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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To cite this Article Kujawski, W. , Poźniak, G. , Nguyen, Q. T. and Néel, J.(1997) 'Properties of Interpolymer PESS Ion-Exchange Membranes in Contact with Solvents of Different Polarities', Separation Science and Technology, 32: 10, 1657 — 1667

To link to this Article: DOI: 10.1080/01496399708000726

URL: http://dx.doi.org/10.1080/01496399708000726

SEPARATION SCIENCE AND TECHNOLOGY, 32(10), pp. 1657–1667, 1997

Properties of Interpolymer PESS Ion-Exchange Membranes in Contact with Solvents of Different Polarities

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ABSTRACT

PESS membranes with sulfonic ion-exchange groups were prepared by chemical modification of a polyethylene/poly(styrene-*co*-divinylbenzene) interpenetrating polymer network with varying content of the crosslinking agent (DVB). PESS membranes were loaded with different alkali metal ions as counterions. Swelling and pervaporation properties of these membranes in contact with water and aliphatic alcohols were obtained. The obtained data show that properties of PESS membranes depend strongly on the kind of counterions, the degree of crosslinking, and the solvent polarity.

INTRODUCTION

Ion-exchange membranes are widely used in a number of separation techniques like electrodialysis, electroelectrodialysis, and diffusion di-

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alysis (1–3). It has also been reported that ionic membranes can be used in pervaporation for the fractionation of different liquid mixtures (4–11). 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 are expected to depend strongly on (12):

The nature of the polymeric backbone
The kind of ion-exchange sites
The kind of counterion

The PESS cation-exchange membranes obtained by chemical modification of an interpenetrating polymer network (13), such as the polyethylene/poly(styrene-*co*-divinylbenzene) [PE/poly(St-*co*-DVB)] system, have excellent osmotic and mechanical stability, and have high selectivity and good ion-exchange properties. These membranes are used for active transport of cations (14, 15) as well as for deacidification of aqueous solutions by means of diffusion dialysis (16, 17), Donnan dialysis, and/or Poźniak dialysis (18). The PESS membranes also show very good transport and selective properties in the separation of water–pyridine mixtures by pervaporation (8).

This work was aimed in the investigation of swelling and pervaporation properties of PESS membranes in contact with solvents of different polarity. The PESS membranes were obtained from the PE/poly(St-*co*-DVB) system with varying the content of the crosslinking agent (DVB) and were loaded with different counterions.

EXPERIMENTAL

Preparation and Physicochemical Properties of Interpolymer Cation-Exchange Membranes (PESS)

The PESS membranes were prepared by the chemical modification of the PE/poly(St-*co*-DVB) interpolymer system according to the following procedure (19).

The interpolymerization was carried out with a 1 wt% content of benzoyl peroxide (BPO). The PE/poly(St-*co*-DVB) interpolymer systems contained 30 wt% of poly(St-*co*-DVB) crosslinked with 1, 3, or 10 wt% of DVB. The interpolymer was chlorosulfonated at room temperature with a 30 vol% solution of chlorosulfonic acid in 1,2-dichloroethane for 4 hours and then hydrolyzed with 20 wt% NaOH aqueous solution for 18 hours.

Membranes that were prepared using 1, 3, or 10 wt% of divinylbenzene are denoted throughout this paper as PESS-1, PESS-3, and PESS-10, respectively.

In order to avoid any slow structural changes during the experiments, the samples of PESS membranes 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 swollen in water at 50°C for 4 hours.

Samples in a given ionic form were obtained by immersion of a sample of the hydrogen form for 24 hours in a 1-M solution of the appropriate hydroxide (Li^+, Na^+, or K^+), followed by repeated washing to remove any excess of caustic solutions. A schematic of the molecular structure of the sulfonated poly(St-*co*-DVB) is presented in Fig. 1.

The total cation-exchange capacity and water content were determined using standard methods (20, 21).

The specific resistance was measured in 0.1 M NaCl by the modified procedure described by Gryte and Gregor (22). The tensile strength and the elongation at break of the membrane swollen in water (in the hydrogen form) were measured with a tensile testing device ZT-40 (19).

Table 1 summarizes the determined physicochemical properties of PESS membranes.

Swelling Measurements

Membrane swelling caused by the sorption of solvents into the membrane was determined gravimetrically. The weight swelling ratio (S_W) and molar swelling ratio (S_M) of a given membrane were calculated according to the following equations:

$$S_W = (m_s - m_d)/m_d \quad \text{(g solvent/g dry membrane)} \qquad (1)$$

$$S_M = (S_W/M_{sol}) \quad \text{(mole solvent/kg dry membrane)} \qquad (2)$$

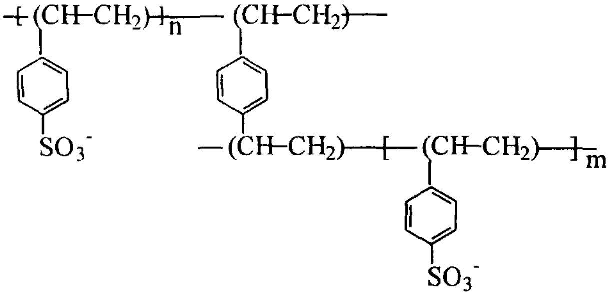

FIG. 1 Schematic of the molecular structure of the sulfonated poly(St-*co*-DVB).

TABLE I
Physicochemical Properties of PESS Membranes in the Hydrogen Form

Membrane	Water content (g/g)	Specific resistance[a] (Ωm)	Tensile strength (MPa)	Elongation at break (%)
PESS-1	0.830	1.2	9.8	120
PESS-3	0.650	1.6	10.5	88
PESS-10	0.336	2.8	12.3	36

[a] Determined for membranes in the sodium form.

where m_s = the weight of the swollen membrane
m_d = the weight of the dry membrane
M_{sol} = molecular weight of the solvent

Swelling measurements were performed for PESS-1, 3, and 10 membranes loaded with lithium, sodium, or potassium counterions and in the contact with following solvents: water, methanol, ethanol, isopropanol, and isobutanol.

Pervaporation Experiments

The vacuum pervaporation experiments were performed by using the standard setup described elsewhere (8). The system was operated at 25° C and at a pressure on the permeate side below 1 mbar.

The following solvents were used as a single component feed: water, methanol, ethanol, propanol, and isopropanol. Experiments were performed with the PESS-1 membrane in the lithium form. The permeate flux (J_{PV}) was determined for each solvent during experiments. The pervaporation permeability coefficient (P_{PV}) was calculated according to the following equation (23):

$$J_{PV} = P_{PV} \frac{\Delta p}{l} \tag{3}$$

where Δp = difference in the vapor pressure between feed and permeate side (Pa)
l = thickness of the membrane (m)

Infrared Spectra

IR spectroscopic measurements were carried out with the attenuated total reflectance (ATR) mode on an FT-IR Bruker spectrometer. Usually

128 interferograms were co-added, and the Fourier transform was calculated at a resolution of 2 cm^{-1}. The spectra were recorded in the 4000–400 cm^{-1} range at 20°C. Spectra were collected for the PESS-I dry membrane and solvent-swollen membranes in different alkaline ionic forms (7, 24).

RESULTS AND DISCUSSION

Membrane Swelling

The molar swelling ratio (S_M) gives a qualitative indication of the membrane affinity for a given solvent or liquid mixture.

Swelling of ion-exchange membranes in polar solvents is caused by the solvation tendency of fixed ionic groups and counterions, the osmotic activity of the counterions, and the electrostatic repulsion between dissociated fixed ionic groups. The membrane expands until swelling equilibrium is attained, i.e., when the osmotic and electrostatic forces are balanced by the tendency of the expanding polymer matrix to contract.

Results presented in Table 2 indicate that for all membranes swollen in water, S_M decreases with increasing degree of membrane crosslinking. The highly crosslinked membrane PESS-10 possesses only a limited ability to swell, which is consistent with results obtained for ion-exchange resins equilibrated with water (26).

The swelling ratio in water changes also when, for a given membrane, the counterions are replaced by others. For the ionic forms of PESS membranes investigated, the swelling ratio decreases in the order similar to that of the cation hydration numbers (25): $H^+ > Li^+ > Na^+ > K^+$.

The swelling behavior of PESS membranes in contact with different solvents is presented in Table 3. In this table the values of dielectric constants and the molar volumes of solvents are also given. The dielectric constant is often used as a factor of solvent polarity, whereas the molar volume gives information about the space hindrances exerted by the solvent during sorption and transport through the membrane.

TABLE 2
Molar Swelling Ratio (S_M) of PESS Membranes Swollen in Water

Ionic	S_M (mole/kg dry membrane)			Hydration number
form	PESS-1	PESS-3	PESS-10	of cation (25)
Hydrogen	46.1	36.1	18.9	3.9
Lithium	43.2	33.2	17.8	3.3
Sodium	33.9	26.0	16.6	1.5
Potassium	26.2	19.9	14.4	0.6

TABLE 3
Molar Swelling Ratio (S_M) of the PESS/Li$^+$ Membranes in Contact with Different Solvents

Solvent	S_M (mole/kg dry membrane) PESS-1	PESS-3	PESS-10	Dielectric constant (27) (—)	Molar volume (cm^3/mol)
Water	43.3	33.4	17.8	80.2	18.0
Methanol	12.4	10.7	8.3	31.2	40.5
Ethanol	7.4	5.1	4.9	24.3	58.4
n-Propanol	2.3	2.2	2.1	22.2	74.7
i-Propanol	4.5	3.8	3.5	13.8	76.5
i-Butanol	1.6	1.5	1.4	18.0	92.9

For a given membrane, swelling decreases strongly with decreasing solvent polarity. The membrane swelling in different solvents also decreases with an increasing degree of crosslinking. However, this relationship is less pronounced for membranes equilibrated with higher alcohols.

An explanation of the swelling behavior of PESS membranes in contact with different solvents can be made by using the results of IR experiments. The sulfonic anions have two active stretching vibrations in the infrared region (28, 29).

1. A symmetric stretching vibration (ν_s) at 1030–1050 cm^{-1}. The position of the symmetric stretching vibration band of the sulfonic group (ν_s) is related to the state of its local chemical environment (24, 29).
2. An antisymmetric stretching vibration (ν_{as}) at about 1200 cm^{-1}, which occurs as a doublet. The splitting of the antisymmetric stretch is caused by the polarization of one of the S—O bonds due to asymmetric attachment of the monovalent counterion to the sulfonic group (Fig. 2). The splitting of the antisymmetric stretching vibration band (ν_{as}) increases with increasing electrostatic field of the cation (28, 29).

Table 4 presents the frequencies of the ν_s band for different ionic forms of the PESS-1 membrane in the dry state or swollen in chosen solvents.

For all dry membranes the frequency ν_s shifts toward higher wavenumbers when the counterion is changed from K$^+$ to Li$^+$; that is, when the induced polarization of the S—O dipole increases (28, 29).

In pure water, all counterions lead to the same frequency of the S—O symmetric stretch. This behavior means that the same environment was obtained for the sulfonic group, whatever the counterion. All types of alkaline sulfonates undergo dissociation and hydration, and the sulfonate

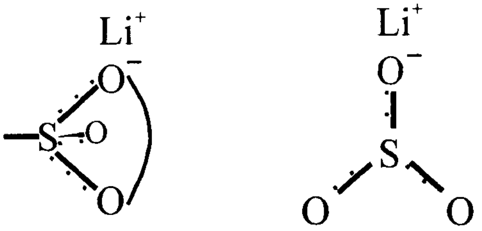

FIG. 2 Asymmetrical attachment of the lithium counterion to the sulfonic anion.

groups are shielded from the influence of the electrostatic field of cations (28, 29).

On the other hand, it is seen from Table 4 that after equilibration with pure alcohols, the position of the ν_s band in the PESS-1 membranes remains close to that in the dry membranes. This suggests that the alcohol molecules cannot dissociate the contact ion-pairs. That difference between the influence of water and alcohol molecules resides in the different abilities of these solvents to dissociate contact ion-pairs. Due to their low dielectric constant (Table 2), alcohols as solvents are known to possess lower dissociation abilities. Following the concept of the multistep mechanism of ion-pairs in electrolytic solutions as proposed by Eigen et al. (30), one can conclude that in the PESS membrane equilibrated with water, the sulfonic anion–lithium counterion pairs form completely dissociated hydrated ion-pairs (Fig. 3A). However, when the membrane is equilibrated with pure alcohols, the sulfonic anion–lithium counterion pairs remain undissociated and form so-called inner-sphere complexes (Fig. 3B) (31). The absence of dissociation of alkali sulfonates in alcohols means

TABLE 4
Frequency of the Symmetric Stretching Vibration Band of the Sulfonic Anion (ν_S) in PESS-1 Membranes

Ionic form	Position of symmetric stretching vibration band ν_S of SO_3^- anions (cm^{-1})			
	Dry	Water	Ethanol	i-Propanol
Lithium	1046.3	1035.7	1046.3	1044.0
Sodium	1039.6	1035.7	1040.5	1039.6
Potassium	1037.6	1035.7	1037.6	1036.7

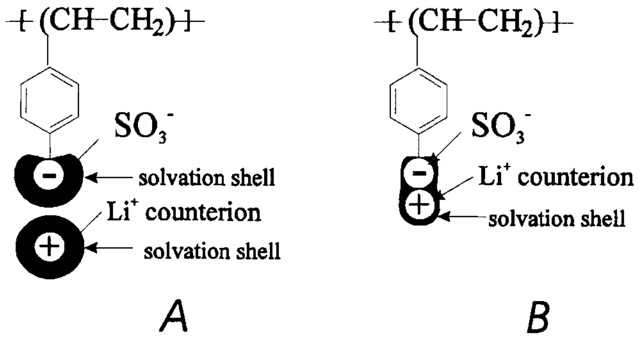

FIG. 3 Solvation-mediated dissociation equilibrium between styrene-sulfonic groups and lithium counterions in PESS membrane. A: Completely dissociated solvated ion-pairs (PESS membrane equilibrated in water). B: Undissociated inner-sphere complex (PESS membrane equilibrated in pure alcohol).

that interactions between the solvents and the ions are not strong enough to overcome the attractive energy in contact ion-pairs (30, 31).

Pervaporation

Table 5 presents the values of molar pervaporation flux and the permeability coefficient of different solvents, calculated according to Eq. (3).

The results presented prove the high preference of the PESS ion-exchange membrane toward the transport of water molecules. Pervaporation permeate flux decreases with increasing hydrophobicity of the transported alcohols. The permeability coefficient for water is 20–30 times higher than

TABLE 5
Pervaporation Flux (J_{PV}) and Permeability Coefficient (P_{PV}) of Solvents in the Single Component Pervaporation Transport through PESS-1/Li$^+$ Membrane

Solvent	Pervaporation flux J_{PV} (10^{-4} mol/m^2·s)	Permeability coefficient P_{PV} (10^{-11} mol/m·s·Pa)
Water	86.7	81.2
MeOH	21.1	3.32
EtOH	7.43	2.58
i-PrOH	0.42	2.53
n-PrOH	0.19	2.25

TABLE 6
Pervaporation Fluxes (J_{PV}) of Water and Alcohol in the Binary Mixtures through PESS-1/Li^+ Membrane

	Water concentration (wt%)		J_{PV} (10^{-4} mol/m^2·s)	
Mixture	Feed[a]	Permeate	Water	Alcohol
Water/EtOH	4.6	12.6	2.64	5.49
Water/*i*-PrOH	12.0	63.0	5.83	1.03
Water/*n*-PrOH	26.8	75.2	10.67	1.06

[a] Azeotropic composition.

that for alcohols (Table 5). It should be added, however, that in binary water/alcohol mixtures, the selectivy and transport properties of a membrane depend strongly on the feed composition. The selectivity is usually lower than that expected from single component data (Tables 5 and 6). This is due to the synergetic effects between transported molecules and between mixture components and the membrane material (5).

The results presented above are consistent with the results of sorption experiments and IR observations. On the basis of the above results, we can conclude that the transport properties of the PESS ion-exchange membrane depend strongly on the state of the ion pairs of the ionic groups. If the membrane is equilibrated with water, all ion pairs are dissociated and mass transfer occurs through hydration shells and water clusters. On the other hand, if the membrane is equilibrated with alcohols, the ion pairs in the PESS membrane remain undissociated. In this latter case the permeation of alcohol molecules occurs via a solution–diffusion mechanism through both charged segments and the amorphous matrix of the membrane.

CONCLUSIONS

The PE/poly(St-*co*-DVB) system is known to be microheterogeneous; isolated microdomains of poly(St-*co*-DVB) are distributed within a PE network. In this type of membrane, PE serves as the inert matrix and poly(St-*co*-DVB) with sulfonic groups serves as the crosslinked polyelectrolyte. Both the amount of DVB in the copolymer and the kind of counterion influence the properties of PESS ion-exchange membranes.

An increase of DVB content leads to a decrease in membrane swelling. The swelling behavior is also highly dependent on the type of counterion in the membrane. For the alkali cation series, swelling decreases in the following sequence: $H^+ > Li^+ > Na^+ > K^+$.

The swelling and transport properties of PESS membranes also depend strongly on the polarity of the given solvent. The swelling and permeation rates decrease with decreasing polarity of the solvent. Such membrane behavior can be attributed to the solvent-mediated dissociation equilibrium between unbounded counterions and sidechain-bonded sulfonic groups. PESS membranes show good swelling and transport properties in contact with water and show much poorer properties in contact with alcohols.

Such results suggest that PESS ion-exchange membranes could be used for the separation of organo-aqueous solutions by pervaporation. The results of our investigation of the swelling and transport properties of PESS membranes in contact with water–organic solutions will be reported soon from our laboratory.

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Received by editor January 3, 1996
Revision received November 1996