Pervaporation Separation of Water–Ethanol Mixtures Using Metal-Ion-Exchanged Poly(vinyl alcohol) (PVA)/Sulfosuccinic Acid (SSA) Membranes

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ABSTRACT: Poly(vinyl alcohol)/sulfosuccinic acid (PVA/SSA) membranes in the hydrogen form were converted to monovalent metal ion forms Li^+, Na^+, and K^+. The effect of exchange with metal ions was investigated by measuring the swelling of water–ethanol (10/90) mixtures at 30 °C and by the pervaporative dehydration performance test for aqueous ethanol solutions with various ethanol concentrations at 30, 40, and 50 °C. In addition, electron spectroscopy for chemical analysis (ESCA) analysis was carried out to study the quantity of metal ions in membranes. From the ESCA analysis, the lithium ion quantity in the resulting membranes is greater than that of any other metal ions in question because of the easy diffusion of a smaller metal ion into the membrane matrix. The swelling ratio was in the following order: PVA/SSA-Li^+ > PVA/SSA-Na^+ > PVA/SSA-K^+ membranes. For pervaporation, the PVA/SSA-Na^+ membrane showed the lowest flux and highest separation factor for all aqueous ethanol solutions. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1867–1873, 2002

Keywords: PVA/SSA; metal-ion-exchanged membranes; monovalent metal ions; ESCA; swelling measurement; pervaporation; water–ethanol mixtures

INTRODUCTION

The pervaporation separation technique is very interesting because of its ability to separate azeotropic, close boiling, or aqueous-organic mixtures while saving energy. Many studies have been successfully carried out on the separation of water-ethanol mixtures. Pervaporation membrane materials are being developed worldwide. Poly(vinyl alcohol) (PVA) is still the object of pervaporation researchers because of its chemical and physical natures and its excellent permselective characteristics, even though the PVA composite membrane material known as GFT membrane has been commercialized.

In membrane material science, it is difficult to develop polymer membranes that are suitable for separating mixture systems because of complex interactions between the membrane material and the feed mixture. In addition, the permselective characteristics of the membranes have to be considered to achieve the goal of commercialization. A number of papers have been published on the development of membrane materials by several techniques, such as cross-linking a polymer, grafting selective species onto an inert film, copolymerization, and blending polymers. In particular, the sulfonation of polymer membrane materials is a very effective method that has been used in the ultrafiltration field to increase permeabilities.

Ihm and Ihm[1] investigated the pervaporation of water–ethanol mixtures through sulfonation of polystyrene membranes by plasma graft-polymerization onto porous poly(vinylidene fluoride) membranes. The flux of sulfonated polystyrene (PSS) membrane decreased with increasing the grafted amount because of pore blocking in spite of the introduction of hydrophilic group. However, the sodium exchanged (PSS-Na) membranes had a much higher permeation rate than the plain PSS membranes. They explained this result in terms of the so-called swelling or salting effect. The PSS-Na membranes with a grafted amount of polystyrene of 14 mg/cm^2 had a high permeation rate of 6.6 kg/m^{2}h and a separation factor of 21 for an aqueous 60 wt% ethanol solution at 50 °C. Chen and Martin[2] investigated the effect of the introduction of metal counterions, Na$^+$ and Mg^{2+}, into sulfonated polystyrene (PSS) membranes coated onto microporous alumina support membranes on the pervaporation separation of methyl t-butyl ether–methanol mixtures. They showed that both the flux and the separation factor of PSS-Mg membranes were much higher than those obtained from PSS-Na membranes. In particular, separation factors of the 27.5% sulfonated PSS-Mg are the highest for any polymer investigated to date. Chen et al.[3] studied the pervaporation separation of ethanol–water mixtures by PSS-Na–alumina and PSS-Mg–alumina composite membranes. They reported that membranes in the Na$^+$ counterion form showed higher separation factors than membranes with Mg^{2+} as the counterion. The separation factors for the lower sulfonated membranes are greater than those for the higher sulfonated membranes. Freger et al.[4,5] investigated the preferential sorption and the transport mechanism in ion-exchange pervaporation membranes of sodium polyethylene sulfonated (Na-SPE) for water–ethanol mixtures. Based on the results of this study; they reported that sorption selectivity toward water increases as capacity increases the per equivalent uptake of water is determined primarily by water activity in the outside solution and the presence of ethanol plays only a minor role. Cabasso and Liu[6] investigated the permselectivity of Nafion 811 hollow fiber membranes for nonelectrolyte liquid mixtures, alcohol–water solutions. They reported that flux decreased in the sequence H > Li > Na > K > Cs for the alkali cation series, and that this sequence is reversed for the separation factor. The trend for their swelling studies for the same membranes was very similar to the results of the

flux studies, and these results were related to the hydration shells of the alkali cations. Cabasso et al.[7,8] studied the effect of counterions (H$^+$, Li$^+$, Na$^+$, K$^+$, Cs$^+$) on flux and separation of water–isopropyl alcohol mixtures with sulfonated polyethylene membranes. Flux-decreased from the H$^+$ membrane to the K$^+$ membrane and then increased for the Cs$^+$ membrane, whereas the separation factors showed the opposite tendency.

In our previous work we developed, novel ion-exchange membranes made of PVA cross-linked with sulfosuccinic acid (PVA/SSA), which has dicarboxylic acid and sulfuric acid groups.[9,10] These membranes have been successfully exposed to pervaporation separation of water–alcohol mixtures.

In the present work, PVA/SSA membranes are exchanged with monovalent counterions, such as Li$^+$, Na$^+$, K$^+$, and then the resulting membranes are quantitatively characterized by electron spectroscopy for chemical analysis (ESCA). Pervaporation performance was measured for each metal-ion-exchanged PVA/SSA membrane, varying the operating conditions.

EXPERIMENTAL

Materials

Fully hydrolyzed PVA with a molecular weight of 50,000 and PAA with a molecular weight of 2000 (25 wt% in water) were purchased from Showa Chemical Company (Tokyo, Japan) and Aldrich Chemical Company (Milwaukee, WI), respectively. SSA and ethanol were analytical grade from Aldrich Chemical. Ultrapure water produced with the Sun-Kyung Chemical Company system was used. The metal compounds used in this study, LiOH, NaOH, and KOH, were analytical grade from Aldrich Chemical.

Membrane Preparation

Aqueous 10 wt% PVA solutions were prepared by dissolving preweighed quantities of dry PVA in ultrapure water and heating at 90 °C for at least 6 h. Aqueous 25 wt% PAA solutions were diluted to 10 wt% solutions, and the aqueous 10 wt% SSA solutions were prepared. Then, two polymer solutions were mixed together for at least 1 day at room temperature to form a homogeneous solution containing 5% SSA. Homogeneous membranes were cast onto a Plexiglass plate with a
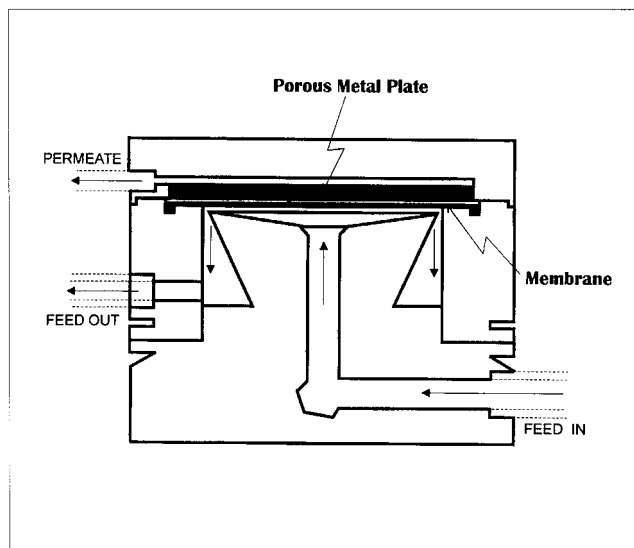
Figure 1   Configuration of the pervaporation cell used in this study.

Gardner knife with a predetermined drawdown thicknéss. The membranes were allowed to dry in air at room temperature, and completely dried membranes were then peeled off. The dried and blended membranes were then heated in a thermostated oven at 150 °C for 1 h. The resulting membranes were 13–15 μm thick.

For the metal-ion-exchanging reaction, the prepared PVA/SSA membranes were soaked in 1 N aqueous solutions containing each metal compound, with light stirring for at least 24 h at room temperature. The resulting membranes, PVA/SSA-Li$^+$, PVA/SSA-Na$^+$, and PVA/SSA-K$^+$, then were washed with water several times and finally stored in solutions (5, 10, and 20 wt% ethanol) to be separated for further use.

ESCA Analysis

To investigate the chemical changes and contents due to the metal exchanging reaction with H$^+$ in -SO$_3$H of PVA/SSA membranes, the (ESCALAB MK II, V. G. Scientific Company, U. K.) equipped with A1Kα radiation source at 1487 eV and 300 W at the anode was used. Survey scan and carbon 1S core level scan spectra were taken to analyze the film surfaces.

Swelling Measurement

The sorption capacity of the membrane was measured by immersing the membrane samples in the mixtures of water and ethanol at 30 °C. The homogeneous membranes were cut into slabs with dimensions of 10 $\times$ 50−80 (mm). The slab soaked in the mixtures for 2 days for an equilibrium swelling. The swollen slab was taken out and then wiped with the cleansing tissue. Both ends of the slab were marked with a pen as quickly as possible, and the distance (L) between the marks was measured with Venier Caliper with an accuracy of ± 10 μm. After drying, the lengths (L_o) of the dry slabs were checked. The solubility of the mixtures in the swollen membrane, ϕ, was calculated from

$$\phi = \frac{R_L^3 - 1}{R_L^3} \tag{1}$$

where $R_L = L/L_o$.

Pervaporation

The membrane cell and the experimental apparatus used in this study are illustrated in Figures 1 and 2, respectively. The pervaporation separation experiments were performed with two stainless steel pervaporation cells (Figure 1). A feed mixture enters the cell through the center opening, flows radially through the thin channel, and leaves the cell through the side opening, which allows relatively high fluid velocity parallel to a membrane surface. The effective membrane area was 14.2 cm^2. The pervaporation experiments with water–ethanol mixtures were conducted at 30, 40, and 50 °C. On reaching steady-state flow conditions, product samples were collected at
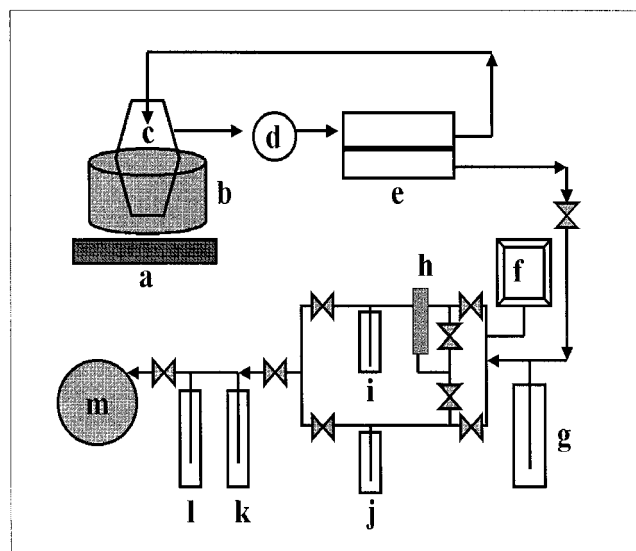
a – stirrer
b   Temperature Controller
c   Feed Tank
d – Micro Pump
e – Permeation Cell
f – Vacuum Manometer
g – Trap
h – Drying Tube
i, j – Cold Traps for collecting samples
k, l – Cold Traps
m – Vaxuum Pump

Figure 2 Schematic diagram of pervaporation apparatus used in this study.

timed intervals, isolated from the vacuum system, and weighed. During the experiments, a downstream pressure of 0.3–1 Torr was maintained. Composition analysis of the permeate was accomplished by gas chromatography with a Porapak Q column. The following relationship was used to calculate the separation factor:

$$\alpha_{i/j} = (y_i/y_j)/(x_i/x_j) \tag{2}$$

where x is the feed composition, y is the permeate composition, and i is the preferentially permeating component.

RESULTS AND DISCUSSION

ESCA Analysis

The results of ESCA analysis for PVA/SSA membranes are shown in Table I. The larger the molecular size of the metal ion, the smaller the quantity in the membranes. Lithium ions could penetrate or diffuse into the membranes through the film surface and react with SO_3^- H^+ because of their size. However, the penetration of larger molecular size ions would be hindered because the PVA/SSA membranes are crosslinked. Therefore,

Table I Results of ESCA Analysis of PVA/SSA Membranes Exchanged with Various Monovalent Metal Ions

Membrane	Li 1s	Na 1s	K 2p	C 1s	O 1s	S 2p
PVA/SSA-Li$^+$	2.176	—	—	73.361	23.209	0.255
PVA/SSA-Na$^+$	—	0.873	—	75.326	22.547	0.254
PVA/SSA-K$^+$	—	—	0.336	78.071	21.328	0.259
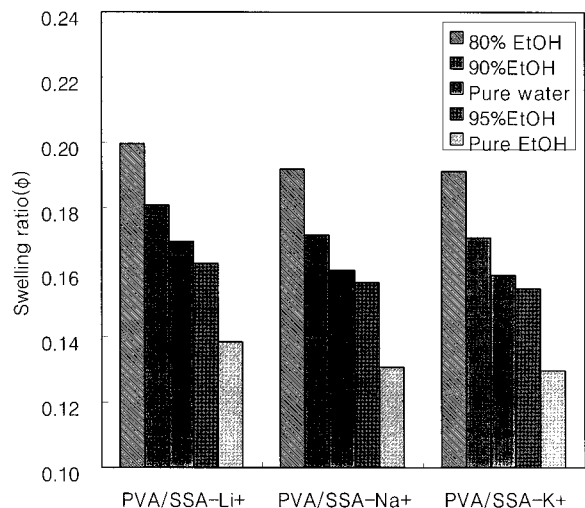
Figure 3 Swelling ratio of PVA/SSA membranes exchanged with monovalent metal ions for 10/90 water–ethanol solutions at 30 °C.

the proportion of lithium ions in membranes is larger than that of sodium or potassium.

Swelling Measurement

The results of the swelling experiments for the crosslinked PVA membranes containing 5% SSA with monovalent metal ions Li^+, Na^+, and K^+ at 30 °C are shown in Figure 3. In principle, selective uptake of water from aqueous organic solutions by ion-exchange materials has the same origin as salting-out (electrostatic rejection of organic molecules by ions in aqueous media) and preferential sorption.[4] The uptake of a polar solvent like water by an ion-exchanging material is essentially solvation of ions comprising ionogenic groups. As is known, organic solvents solvate inorganic ions to a much lesser degree than water. Water molecules fill the first coordination shells of the groups where the field of ions is strongest, whereas organic molecules are lodged in the higher shells and thus do not affect the water–ion interaction. As expected, the swelling ratio for pure ethanol is lower than any other feed compound because the resulting membrane with highly polar ionogenic groups interacts much more strongly with water than organic substances. And, because the water component of feed contains larger portions, the swelling ratio increases. Even though the salting-out effect and preferential sorption act on the membranes in question, it could be theorized that a possible way for ethanol to enter the membrane phases is to dissolve in water adsorbed by the membranes. Therefore, it can be considered that sorption is getting greater as the ethanol concentration in feed increases. However, the swelling ratio for pure water lies between the values of 90 and 95% ethanol feed solutions. These results are very similar to the sorption studies of water–isopropyl alcohol(IPA)–Nafion 811 membranes exchanged with various alkali cations,[4] water–IPA–SPE–Na, and water–ethanol–SPE–Na membrane systems.[6] All systems clearly showed that a maximum absorption was observed in the middle range; that is, the composition of $50 \pm 5\%$ in solution and the absorption of either pure IPA or pure water was relatively low. In particular, the absorption at the concentration close to pure water was in the absorption range of the high concentration of ethanol for SPE-Na, −K, and −Cs membranes. Attempts to explain this observations failed. However, it could be considered that water and ethanol molecules struggle with each other in the formation of hydration shells around the alkali cations within the ranges 90–95% ethanol solutions.

Also, the swelling ratio decreases with increasing size of metal ions. Because lithium ions are smallest, they can penetrate deep inside membranes, whereas potassium ions may react with sulfuric acids existing on only membrane surfaces because of its size effect. However, because the interaction properties of lithium ions with water in feed might be much stronger than those of potassium ions, a lithium cation would carry a substantial amount of water molecules into an ion-exchange polymer matrix and therefore the swelling ratio for PVA/SSA-Li$^+$ becomes larger than that for PVA/SSA-K$^+$. Therefore, the swelling ratio appears in the following order: $Li^+ > Na^+ > K^+$.

Pervaporation Studies

Because highly polar ionogenic groups interact much more strongly with water than with organic substances, such membranes have a great potential in the pervaporative dehydration of organic solvents. Pervaporation experiments were carried out to separate water–ethanol mixtures with metal-ion-exchanged PVA/SSA membranes at various operating temperatures.
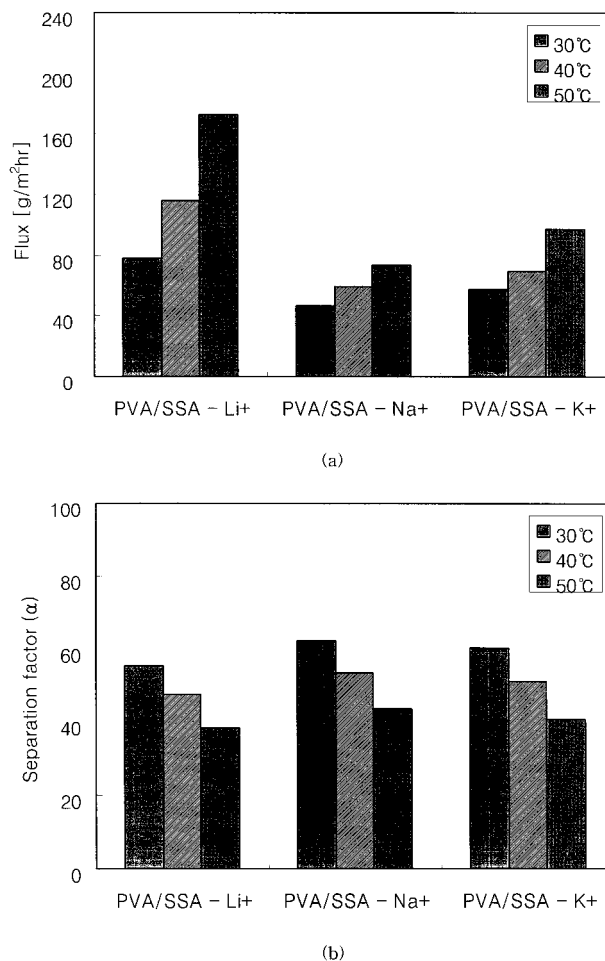
The flux and separation factors for water–ethanol (0/90) solutions are illustrated in Figure 4. The flux decreases with passing the minimum at PVA/SSA-Na$^+$ and then increases. In most ion

exchange membranes, such as Nafion 811 membranes, the flux decreases with increasing molecular sizes of counterions.[6] Only sulfonated polyethylene membranes with exchanges of various metal counterions showed the same trends as in our studies.[4] In their investigations,[4] the flux decreased with increasing molecular size of metal ions up to K^+ and then increases at Cs^+. Until now, this phenomena is not still explained well enough. However, a common fact is that flux of just sulfonated membranes is greater than that of metal-ion-exchanged membranes in all three membranes. In the literature, the flux of PVA/SSA membrane for 10/90 water–ethanol solutions at 60 °C was ~510 g/m²h,[9] whereas the flux of the PVA/SSA-Li^+ membrane for the same solution at 50°C was ~70 g/m²h (membrane thickness is different in each case). A sudden decline of the flux
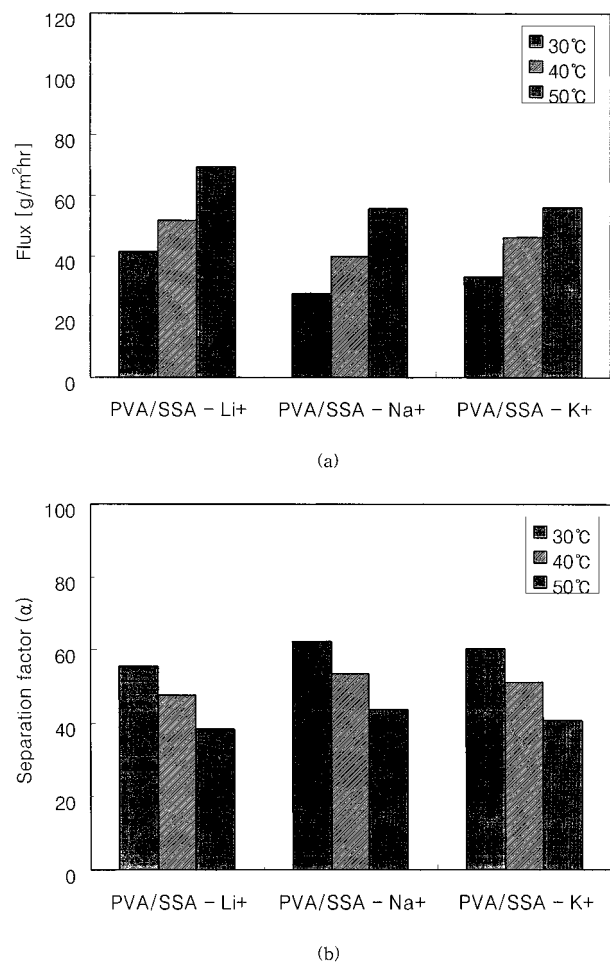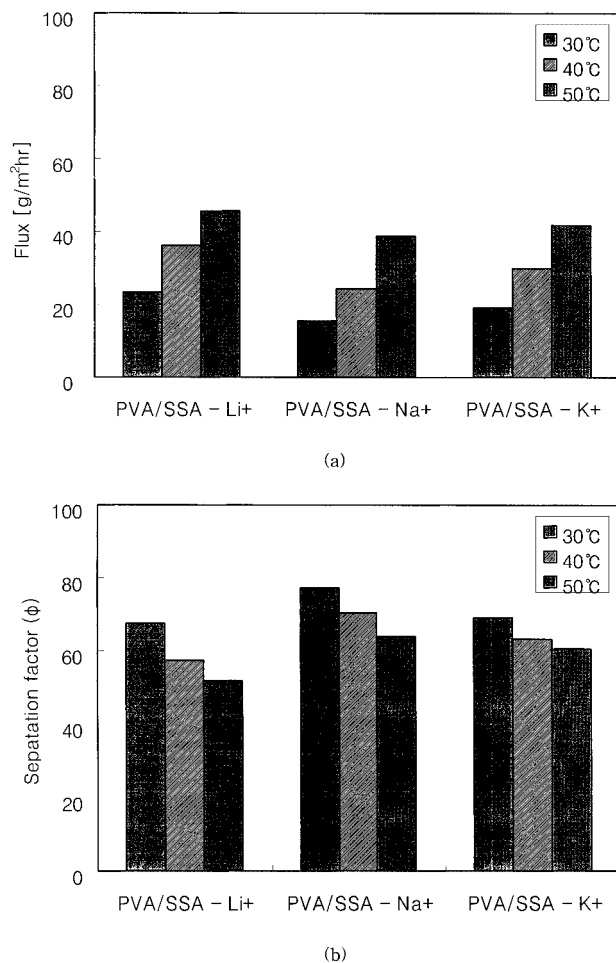

Figure 4 Flux and separation factors of PVA/SSA membranes exchanged with monovalent metal ions for 10/90 water–ethanol mixtures at various operating temperatures.

Figure 5 Flux and separation factors of PVA/SSA membranes exchanged with monovalent metal ions for 20/80 water–ethanol mixtures at various operating temperatures.

may be described with the concept of salting-out effect (the reduction of solubility of organic substances in aqueous–electrolyte solutions). Because the PVA/SSA membrane itself has SO_3^- H^+ groups inside membranes, counterions in question could penetrate inside the membranes and react with H^+ even if the degree of penetration would be different with the sizes of counterions. The metal ions inside the membranes inhibit the ethanol transport into the membrane phases by dissolving in water adsorbed by the membranes. Typical permselectivity results indicated that the flux was ~59 g/m²h and the separation factor was ~44 for water–ethanol (0/90) mixtures at 50 °C.

The flux and separation factors for 20/80 and 5/95 water–ethanol solutions are shown in Figures 5 and 6, respectively. The trends in both cases are very similar to that of the 10/90 water–ethanol solution.

Figure 6 Flux and separation factors of PVA/SSA membranes exchanged with monovalent metal ions for 5/95 water–ethanol mixtures at various operating temperatures.

CONCLUSIONS

PVA/SSA membranes in the hydrogen form were converted to metal ion forms, PVA/SSA-Li$^+$, PVA/SSA-Na$^+$, and PVA/SSA-K$^+$. These membranes were characterized by ESCA. The effect of exchange with metal ions was investigated with swelling and pervaporation experiments. The following conclusion can be drawn from the results:

1. The quantity of lithium ion in metal-ion-form membranes is greater than any other metal ion because of its small molecular size that allows easy penetration or diffusion into the membranes. The lithium was 2.176%, whereas sodium and potassium were 0.873 and 0.336% in the membranes, respectively.
2. The swelling ratio appeared in the following order: PVA/SSA-Li$^+$ > PVA/SSA-Na$^+$ > PVA/SSA-K$^+$. The salting-out effect and preferential sorption are dominant in the membrane swelling for mixtures.
3. For all water–ethanol mixtures, the flux for PVA/SSA-Li$^+$ membrane decreased with passing the minimum for PVA/SSA-Na$^+$ membrane and then increased. The separation factor results were opposite to what was expected. A typical result was that the flux was ~59 g/m^{2}h, and the separation factor was ~44 for 10/90 water–ethanol mixtures at 50 °C.

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