Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Wojciech Kujawski[a]; Gryzelda Poźniak[b]
[a] Faculty of Chemistry, N. Copernicus University, Toruń, Poland [b] Institute of Organic and Polymer Technology, Wroclaw University of Technology, Wrocław, Poland

To cite this Article Kujawski, Wojciech and Poźniak, Gryzelda(2005) 'Swelling Properties of Ion-Exchange Membranes in Contact with Water-Alcohol Mixtures', Separation Science and Technology, 39: 9, 2137 — 2154
To link to this Article: DOI: 10.1081/SS-120039303
URL: http://dx.doi.org/10.1081/SS-120039303

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 9, pp. 2137–2154, 2004

Swelling Properties of Ion-Exchange Membranes in Contact with Water–Alcohol Mixtures

Wojciech Kujawski[1,*] and Gryzelda Poźniak[2]

[1]Faculty of Chemistry, N. Copernicus University, Toruń, Poland
[2]Institute of Organic and Polymer Technology, Wroclaw
University of Technology, Wrocław, Poland

ABSTRACT

Cation exchange membranes polyethylene sulfonated polystyrene (PESS) were prepared by sulfonation of an interpolymer polyethylene/poly (styrene-*co*-divinylbenzene) [PE/poly(St-*co*-DVB)] with 1 or 3 wt% of the cross-linking agent divinylbenzene (DVB). Swelling properties of the PESS ion-exchange membranes in contact with water–aliphatic alcohols mixtures were investigated. The 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, the degree of cross-linking, and the difference in the polarities between water and the organic component of the

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*Correspondence: Wojciech Kujawski, Faculty of Chemistry, N. Copernicus University, ul. Gagarina 7, 87-100 Toruń, Poland; E-mail: kujawski@chem.uni.torun.pl.

DOI: 10.1081/SS-120039303
0149-6395 (Print); 1520-5754 (Online)

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binary mixture. Results obtained for PESS membranes were compared with data obtained for the Nafion 117 ion-exchange membrane.

Key Words: Swelling properties; Ion-exchange membrane; Water–alcohol mixture; Binary mixture.

INTRODUCTION

Pervaporation is a membrane-based technique used for separation of liquid mixtures. According to the commonly used qualitative description of pervaporation, the overall separation of components in the process is affected by the preferential sorption of one of those components into the membrane, diffusion of sorbed components across the membrane, and fast desorption of vapors into the vacuum or sweeping gas.[1] For a given liquid mixture, the pervaporation separation factor α^{PV} can be divided into, at least, the sorption separation factor α^{S} and the diffusion separation factor α^{D}:[2]

$$\alpha^{\mathrm{PV}} = \alpha^{\mathrm{S}}\alpha^{\mathrm{D}} \tag{1}$$

An indication of the membrane suitability for a separation of a given liquid mixture can be estimated from the swelling properties. The behavior of a given membrane in equilibrium with a water–alcohol mixture can be described on the basis of the swelling degree S [Eqs. (2) and (3)], the sorption separation factor α^{S} [Eq. (2)], and the sorption ratio Φ_i [Eq. (3)].[2–4]

The total swelling degree (S) of a given membrane can be calculated according to the following equation:

$$S = \frac{(m_{\mathrm{s}} - m_{\mathrm{d}})}{m_{\mathrm{d}}} \qquad (\text{g solution/g dry membrane}) \tag{2}$$

The partial swelling S_i of a given mixture component (i = water, alcohol) was calculated according to the following equation:

$$S_i = S w_i^{\mathrm{S}} \tag{3}$$

The sorption separation factor α^{S} was calculated according to the following formula:

$$\alpha^{\mathrm{S}} = \frac{w_{\mathrm{H_2O}}^{\mathrm{S}} / w_{\mathrm{Alc}}^{\mathrm{S}}}{w_{\mathrm{H_2O}}^{\mathrm{F}} / w_{\mathrm{Alc}}^{\mathrm{F}}} \tag{4}$$

Whereas, the sorption ratio is described as follows:

$$\Phi_i = \frac{S_i}{w_i^{\mathrm{F}} S_{i,0}} \tag{5}$$

The meaning of the symbols used in Eqs. (2)–(5) is the following: m_{s} is the weight of the swollen membrane; m_{d} is the weight of the dry membrane; w_i^{S} is weight fraction of i sorbed into the membrane; w_i^{F} is weight fraction of i in the external solution; S_i is partial uptake of i component from the external solution onto a dry membrane, according to Eqs. (4) and (5); $S_{i,0}$ is swelling degree of the membrane in the pure i solvent.

The sorption ratio indicates the synergetic effects between components of the mixture during sorption into the membrane, $\Phi_i = 1$ denotes the independent sorption of each component into the membrane. If Φ_i is greater than unity, then the sorption of i is increased by the presence of another component, whereas, $\Phi_i < 1$ points to a hindered sorption.

Ion-exchange membranes frequently are used in the pervaporation process for the separation of different liquid mixtures.[5–10] Taking into account the supermolecular structure of the ion-exchange membranes, it can be stated that the selectivity and transport properties of these kinds of membranes should depend on the following: (1) the nature of the polymeric backbone; (2) the kind of ion-exchange sites; and (3) the kind of counterion.[11]

In a previous work, the swelling and pervaporation properties were present in polyethylene sulfonated polystyrene (PESS) cation exchange membranes in contact with pure solvents of different polarity.[12] The aim of this work was to investigate swelling properties of PESS membranes loaded with different counterions in contact with different water–alcohol mixtures. Results obtained for the PESS membrane were compared with those of a Nafion membrane. The PESS and Nafion membranes both possess sulfonic ion-exchange groups, but the strength of these ion-exchange groups as well as the supermolecular structure are different in both membranes.[13] In the Nafion membrane, ion-exchange sites form clusters.[14] whereas, in the PESS membrane, ion-exchange sites are distributed much more uniformly within the polymeric matrix, forming the continuous polyelectrolyte network.[15]

EXPERIMENTAL

Membranes

The PESS membranes were prepared by the chemical modification of the polyethylene/poly(styrene-*co*-divinylbenzene) [PE/poly(St-*co*-DVB)] interpolymer system, according to the following procedure.[12,16]

The low-density PE (Petrochemia Blachownia S.A., Kedzierzyn-Kozle, Poland) was used. The interpolymerization was carried out with a content of 1 wt% benzoyl peroxide. The two-phase reaction mixture contained 70 wt% of PE (granulate) and 30 wt% of styrene (St) and divinylbenzene (DVB); the proportion of DVB in the monomer mixtures was 1 or 3 wt%. The resulting PE/poly(St-*co*-DVB) interpolymers (granulate) were formed into a sheet, chlorosulfonated at room temperature with a 30 vol% solution of chlorosulfonic acid in 1,2-dichloroethane for 4 hr, and then hydrolyzed with a 20 wt% NaOH aqueous solution for 18 hr. In this type of interpolymer, PE serves as the inert matrix and poly(St-*co*-DVB) with sulfonic groups serves as the cross-linked polyelectrolyte.

Membranes containing 1 or 3 wt% of DVB as the cross-linking agent are denoted throughout this paper as PESS-1 and PESS-3, respectively.

The Nafion 117 membrane is a well-known perfluorinated ion-exchange material, which is used in many industrial applications.[17–21]

To avoid any slow structural changes during experiments, the membrane samples underwent the following pretreatment before use. All new samples of membranes were reexchanged 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 hr.

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

Table 1 summarizes the main physicochemical properties of investigated membranes.

Table 1. Physicochemical properties of investigated sulfonic membranes.

Membrane	Chemical structure	Water content[a] (g/g)	Exchange capacity (mmol/g)
PESS-1	Interpenetrating network of polyethylene and sulfonated polystyrene-*co*-divinylbenzene (1% DVB)	0.78	1.98
PESS-3	Interpenetrating network of polyethylene and sulfonated polystyrene-*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.

Swelling Measurements

The membrane swelling caused by the sorption of water–alcohol mixtures into membrane was determined gravimetrically according to the following procedure. Membrane samples were immersed in water–alcohol solutions of a given composition in a thermostatic vessel at 298 K for 24 hr. After blotting off an excess of the solution, the swollen membranes were weighed and then dried in a vacuum oven at 373 K to a constant weight.

The composition of the sorbed mixture was determined by using the desorption method proposed by Uragami.[22] The swollen samples were wiped off with a filter paper and then placed in the sampler (Fig. 1). The vacuum-evaporated vapors were collected in the cold finger immersed in liquid nitrogen and were analyzed thereafter by using a VARIAN GC 3300 gas chromatograph.

Swelling measurements were performed for PESS-1, PESS-3, and Nafion membranes loaded with different counterions and in contact with different water–alcohol mixtures: water–methanol, water–ethanol, water–propanol, and water–isopropanol. Measurements were performed in the whole composition range (i.e., 0–100 wt% of water in the binary water–alcohol mixture).

Infrared Measurements

Infrared (IR) spectroscopic measurements were carried out by the attenuated total reflectance (ATR) mode on the Fourier transform (FT) infrared Bruker spectrometer. Usually 128 interferograms were co-added and the FT

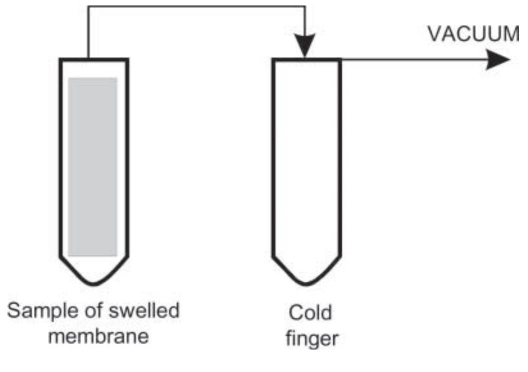

Figure 1. The principle of the setup for the determination of the composition of the sorbed mixture.

was calculated at a resolution of $2\,\mathrm{cm}^{-1}$. The spectra were recorder in the range of $400-4000\,\mathrm{cm}^{-1}$ at 20°C. The spectra were collected for the PESS-1 and Nafion 117 dry and solvent-swollen membranes in different alkaline ionic forms.

RESULTS AND DISCUSSION

The swelling behavior of PESS-1 and PESS-3 membranes in contact with water–EtOH mixtures, determined for the series of hydrogen and alkali counterions, are shown in Fig. 2(A) and (B). Results presented indicate that the membrane swelling decreases with the increasing degree of the membrane cross-linking. It also can be seen that the membrane swelling is closely related to the kind of counterions loaded into the ion-exchange membrane. For the ionic forms of PESS membranes investigated, the swelling decreases in the order similar to that of the cation hydration number:[23]

$$H^+ > Li^+ > Na^+ > K^+$$

Similar observations can be made for the PESS-1 and PESS-3 membranes loaded with hydrogen and alkali metal counterions in contact with water–propanol mixtures [Fig. 3(A) and (B)]. The swelling degree depends both on the kind of counterion and on the degree of the cross-linking.

The water weight fraction in the PESS-1 membrane in contact with water–ethanol and water–propanol mixtures is presented in Fig. 4. It is seen that the sulfonic ion-exchange membrane sorbs water preferentially from the water–alcohol mixture and that the selectivity of a given ionic form increases according to the following order:

$$H^+ < Li^+ < Na^+ < K^+$$

By comparing both orders, one can note that the swelling of the PESS membranes conversely depends on the kind of counterion than the sorption selectivity does [e.g., Figs. 2(A) and 4(A)]. This phenomenon can be explained by taking into account the differences in the ionic radius, the solvation numbers, and the electrostatic field around the counterions (Table 2).[13,23] A lithium ion possesses the smallest ionic radius and this results in the strongest electrostatic field around this ion. This strong electrostatic field allows a build-up of several solvation shells around the lithium cation. These shells contain not only water molecules but also the molecules of a given alcohol. In the case of potassium counterion, the electrostatic field is much weaker (Table 2) and, hence, the solvation shells are thinner and mainly contain water molecules. The PESS/K^+ membrane is much more rigid than

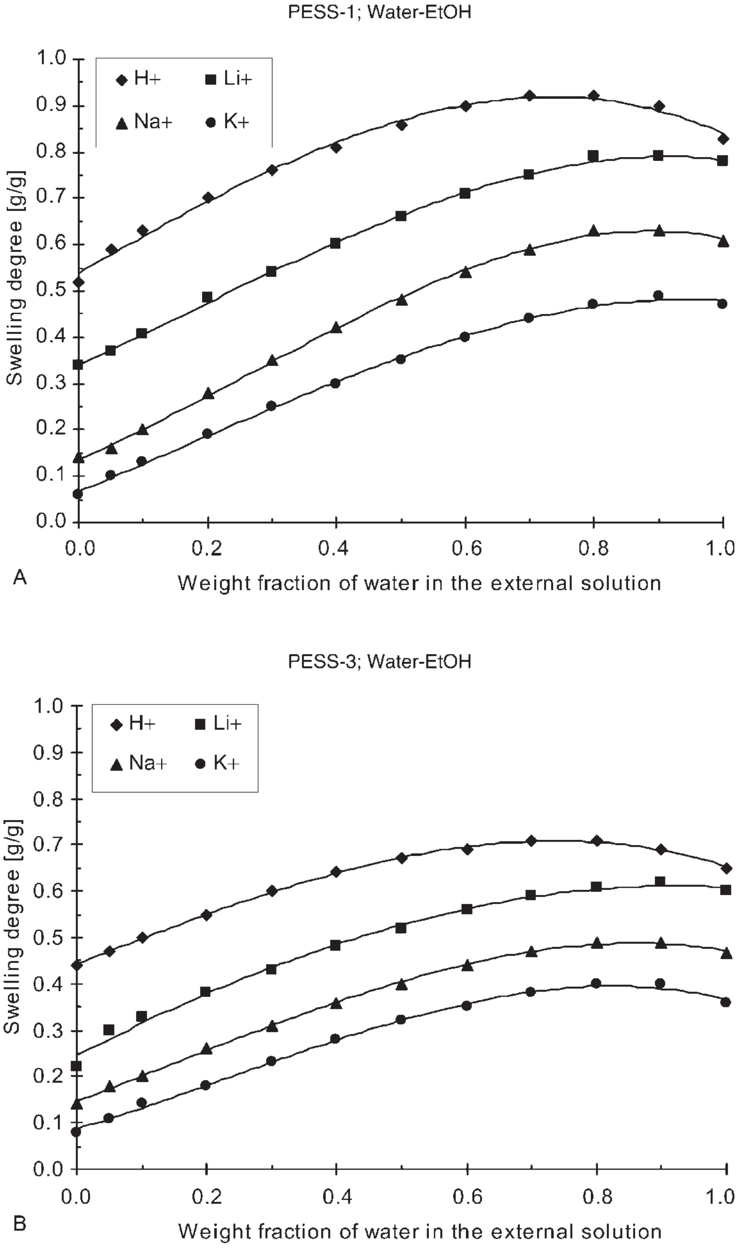

Figure 2. The counterion effect on the swelling degree of PESS-1 (A) and PESS-3 (B) ion-exchange membranes in contact with water–ethanol mixture.

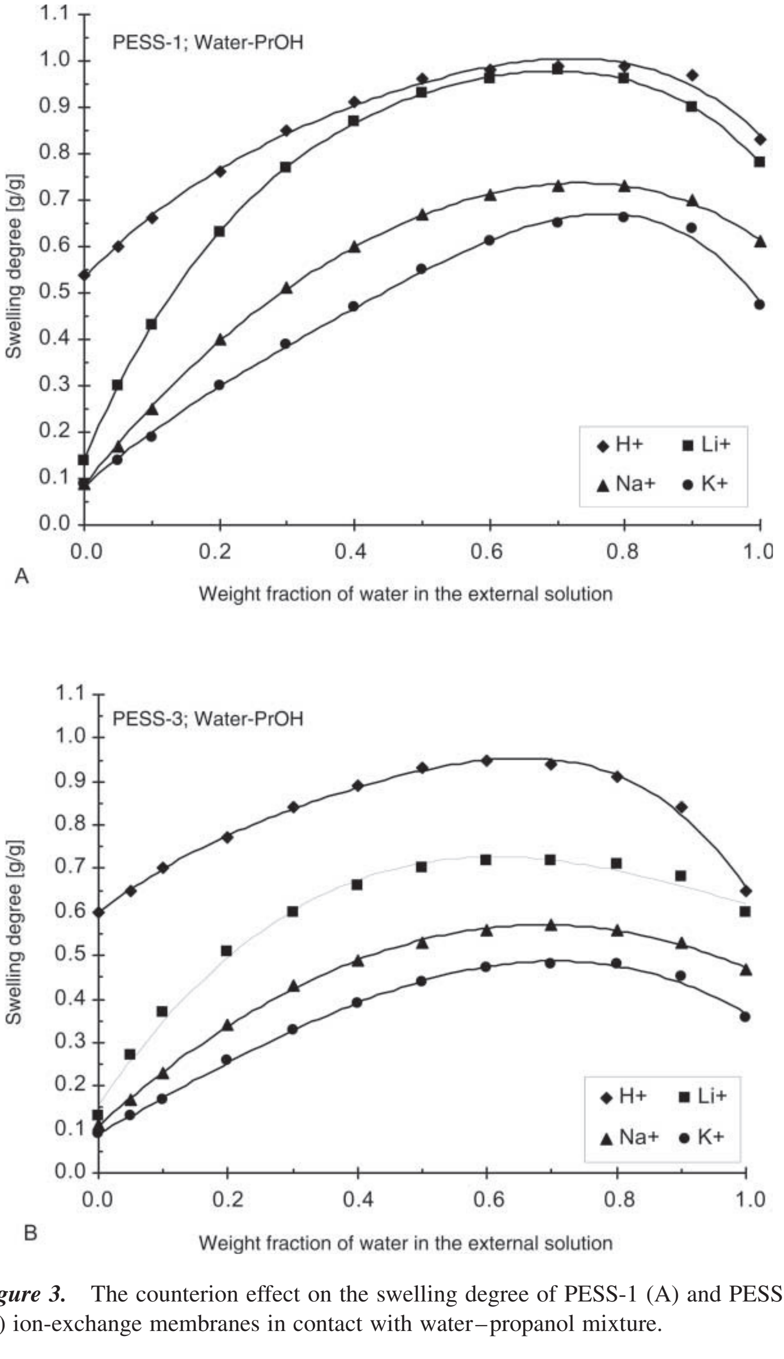

Figure 3. The counterion effect on the swelling degree of PESS-1 (A) and PESS-3 (B) ion-exchange membranes in contact with water–propanol mixture.

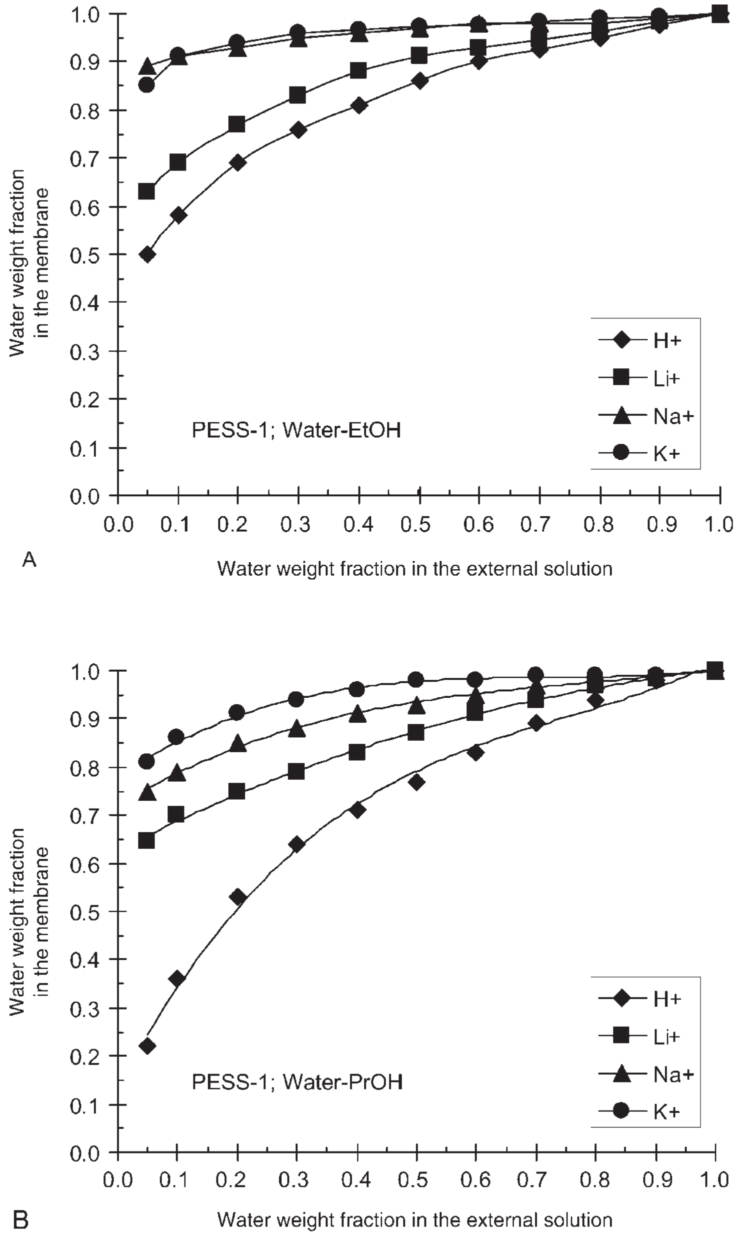

Figure 4. The counterion effect on the water weight fraction in the PESS-1 ion-exchange membrane in contact with water–ethanol (A) and water–propanol (B) mixture.

Table 2. Chosen properties of alkaline cations.

Cation	Ionic radius (Å)	Electrostatic field (10^{-6} ESU cm^{-2})	Hydration number[a]
Li^+	0.68	3.18	3.3
Na^+	0.97	2.08	1.5
K^+	1.33	1.36	0.6

[a] Determined by the extrapolation to the infinite swelling.[23]

the PESS/Li^+ one, swells to a lesser extent, and almost does not sorb alcohol molecules. For example, the PESS-1/Li^+ membrane equilibrated with water–ethanol mixture containing 25 wt% water, sorbs 0.584 g of water/g of dry membrane and 0.146 g of ethanol/g of dry membrane (i.e., the internal solution contains 80 wt% water, whereas, the separation factor is $\alpha^S = 12$). The PESS-1/K^+ membrane in contact with the same external solution, sorbs 0.209 g of water/g of dry membrane and only 0.011 g of ethanol/g of dry membrane (i.e., the internal solution contains 95 wt% of water, and the separation factor is $\alpha^S = 59$).

The concentration dependence of the swelling is similar for both membranes and for all ionic forms investigated. It is seen that the total swelling passes through the slight maximum at the composition of 80 wt% of water in the external solution. Such behavior can be discussed in terms of the sorption ratio Φ_i [Eq. (3), Fig. 5(A) and (B)] and the partial swelling [Fig. 6(A) and (B)]. The sorption ratio for water Φ_{water} is greater than unity within the whole concentration range and is greatest at low water concentration [Fig. 5(A) and (B)]. This means that the presence of alcohol molecules enhances water uptake by the membrane [Fig. 6(A) and (B)]. The sorption ratio for ethanol Φ_{EtOH} [Fig. 5(A)] is smaller than unity, indicating that in the absence of water, the alcohol molecules are placed around the undissociated sulfonic-counterion pairs,[12] and, with increasing water content in the external solution, they are replaced by water molecules [Fig. 6(A)].

The influence of the alcohol polarity on the swelling properties of the PESS-1/Li^+ membrane is presented in Fig. 7. The membrane swelling in pure alcohols decreases with increasing hydrophobicity of a given alcohol [Fig. 7(A)].[12] However, swelling of the PESS membrane in pure isopropanol is greater than in pure propanol, which can suggest that isopropanol, as more hydrophobic, can partially plasticize the amorphous parts of the PESS membrane.[16] With the increasing water content in the external solution, total swelling is much greater in a water–isopropanol than in a water–methanol mixture [Fig. 7(A)]. As sorption selectivity increases with increasing

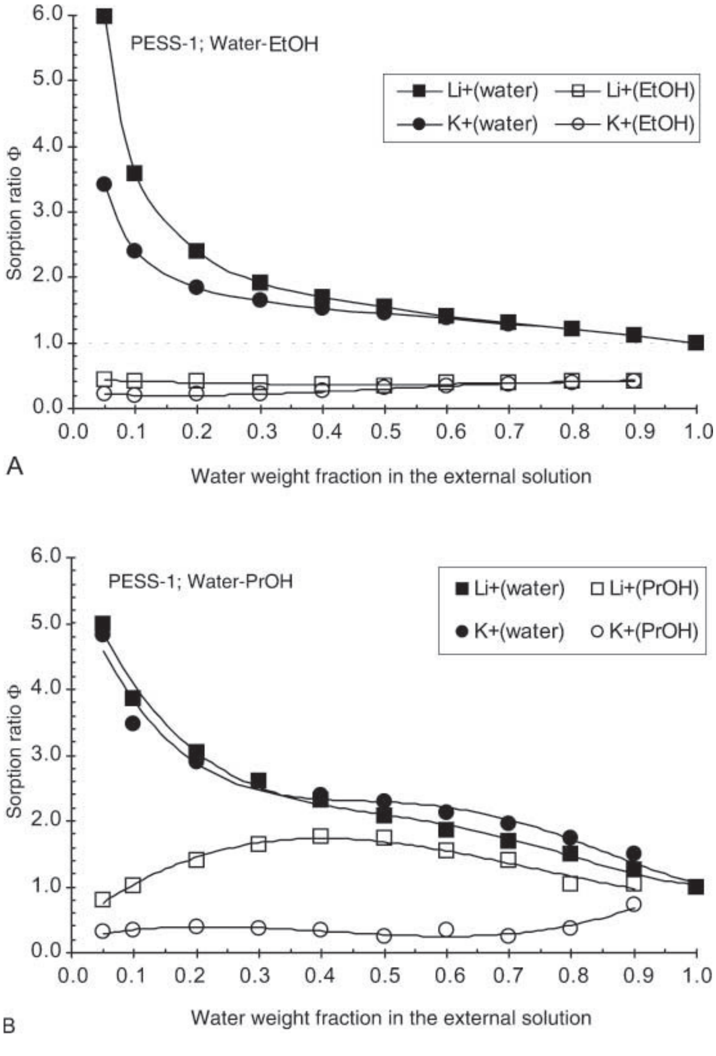

Figure 5. Water and alcohol sorption ratio for PESS-1 ion-exchange membrane in Li^+ and K^+ form in contact with water–ethanol (A) and water–propanol (B) mixture.

hydrophobicity of alcohols [Figs. 7(B) and (C)], one can state that enhanced swelling results from the higher water uptake in the presence of higher alcohols. This can be caused either by the plasticizing of the amorphous parts of a PESS membrane by the higher alcohols, or by the formation of hydration

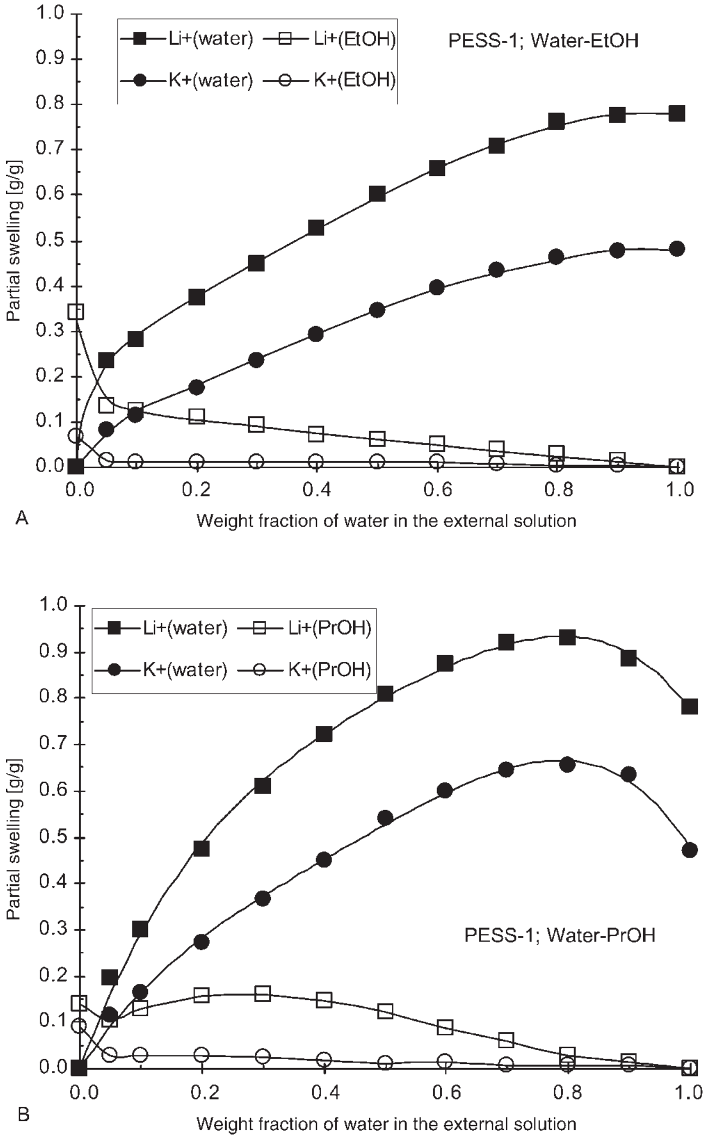

Figure 6. Partial swelling of PESS-1 ion-exchange membrane in Li^+ and K^+ form in contact with water–ethanol (A) and water–propanol (B) mixture.

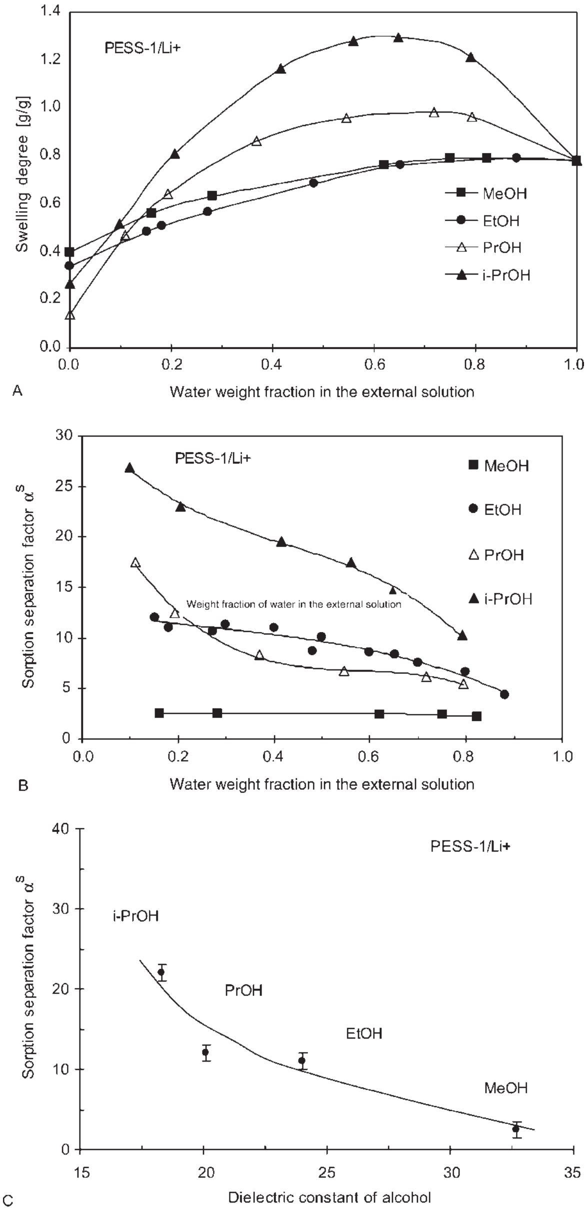

Figure 7. Equilibrium properties of PESS-1/Li$^+$ membrane in contact with water–alcohol mixtures. (A) Swelling degree vs. composition of the external solution. (B) Sorption separation factor vs. composition of the external solution. (C) Sorption separation factor vs. dielectric constant of alcohol.

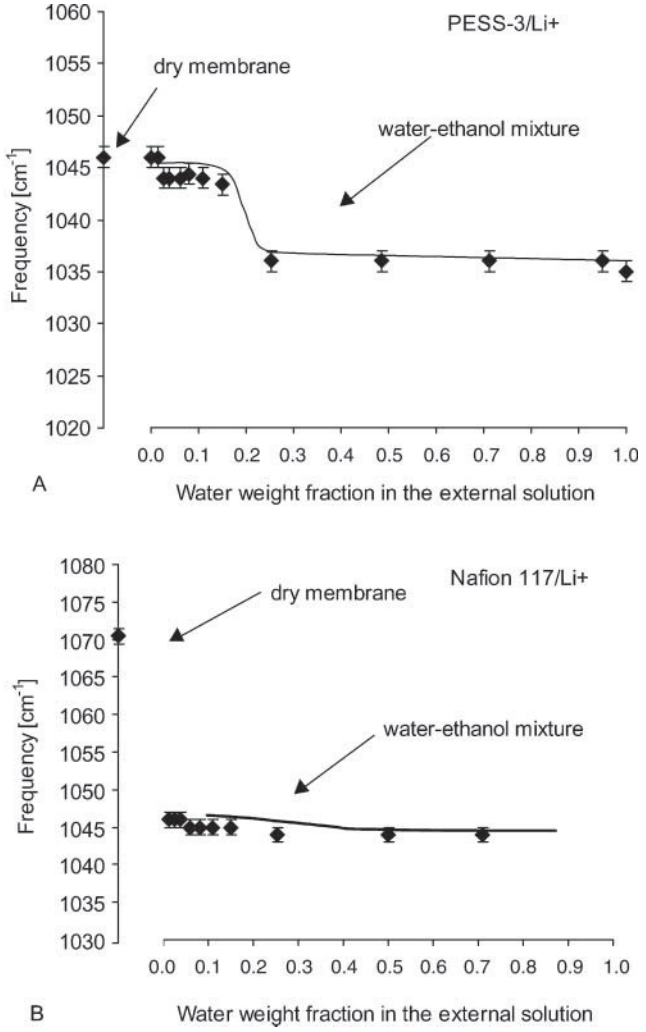

Figure 8. Frequency of the symmetric stretching vibration of the sulfonic group of ion-exchange membranes in lithium form vs. composition of the external water–ethanol solution. (A) PESS-3/Li^+ membrane. (B) Nafion 117/Li^+ membrane.

shells around ionic sites and counterions. In contact with pure alcohols, sulfonic-counterion pairs in PESS membranes remain undissociated and alcohol molecules form only the outer solvation shells around those ion pairs.[12] With an increasing amount of water in the external solution, water

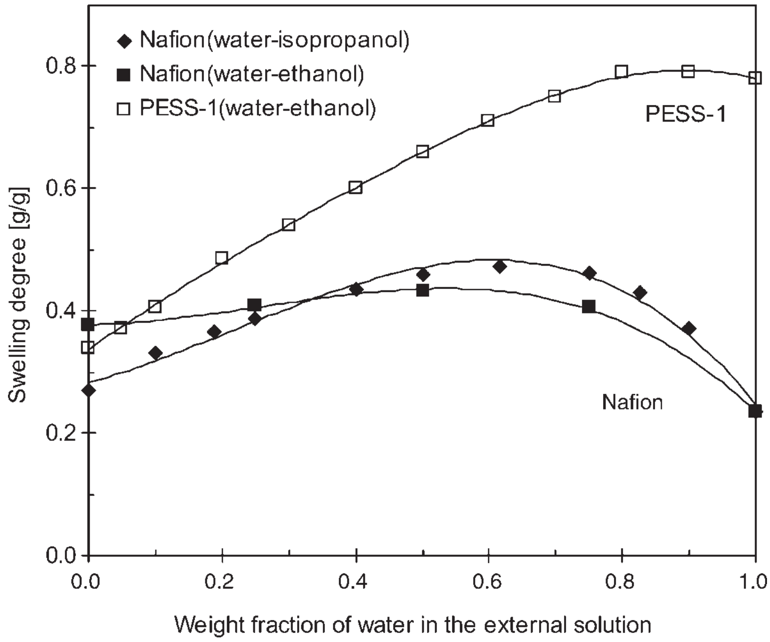

Figure 9. Comparison of the swelling properties of the PESS-3 and Nafion 117 membranes in contact with water–ethanol and water–isopropanol solutions.

molecules replace the alcohol molecules in the solvation shells. As a consequence, anion–cation ion pairs start to dissociate. According to the IR investigations of PESS membranes in contact with water–alcohols mixtures, one can state that this process is completed when the water content of the external solution equals 15–25 wt% [Fig. 8(A)].[12,13] The IR and the swelling results [Figs. 8(B) and 9] obtained with Nafion membrane lead to another conclusion. Swelling of the Nafion membrane in pure alcohol exceeds that in the pure water (Fig. 9). It means that the polarity of ethanol is high enough to cause the total dissociation of ion pairs [Fig. 8(B)].[12,13]

CONCLUSIONS

Swelling of an ion-exchange membrane is caused by the solvation tendency of fixed ionic groups and counterions, the osmotic activity of the counterions, the electrostatic repulsion between dissociated fixed ionic groups, and mutual interactions between components of the sorbed mixture.

The membrane expands until the swelling equilibrium is attained, i.e., when the osmotic and electrostatic forces are balanced by the tendency of the expanding polymeric matrix to contract.

Presented results proved that the swelling properties of ion-exchange membranes depend on the following: (1) the nature of polymeric backbone; (2) the kind of the ion-exchange sites; and (3) the kind of counterion. In the PESS membranes, both the amount of the DVB in the copolymer and the kind of counterion influence the swelling properties of these membranes. Swelling properties also depend on the ionic strength of the sulfonic group. In the PESS membrane, the sulfonic group is bound to the benzene ring and only water molecules can dissociate ion-pairs. Within 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 alcohols.

These results correlate well with our observation for membranes in contact with a pure solvent[12] and with observations of Cabasso[7,24] and Wenzlaff[25] and Freger[26] for other sulfonic ion-exchange membranes contacting water–alcohol mixtures. Results obtained with different sulfonic membranes and with different water–alcohol mixtures suggest that such characteristics prevail in ion-exchange membranes.

The results of our investigations of transport properties of PESS and other sulfonic membranes in contact with water–organic solutions will be reported in the next paper.

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