducing the total pressure on permeate side of the membrane by

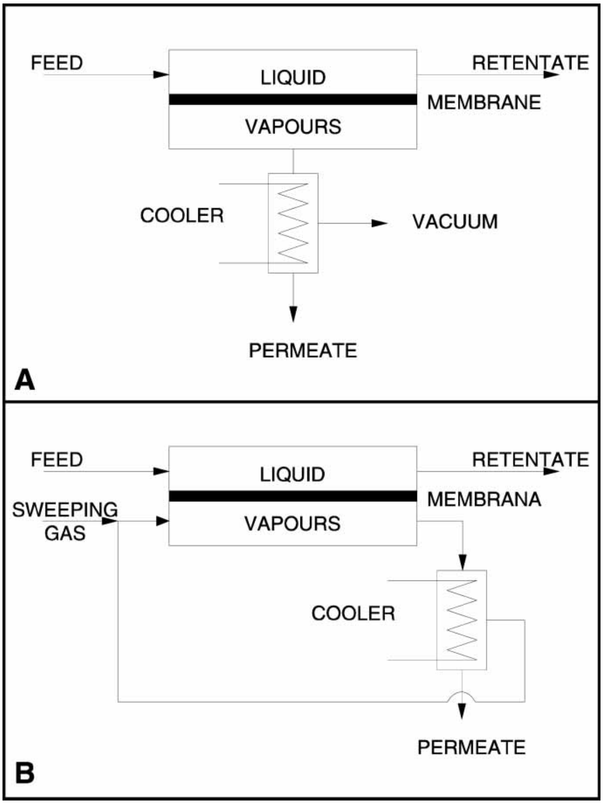

Figure 1. The principle of pervaporation. A. Vacuum pervaporation. B. Sweeping gas pervaporation.

using vacuum pump system or by sweeping an inert gas on the permeate side of the membrane (6, 7).

The performance of a pervaporation membrane in contact with an A/B binary mixture (where A denotes the faster permeating component of the mixture) can be characterized in terms of the pervaporation separation factor α^{PV} (8):

$$\alpha^{PV} = \frac{w_A^P / w_B^P}{w_A^F / w_B^F} \tag{1}$$

where w_i^p—weight fraction of i component in the permeate; w_i^F—weight fraction of i component in the feed mixture.

The other parameters are the total (J_{tot}) and partial (J_i) permeation fluxes. The following relations are hold for the fluxes:

$$J_{tot} = \sum_i J_i \tag{2}$$

$$J_i = J_{tot} w_i^P \tag{3}$$

Due to the coupling effects occurring during the transport of a binary mixture through the membrane, usually there is no linear relationship between the permeation flux and its weight fraction in the feed mixture (9–11). Huang (10) and Drioli (11) introduced the flux ratio parameter Θ_i expressing the deviation of the permeation of a component i when in a binary mixture to a single component permeation:

$$\Theta_i = \frac{J_i}{w_i^F J_{i,0}} \tag{4}$$

where: Θ_i—flux ratio of component i; J_i—permeation flux of component i in binary mixture; $J_{i,0}$—permeation flux of pure component i; w_i^F—weight fraction of component i in the feed mixture.

When $\Theta_i > 1$ the permeation of component i is enhanced by the presence of the other component; whereas for $\Theta_i < 1$ the permeation of component i is retarded by the other one.

The composition and morphology of the membranes are a key to effective use of pervaporation technology. The choice of the membrane material strongly depends on the type of application. It is important which of the components should be separated from the mixture and whether this component is water or an organic liquid. Generally, the component with the smallest weight fraction in the mixture should be preferentially transported across the membrane (12–14). For instance, hydrophilic polymers, like poly(vinyl alcohol) or polyamide, are used as a membrane material for the removal of water from organic solvents (6). On the other hand, hybrophobic polymers, like poly(dimethylsiloxane), are used for the removal of organics from water.

Recently the great increase of interest in the different applications of ceramic membranes area has been also observed (15–17). This kind of membrane opens wide perspectives for commercial applications in many various separation processes such as ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), gas separation (GS), or pervaporation (PV). The main advantage of ceramic over polymeric membranes is that the former ones are very resistant in the corrosive media and at elevated temperatures. Commercial ceramic membranes are usually prepared from metal oxides like alumina, zirconia, and/or titania. These materials originally posses the hydrophilic character due to the presence of the surface hydroxyl (–OH) groups, which can link very easily water molecules. In the case of pervaporation with ceramic membranes, the mass transport mechanism differs from the case of dense membranes. Here, the selectivity is based on the preferential adsorption of one of the components in the micropores and the flux is governed by a surface diffusion mechanism (15–17). One can assume that more polar components will be preferentially adsorbed on the surface of micropores.

Applications of conducting polymers were mainly related to their conductivity and there were few considerations of their chemical affinity and structural properties. Membrane-oriented applications represent a new area where latter aspects play important roles (18, 19). Conducting polymers are normally insoluble in many solvents and this makes it impossible to prepare membranes through the conventional techniques based on the phase-inversion method. Thus, the preparation of membranes from conducting polymers is a one-step fabrication, in which polymerization (via electrodeposition or chemical synthesis) and formation occur simultaneously. For example, after electropolymerization of polypyrrole from the acetonitryle solution containg Bu_4NPF_6, the deposit is obtained in its oxidized state with PF_6^- as counter-ion in it (19). Such membrane possesses the polar properties and can be used to separate, e.g., alcohols from hydrocarbons or ethers.

Ion-exchange membranes are also frequently used in pervaporation process for the separation of different liquid mixtures (20–24). Since during pervaporation interactions exist not only between the components of the liquid mixture but also between these components and the membrane material, the selectivity and transport properties of ion-exchange membrane should depend on:

i) the nature of a polymeric backbone,
ii) the kind of ion-exchange sites, and
iii) the kind of a counterion.

In our previous works we presented the pervaporation of PESS cation exchange membranes in contact with pure solvents of different polarity as well as the swelling properties of PESS membranes in contact with pure solvents of different polarity and with water-alcohol binary mixtures (25, 26). This work was aimed in the investigation of pervaporation properties of PESS membrane loaded with different counter ions in contact with different water-alcohol binary mixtures. Results obtained for PESS membrane were compared with properties of Nafion membrane. The PESS and Nafion

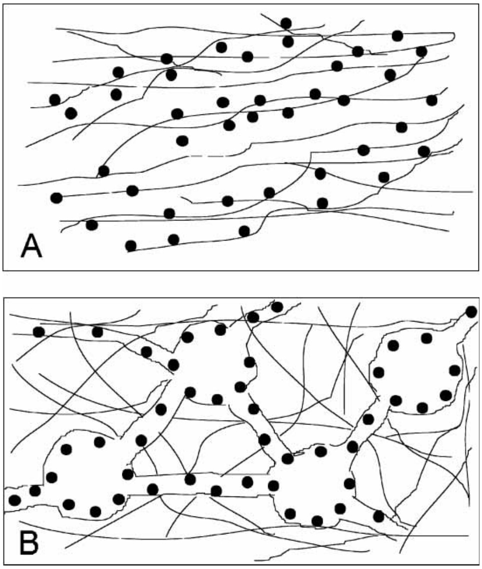

Figure 2. Supermolecular structure of PESS (A) nad Nafion (B) membranes (•—SO_3^- Me^+ site).

membranes both possess sulfonic ion-exchange groups but the strength of the ion-exchange groups as well as the morphology are different in both membranes (27). In the PESS membrane ion-exchange sites are distributed uniformly within the polymeric matrix, forming the continuous polyelectrolyte network. Such structure was observed on a transmission electron micrograph of the polyethylene/poly(styrene-co-divinylbenzen) system (Fig. 2) (28, 29). On the other hand, in the Nafion membrane ion-exchange sites form clusters—Fig. 2 (30–32). In the Nafion membrane sulfonic groups are attached to the fluorocarbon vinyl ether chains and the ionic strength of these ion-exchange groups is much higher than those in the PESS membrane (27).

EXPERIMENTAL

Membranes

The PESS membranes were prepared by the chemical modification of polyethylene/poly(styrene-co-divylbenzene) interpolymer system, according to the procedure described in the details in our previous paper (25). Membranes containing 1 or 3 wt.% of divinylbenzene as the cross-linking agent are denoted throughout this paper as PESS-1 and PESS-3, respectively.

The Nafion 117 membrane used in this study was well-known perfluorinated ion-exchange material, which found already many practical applications (31–35).

In order to avoid any slow structural changes during experiments, the membrane samples underwent the following pretreatment before use. All new samples of membranes were re-exchanged three times from the sodium form into the hydrogen form. Finally, samples in the hydrogen form were expanded in water at 50°C for 4 h.

Samples in a given ionic form were obtained by an immersion of a sample in the hydrogen form for 24 h in 1 M solution of the appropriate hydroxide (Li^+, Na^+ or K^+), followed by repeated washes to remove the excess of caustic solutions.

Table 1 summarizes the main physicochemical properties of investigated membranes.

Pervaporation Experiments

Pervaporation experiments were carried out in the standard laboratory-scale pervaporation system described in the details elsewhere (36). The thermostatic feed solution circulated over the membrane, whereas permeate was collected in cold traps cooled by liquid nitrogen. During experiments the upstream pressure was maintained at the atmospheric pressure, while the downstream pressure was kept below 1 mbar by using a vacuum pump. The flux of permeate was determined by weight, whereas the feed and permeate compositions were determined by using a gas chromatograph (VARIAN 3300). Pervaporation experiments were performed at the temperatures of 298 and 313 K.

The effect of feed composition on flux and selectivity was determined for PESS and Nafion membranes in contact with water-methanol, water-ethanol, water-propanol, and water-isopropanol mixtures.

Table 1. Physicochemical properties of investigated membranes

Membrane	Chemical structure	Water content[a] (g/g)	Exchange capacity (mmol/g)
PESS-1	Interpenetrating network of polyethylene and sulfonated poly(styrene-co-divinylbenzene) 1% DVB	0.78	1.98
PESS-3	Interpenetrating network of polyethylene and sulfonated poly(styrene-co-divinylbenzene) 3% DVB	0.60	1.95
Nafion 117	Poly(tetrafluoroethylene-co-perfluoro-3,6-dioxa-4-methyl-7-octen-sulfonic acid)	0.21	0.91

[a] Determined for membranes in lithium form.

RESULTS AND DISCUSSION

Influence of the Crosslinking Degree on Pervaporation Properties of the PESS Membrane

According to the wide-accepted qualitative model of pervaporation, the separation during this process proceeds in the three consecutive steps, i.e., sorption, diffusion, and desorption (6, 8). However, the selectivity and transport properties depend on the sorption and diffusion steps only (6, 8). As it was found out in our previous investigations, the increase in the crosslinking degree of a given polymeric material resulted in the decrease of the swelling degree and the increase of the sorption selectivity (25, 26). Fig. 3 presents the comparison of sorption (Fig. 3A) and pervaporation (Fig. 3B) selectivities of PESS-1/Li^+ and PESS-3/Li^+ membranes in contact with water-ethanol mixtures. It is seen that with increasing crosslinking degree the selectivity of PESS membrane in contact with water-ethanol mixture increased, but this increase is much less pronounced compared to the swelling selectivity (26). Because the PESS membranes were of different thickness, it was difficult to observe directly the influence of the crosslinking degree on the pervaporation flux. In Fig. 4 the ratios of molar permeate fluxes are presented for PESS-1 and PESS-3 membranes. One can conclude that the increase in crosslinking resulted in the increase of water to ethanol molar permeate ratio. It means that crosslinking not only limits the swelling degree but also limits the diffusivity of both components through the membrane and the bigger molecules (i.e. EtOH) were hindered more than smaller water molecules.

Pervaporation Properties of PESS and Nafion Membranes

Figure 5 compares the selective properties of PESS-3 (Fig. 5A) and Nafion (Fig. 5B) membranes in contact with water-ethanol mixture. The counterion effect on the selectivity of a given membrane is clearly observable. The potassium forms of both membranes were more selective than the lithium ones, which resulted from the different solvating numbers of lithium and potassium ions and from differences in swelling (25, 26). The influence of the type of counterion on the pervaporation selectivity was similar to that found in our observations concerning sorption selectivity in water-alcohol mixtures and pervaporation of pure solvents through PESS membranes (25, 26). For both ionic forms investigated, the pervaporation selectivity of the Nafion membrane was much lower than that of the PESS one. Such a big difference could be explained by the different ionic strength of the sulfonic groups in both membranes. This will be discussed next.

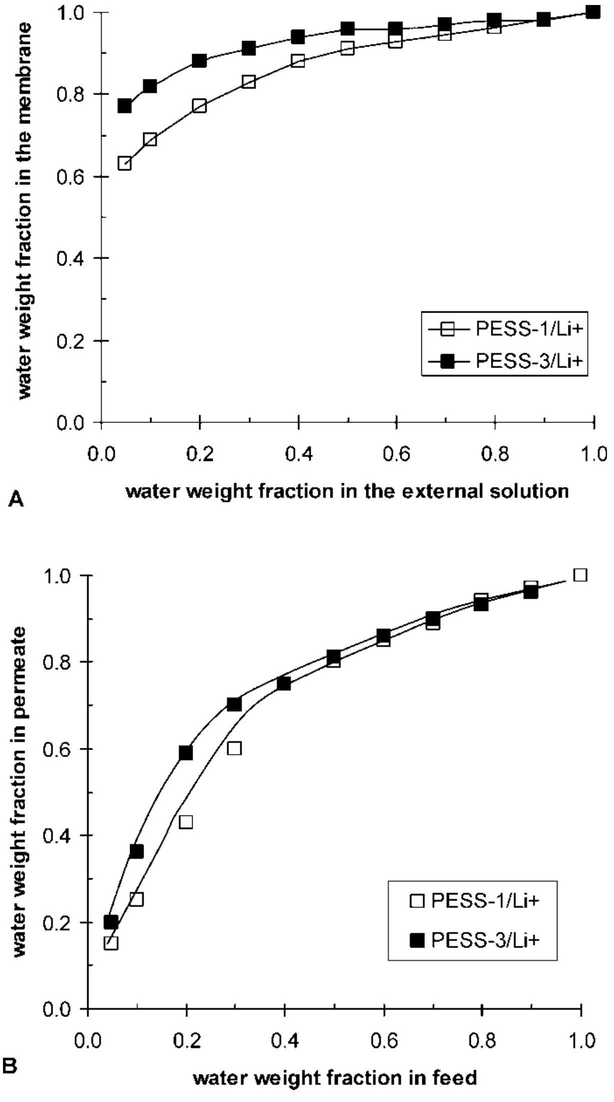

Figure 3. Sorption selectivity (A) and pervaporation selectivity (B) of PESS-1/Li$^+$ and PESS-3/Li$^+$ membranes in contact with water-ethanol mixture.

Figures 6 and 7 present the comparison of transport properties of PESS-3 and Nafion membranes in contact with water-ethanol mixture. Both membranes were less permeable in the potassium form. The water flux increased with increasing water content in the feed mixture. The flux of alcohol molecules passed through the slight maximum at 50–70-wt.% of water in the feed mixture. The difference in the transport mode through both investigated membranes was seen when comparing the

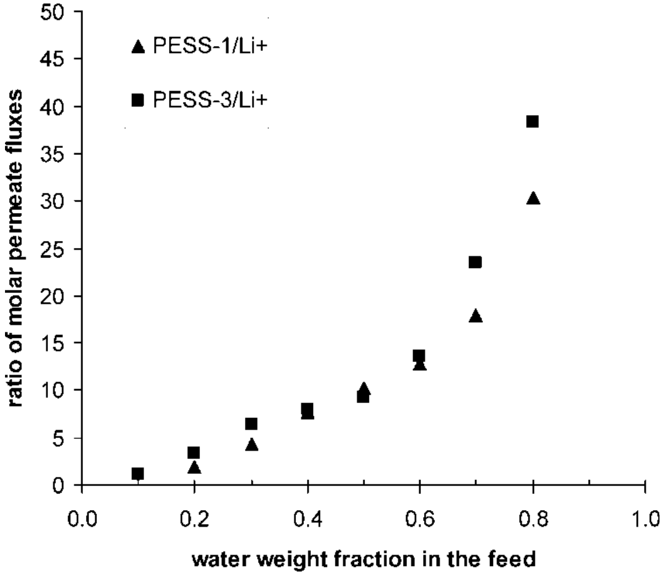

Figure 4. Ratios of water over ethanol molar permeate fluxes for PESS-1/Li$^+$ and PESS-3/Li$^+$ membranes in contact with water-ethanol mixture.

transport of ethanol molecules (Figs. 6A, 7A). The permeability of PESS-Li$^+$ membrane in contact with pure ethanol was relatively small (Fig. 6A). On the other hand, the Nafion-Li$^+$ membrane showed much higher permeability toward pure ethanol (Fig. 7A). This difference can be explained comparing the ionic strength of sulfonic groups in both membranes. In the PESS membrane sulfonic groups are bound to the benzene ring and only water molecules can dissociate ion-pairs. In the Nafion membrane sulfonic groups are attached to the fluorocarbon vinyl ether chains and the dissociation of the ion-pairs occurs even in the presence of alcohol of low polarity. Such behavior of sulfonic groups in both PESS and Nafion membranes was proved by IR investigations (25, 27).

Pervaporation Properties of PESS-1/Li$^+$ Membrane in Contact with Water-Aliphatic Alcohol Mixtures

Figure 8 presents the selectivity of PESS-1/Li$^+$ membrane in contact with water-aliphatic alcohol mixtures. It could be seen that the selectivity of PESS-1/Li$^+$ increased with decreasing polarity of the aliphatic alcohol (Table 2). The highest selectivity was found for the PESS-1/Li$^+$ membrane in contact with water-isopropanol system. The pervaporation separation factor α^{PV} showed the influence of alcohol and feed composition on the

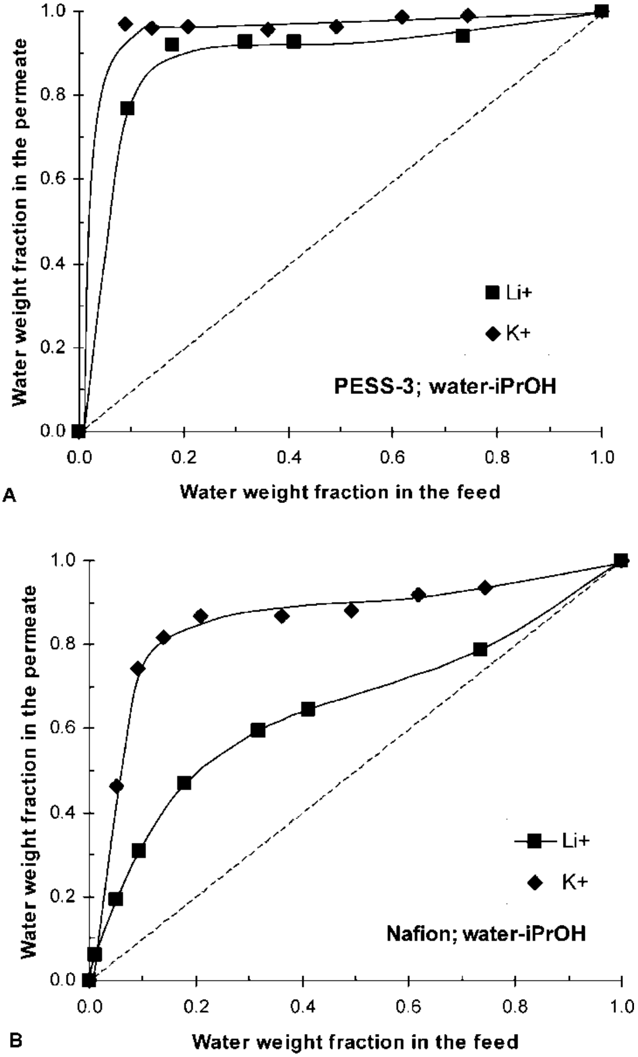

Figure 5. McCabe-Thiele selectivity diagram of PESS-3/Li^+ and PESS-3/K^+ membranes (A) and Nafion 117/Li^+ and Nafion 117/K^+ membranes (B) in contact with water-ethanol mixture.

membrane selectivity (Fig. 9). In the case of methanol and ethanol, selectivity of the PESS-1/Li^+ membrane was relatively low and practically constant within the concentration range investigated. However for water-propanol and water-isopropanol mixtures α^{PV} passed through the maximum at 25–30 wt.% water in the feed. The fast selectivity increase at the low water content mixtures could be explained by the replacement of alcohol

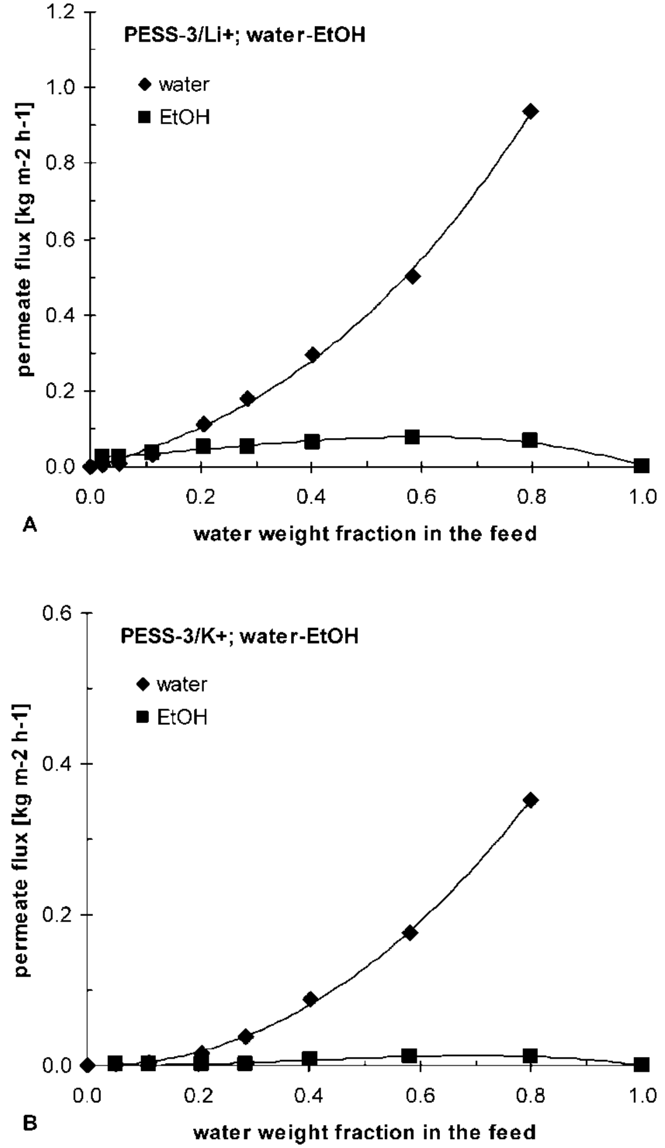

Figure 6. Permeate fluxes of water and ethanol through PESS-3/Li^+ (A) and PESS-3/K^+ (B) membranes in contact with water-ethanol-mixture.

molecules by water molecules in the solvating shells, followed by the dissociation of ion-pairs (Figs. 8, 9) (25, 27). At the feed water content greater than 30 wt.%, the water content in the permeate increased to the much less extent (Fig. 8)—from about 90 wt.% when membrane contacted feed containing 30 wt.% water to 100%wt. when membrane was contacted with

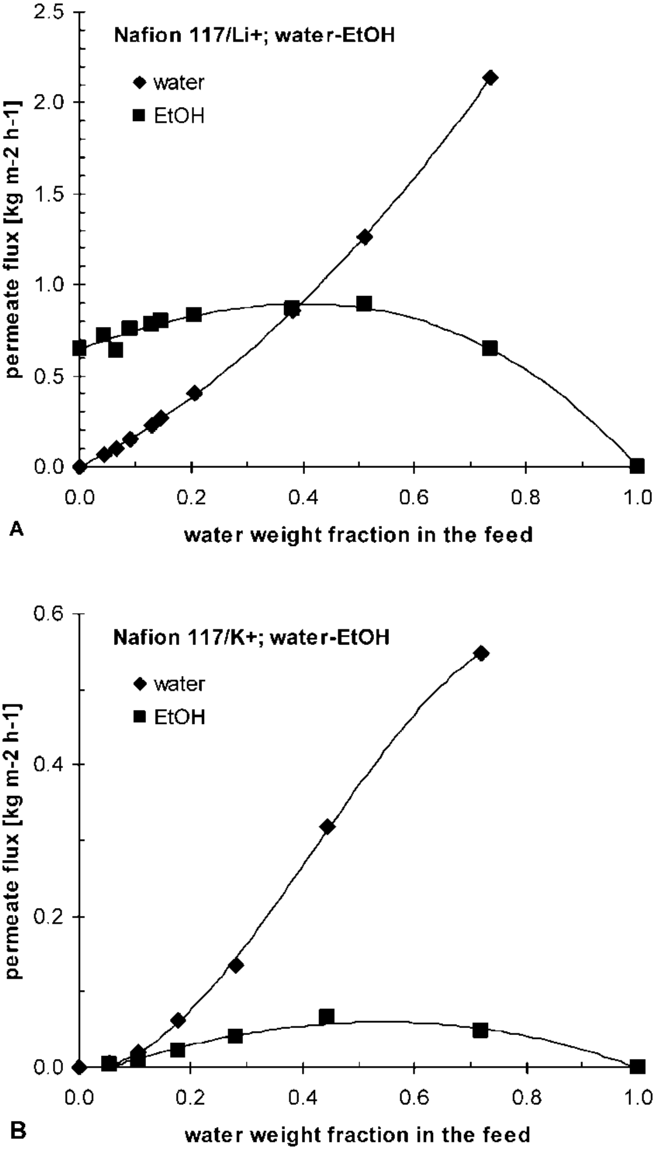

Figure 7. Permeate fluxes of water and ethanol through Nafion 117/Li^+ (A) and Nafion 117/K^+ (B) membranes in contact with water-ethanol-mixture.

pure water. According to the Eq. (1), such concentration dependence resulted in the decrease of the pervaporation separation factor.

The permeate flux of water through PESS-1/Li^+ membrane (Fig. 10) was dependent on the kind of the alcohol in the feed mixture. For the more polar alcohols (i.e., methanol and ethanol) fluxes of water were comparable and

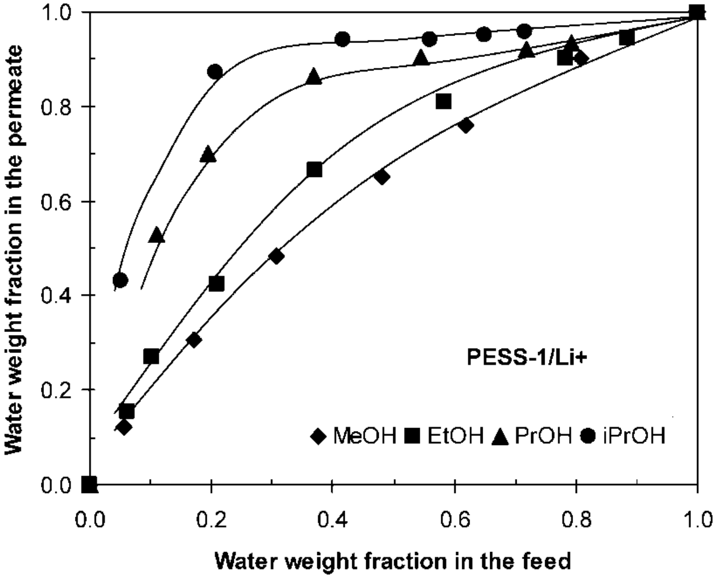

Figure 8. McCabe-Thiele selectivity diagram of PESS-1/Li$^+$ membrane in contact with water-alcohol mixtures.

much higher than in the presence of propanol and isopropanol. It can be explained by the increased swelling of the membrane in the more polar alcohols. On the other hand, it could be also explained in the terms of so-called synergetic effects or couplings between fluxes (9–11, 39). In the absence of synergetic effects, the water flux ratio should be comparable and close to the unity [Eq. (4)], regardless the kind of alcohol. In general, the presence of alcohol molecules suppressed the flux of water; as for all investigated alcohols the molar flux ratio was smaller than unity (Fig. 10B).

Table 2. Chosen physicochemical properties of solvents investigated

Solvent	Molar volume [cm^3/mol]	Dielectric constant[a] (37) [D]	Vapor pressure[b] [kPa]
Water	18.0	78.5	3.15
Methanol	40.5	32.7	16.91
Ethanol	58.4	24.3	7.88
n-Propanol	74.7	20.1	2.76
i-Propanol	76.5	18.3	5.68

[a] At 298 K.

[b] Calculated for 298 K, according to the Antoine equation (38).

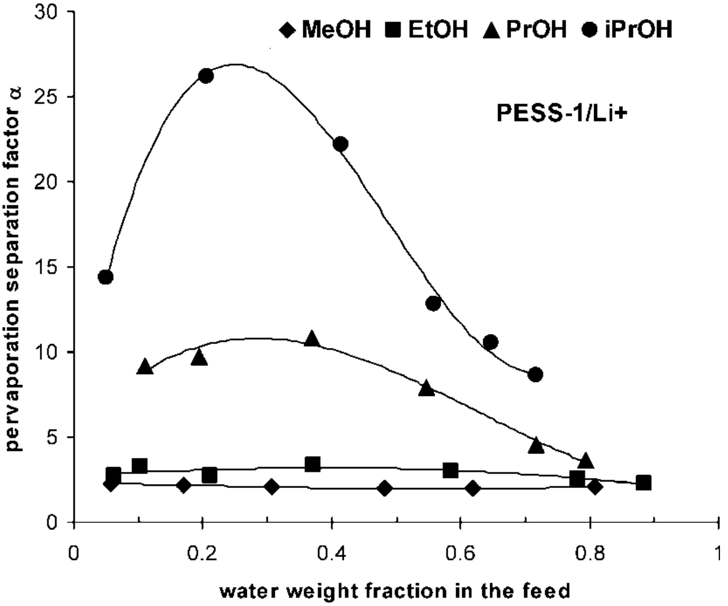

Figure 9. Pervaporation separation factor α^{PV} of PESS-1/Li$^+$ membrane in contact with water-alcohol mixtures.

The permeate fluxes of alcohol were dependent on the alcohol polarity and the dimension of the molecules (Fig. 11A). The flux of pure alcohol was highest in contact with methanol and decreased with increasing hydrophobicity of alcohol, according to the following order (Fig. 11A, (25)):

$$J(MeOH) > J(EtOH) > J(iPrOH) > J(PrOH)$$

The permeate fluxes of alcohols were much smaller than water fluxes (Figs. 10A and 11A) and decreased with increasing water content in the feed. The alcohol flux ratios were practically constant and close to unity for water-methanol and water-ethanol systems but were increasing substantially for water-isopropanol and water-propanol systems (Fig. 11B) indicating the strong synergetic effects.

The detailed discussion of the synergetic or coupling effects in the investigated systems based on the pseudophase-change solution-diffusion model (39) will be presented in a subsequent paper from our laboratory.

CONCLUSIONS

The results presented in this study proved that ion-exchange membranes could be used for the separation of water-alcohol mixtures by pervaporation.

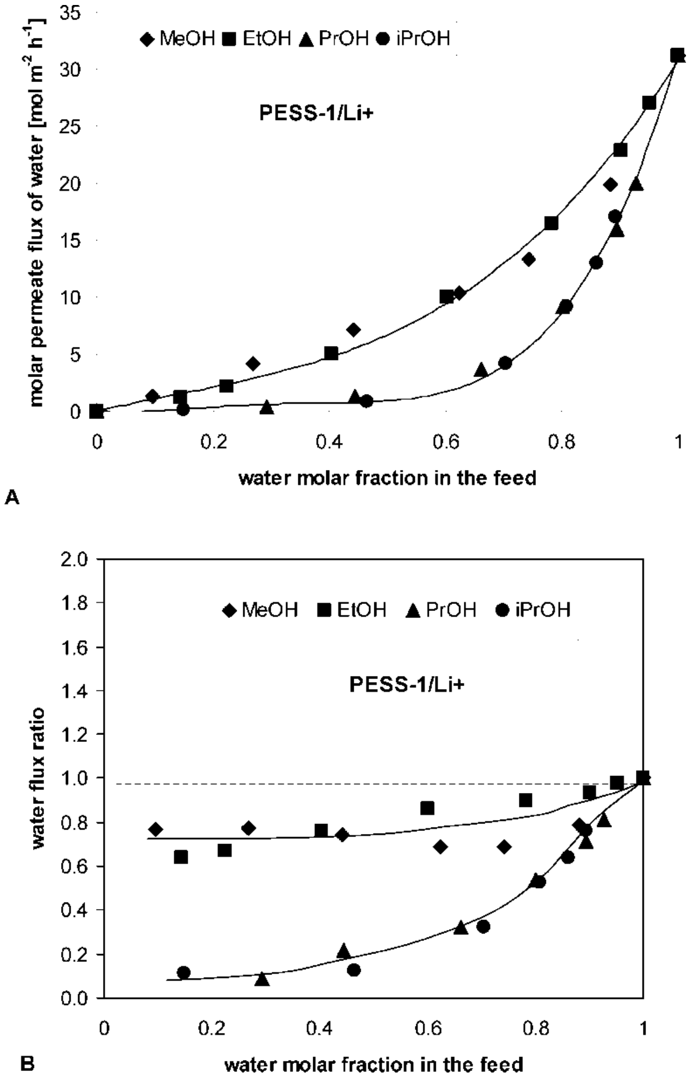

Figure 10. A) Molar permeate fluxes of water through PESS-1/Li$^+$ membrane in contact with water-alcohol mixtures. B) Molar flux ratios of water through PESS-1/Li$^+$ membrane in contact with water-alcohol mixtures.

The selective and transport properties of investigated membranes were dependent on the nature of polymeric backbone, the ionic strength of the sulfonic groups and the kind of counterion.

In the ionomeric materials, the ion-exchange groups are present as clusters or multiplets (28–32). According to our results and results obtained in other laboratories (19–21, 23–26, 40, 41), it was reaffirmed

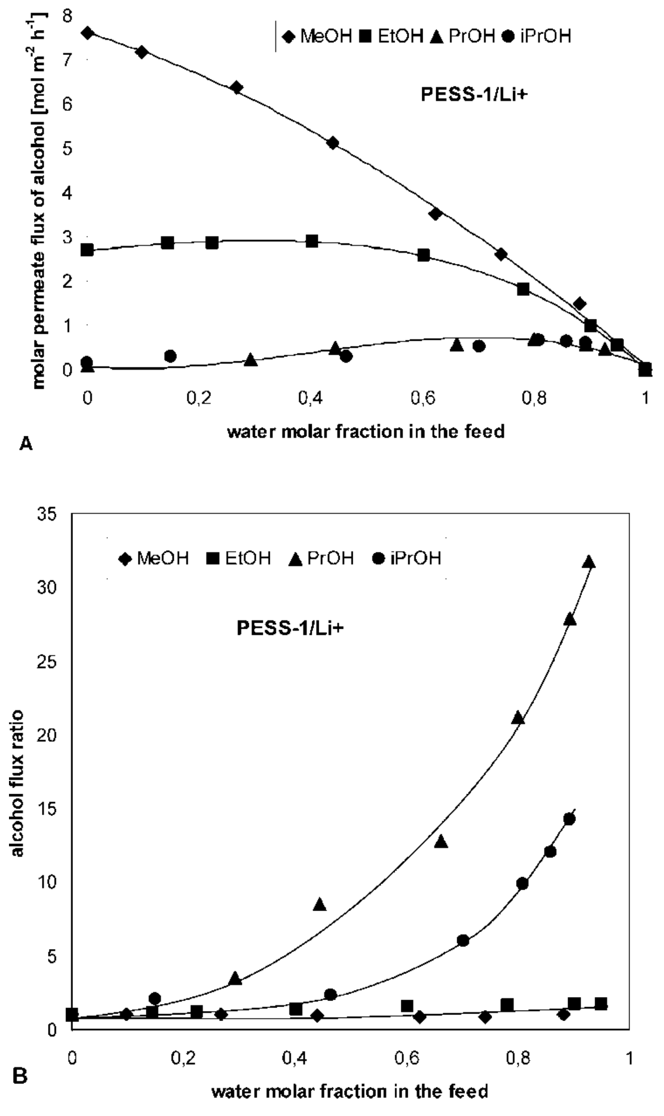

Figure 11. A) Molar permeate fluxes of alcohols through PESS-1/Li^+ membrane in contact with water-alcohol mixtures. B) Molar flux ratios of alcohols through PESS-1/ Li^+ membrane in contact with water-alcohol mixtures.

that transport of water molecules occurs through the hydration shell and water clusters situated in the close vicinity of the ion-exchange sites. The flux ratios demonstrated the presence of interactions in PESS membranes, accelerating the transport of alcohol molecules, especially when the PESS membrane contacted feed mixtures with high water content.

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