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Selective composite cation-exchange membrane based on S-PVDF

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ABSTRACT

A novel cation-exchange membrane composed of a blend of polyvinylidene fluoride (PVDF) and sulfonated PVDF (S-PVDF) was synthesized. The membranes were prepared with different fractions of S-PVDF to optimize their performance in desalination. The ion-exchange capacity (IEC), transport number, apparent selectivity, ion conductivity, crystallinity, water uptake, contact angle, and performance in electrodialysis (ED) were evaluated. With increasing S-PVDF fractions, the transport number and permselectivity decreased, while the IEC and membrane conductivity increased. Finally, the salt extraction in ED obtained for a 70% S-PVDF membrane was 67.6%, which had a better performance than that of a commercial membrane. Also the membranes showed a good selectivity for bivalent cation removal. Membrane structure was evaluated by XRD and showed a decrease in ordering by increase in S-PVDF.

Keywords: Sulfonated PVDF; Cation-exchange membrane; Electrodialysis; Composite membrane; Cation selectivity

1. Introduction

Ion-exchange membranes (IEMs) have many applications in electrodialysis (ED) such as desalination of brackish water [1,2] and water softening by selective permeation of bivalent cations [3]. One of the common methods in the synthesis of cation-exchange membranes (CEMs) is sulfonation of polymers thus providing the required ion-exchange capacity (IEC) and cation conductivity in membrane [4,5]. A major drawback in sulfonated membranes is their dimensional instability, related to the increase in water affinity of the sulfonated polymer. Another problem is the dissolution in water of sulfonated polymers with a high degree of sulfonation, which requires a balanced sulfonation reaction [6]. To overcome this drawback, polyvinylidene fluoride (PVDF), was selected as a hydrophobic and chemically stable polymer to be sulfonated.

In the synthetic method of this work, the polymer powder was directly sulfonated by suspension in acid. Since acid molecules can diffuse easily between the powders and the reaction area is increased, a high reaction yield can be obtained. To improve the thermal

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and mechanical stabilities of the membrane, the prepared sulfonated PVDF (S-PVDF) was blended with PVDF in different percentages by solution blending.

Systematic characterization of the composite S-PVDF/PVDF membranes was conducted to investigate the relation between synthetic conditions and membrane properties in view of optimum performance of composite membranes in ED application.

2. Experimental

2.1. Materials

PVDF (grade Solef® 6020) was purchased from Solvay. Other materials that were used include 1, 2-dichloroethane (≥98%) from Merck, chlorosulfonic acid (≥95%) from Fluka, and N-methyl-2-pyrrolidone (NMP) (ACS reagent, 98%) from Acros. Commercial CEM (FKS-PET-130) and anion-exchange membranes (AEM) (Fumasep® FAB) membranes were bought from FuMA-Tech (Germany). These membranes were selected because of their high permselectivity, low resistivity, and very high mechanical stability. Hydrochoric acid (HCl) 1 N and sodium hydroxide (NaOH) (beads with 97% purity) were prepared from VWR chemicals.

2.2. Synthesis of S-PVDF

Ten grams of PVDF powder was added to 50 ml chlorosulfonic acid and mixed at a temperature of 80˚C for 45 min. The product was precipitated first in 1,2- dichloroethane and then in deionized water. The resulting precipitate was filtered (by 0.45 μm glass fiber filters) and washed with 1,2-dichloroethane and deionized water. The obtained S-PVDF was then dried in a vacuum oven at 50˚C for 1 h.

2.3. Synthesis of S-PVDF/PVDF composite membrane

S-PVDF/PVDF membranes were prepared using the co-dissolution method in N-methyl-2-pyrrolidone (NMP) (ACS reagent, 98%). A 10% solution of S-PVDF in NMP and a 10% solution of PVDF in NMP were prepared separately and then added in an appropriate amount under stirring to form S-PVDF/PVDF blends with the share of S-PVDF ranging from 30 to 70%. The blended solutions were casted on a glass plate with a casting knife and then dried in a vacuum oven at 60˚C overnight. Then, the synthesized membranes were peeled off by immersion of the glass plate in water and were put in 1 M NaCl in solution for at least 24 h to reach equilibrium conditions (maximum exchange of Na^+ and membrane proton).

The prepared membranes were characterized by different methods to evaluate the effect of membrane properties on their performance in desalination and cation selectivity. Also, ED performance of synthesized membranes was compared with a commercial CEM to find the best preparation conditions.

2.3.1. Morphology

The ordering and crystallinity of membranes were evaluated by X-ray diffraction (XRD) method. The XRD studies were performed on a Philips X-ray diffractometer (PW1830 model) using a Cu Kα radiation source (1.542 Å). The scan range (2θ) was 5–50˚ at a scan rate of 2˚ $\min^{-1}$.

2.3.2. Water uptake

All composite membranes were dried in vacuum at 80˚C for 4 h before testing. The sample membranes were soaked in deionized water at room temperature for 24 h. The water remaining on the surface of the wetted membrane was removed using tissue paper before weighing. The water uptake was calculated by:

$$\text{Uptake} = [(w_{\text{wet}} - w_{\text{dry}})/w_{\text{dry}}] \times 100\% \tag{1}$$

where w_{wet} and w_{dry} were the masses of dried and wet samples, respectively.

2.3.3. Contact angle

The contact angles of water on membranes were determined at room temperature with a Kruss device (DSA 10-MK2, Germany) according to the plate method. At least three angles were measured and averaged for every sample.

2.3.4. Transport number and permselectivity

The value of the counter-ion transport number in the membrane phase (t_+^m) was estimated from membrane potential data using Eq. (2):

$$\Delta E = \left(2t_+^m - 1\right)\frac{RT}{nF}\ln\left(\frac{\alpha_1}{\alpha_2}\right) \tag{2}$$

where α_1 and α_2 are the mean activities of electrolytic solutions, n is the electrovalence of counter-ion, R is the universal gas constant (~8.314 J K^{-1} mol^{-1}), F is the Faraday constant (~96,485.3 C mol^{-1}), and T is the temperature in Kelvin [7]. The membrane potential was measured by a two-compartment cell, in which a membrane with 22 cm^2 effective area separated two NaCl solutions of different concentrations (0.01 and 0.1 M).

The permselectivity (P_S) is a measure for the preferable transport of counter-ions in the membrane, thus, it is related to the ion fluxes in the membrane. The permselectivity is defined as:

$$P_S = \frac{t_+^m - t_+^{sol}}{1 - t_+^{sol}} \tag{3}$$

where t_+^{sol} is the solution transport number of the counter ion in the membrane (with no concentration profiles in the solution) [8]. Sodium chloride has a solution transport number of approximately 0.39 for its cation in water at 25°C [9].

2.3.5. Membrane conductivity

Conductivity was measured according to the procedures described earlier [10]. A clip cell was used which was composed of two graphite electrodes fixed in Plexiglass container with an effective area of 22 cm^2. The membrane was first equilibrated in a 1 M NaCl solution before being placed in the cell. The resistance of the membranes was measured at room temperature by impedance spectroscopy using a digital LCR meter (HP 4262A) at a frequency of 1,500 KHz and in a 0.5 M NaCl solution. Then, the membrane resistance (R_{mem}) was calculated by subtraction of the electrolyte resistance (here, R_{sol} is the resistance of electrolyte in the cell measured without any membrane) from the membrane resistance equilibrated in electrolyte solution (R_{cell}), according to the equation $R_{\text{mem}} = R_{\text{cell}} - R_{\text{sol}}$. Based on the electrical resistance measurement, the conductivity (σ, S cm^{-1}) of the membranes was calculated according to the following equation;

$$\sigma = \frac{L}{R_{\text{mem}} A} \tag{4}$$

where L is the thickness of the membrane (cm) and A is the effective area of the membrane (cm^2).

2.3.6. Ion-exchange capacity

The IEC of the membranes was estimated by a conventional titration method [10]. A piece of membrane was exchanged with H$^+$ by immersing the sample in 50 ml of 1 M HCl solution for 24 h. The membrane was washed with distilled water until neutral pH to remove any excess of H$^+$ ions. Then, the sample was dried at 80°C overnight in vacuum and weighted (W_{dry} in g). Afterwards, the membrane was immersed in 25 ml of a 1 M NaCl solution during 24 h to exchange the H$^+$ with Na$^+$. The resultant solution was then titrated by an aqueous solution of 0.01 M (C_{NaOH}) NaOH (equivalent volume = V_{NaOH} in ml). The ion-exchange capacity was expressed in milliequivalents of sulfonic groups per gram of dry polymer (meq/g) and was obtained by the following equation:

$$\text{IEC} = C_{\text{NaOH}} \times V_{\text{NaOH}} / W_{\text{dry}} \tag{5}$$

2.3.7. Electrodialysis

For the ED experiments, a Berghof BEL-500 system was used, which included two AEM and two CEM. The CEM was in contact with the anode in order to prevent Cl_2 production ($2Cl^- \rightarrow Cl_2 + 2e^-$) at the anode [11]. The effective surface area of the ED stack was 58 cm^2 for each membrane. The equipment consisted of three separated circuits for the diluate, the concentrate, and electrode rinsing solutions, each with a volume of 3 L and recirculated by a separate centrifugal pump. The initial concentration in the diluate and concentrate compartments was 0.01 M NaCl; the concentration of Na_2SO_4 in the rinsing circuit was 0.1 M. The membrane stack was connected to a DC electrical potential through TiO_2-coated titanium electrodes. During a 2 h experiment, the voltage was kept constant at 5 V. The synthesized and commercial membranes were cut in 10 cm × 10 cm pieces and perforated to fit in the ED system.

For two cation mixtures, the initial concentration in the diluate and concentrate compartments was 0.01 M NaCl + 0.01 M $MgCl_2$. The ED performance was evaluated by conductivity measurement (using a CDM 83 conductivity meter) of diluate each 30 min. The ion selectivity was calculated as [12]:

$$P_{\text{Na}}^{\text{Mg}} = \frac{t_{\text{Mg}}/t_{\text{Na}}}{C_{\text{Mg}}/C_{\text{Na}}} \tag{6}$$

where t_{Mg} and t_{Na} are the transport numbers of the divalent cation (Mg) and the monovalent cation (Na) in the membrane, and C_{Mg} and C_{Na} are the average concentrations of magnesium and sodium during electrodialysis. The concentration of initial and final samples was measured by atomic absorption spectroscopy (AAS) (Perkin Elmer AAnalyst 100).

3. Results and discussion

3.1. Water uptake and contact angle

Table 1 summarizes the water uptake and contact angle of different composite membranes.

An enhanced water uptake with decreasing contact angle and consequently increasing surface hydrophilicity was observed by increasing the amount of S-PVDF. The molecular structure of S-PVDF is composed of a hydrophobic backbone and hydrophilic sulfonic acid groups, and the hydrophilic ion clusters are basically responsible for the water uptake of the polymer [13].

3.2. Morphology

Membrane structure and morphology were evaluated by X-ray diffraction to indicate the chain ordering and crystallinity in composite membranes. The XRD patterns for different composite membranes are given in Fig. 1. As shown, no distinctive crystal structure was observed. Warren and co-workers [14] found that the ratio of half-width- to-height (HW/H) of the X-ray diffraction peak reflects ordering in the polymer backbone. The smaller the value of HW/H is, the higher the ordering [15]. Therefore, the values of HW/H were determined for different membranes (Table 2).

According to the obtained data, HW/H raised by increase in S-PVDF amount and shows that the higher the amount of S-PVDF, the less ordered the structure becomes. This is due to sterical hindrance of S-PVDF for chains alignment compared to PVDF.

3.3. Transport number and permselectivity

The transport number and permselectivity were decreased by an increase in the S-PVDF percentage (Table 3). This phenomenon can be explained by the membrane potential.

The membrane potential equation proposed by Meyer–Severs–Teorell [16] is a sum of the Donnan potential at both sides of the membrane and the diffusion potential through the membrane. Increase in S-PVDF amount in the matrix, and consequently of the number of sulfonic groups, will improve the Donnan potential at the two sides of the membrane. The enhanced water uptake and enlargement of the ionic transfer channels in the membrane matrix due to the decrease in composite chains ordering leads to diffusion of co-ions through the membrane and a decrease in the diffusion potential for counter-ions [8]. This idea was confirmed by XRD measurements (see Table 2).

Table 1
Water uptake and contact angle of S-PVDF/PVDF membranes

S-PVDF (wt.%)	30	50	70
Water uptake (wt.%)	**4.3**	**8.4**	**14.6**
Contact angle (º)	**72.5**	**65.8**	**61.8**

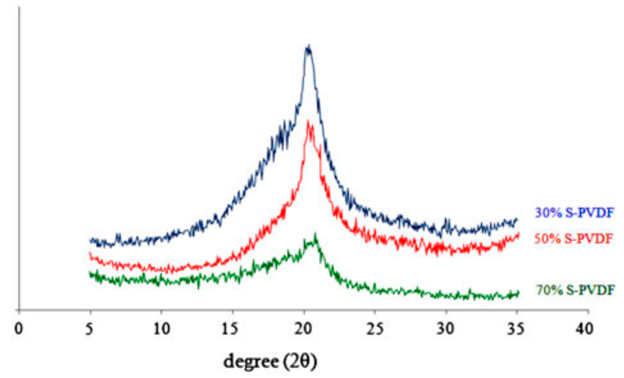

Fig. 1. X-ray diffraction patterns of different composite membranes.

3.4. Ion-exchange capacity (IEC)/membrane conductivity

IEC and membrane conductivity data are plotted in Fig. 2. These two parameters are improved with increasing S-PVDF percentage. This is due to the increase in sulfonic groups, which allow for cation-exchange and ion conductivity in the membrane. Ion-exchange membrane properties are closely related with IEC, considering the fact that the amount, and species, of ion-exchange groups determine the membrane's performance [17].

3.5. Electrodialysis

Finally, the performance of the synthesized membranes was evaluated by carrying out ED experiments, measuring the NaCl removal with the newly produced membranes and comparing them to the commercial membrane. Also the performance of binary cation solution and the selectivity of magnesium to sodium were calculated for composite membranes. The amounts of NaCl removal after 2 h are shown in Fig. 3.

The final NaCl removal results in a negligible increase from the 30% S-PVDF membrane to the 50% S-PVDF membrane. A clear increase in NaCL improvement was shown in the 70% S-PVDF

Table 2
X-ray diffraction pattern analysis of composite membranes

	Amorphous peak (°)	*d*/amorphous (Å)	*W* (°)	*H* (CPS)	*HW*/H
30% S-PVDF	20.4	4.35	13.2	291	0.023
50% S-PVDF	20.4	4.36	14.6	220	0.033
70% S-PVDF	20.7	4.28	10.5	69	0.076

Table 3
Transport number and permselectivity

S-PVDF %	Transport number	Permselectivity
30	0.97	0.95
50	0.95	0.92
70	0.94	0.90

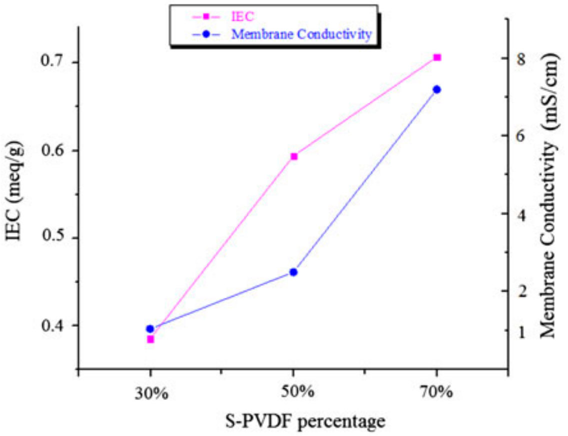

Fig. 2. IEC and membrane conductivity of composite membranes.

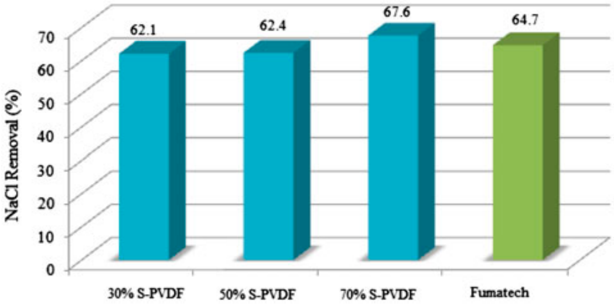

Fig. 3. NaCl removal chart for different membranes after 2 h.

membrane, which performed almost better than the commercial one. There is a trade-off between membrane permselectivity, on the one hand and IEC and membrane conductivity, on the other. This challenge can explain why at 50% amount of S-PVDF the performance cannot improve well. At lower percentages of S-PVDF, the higher selectivity of the membrane can compensate the lower IEC and conductivity, so that the performances at 30% and 50% are similar. However, at higher percentage (70%), the IEC and conductivity increase significantly, which surmount the lower transport number and selectivity.

The reduction in solution conductivity of diluate for a binary mixture of NaCl and $MgCl_2$ is presented in Fig. 4. As shown, the conductivity reduces as the same trend of monovalent salt removal and therefore, with increase in S-PVDF amount, the final ion removal will increase.

Furthermore, the separate cation removal values for each membrane after 2 h with the corresponding selectivities are given in Fig. 5 and Table 4, respectively. The result indicates that all membranes are selective for Mg^{2+} and the 50% S-PVDF membrane has the highest selectivity (>3.4). This indicates that these membranes are suitable for water softening.

To explain the selectivity of these membranes, the diffusion theory of cations through a CEM can be applied. Firdaous et al. [18] argue that cations diffuse in a membrane by their hydration shell, but the passing of a solution–membrane interface requires

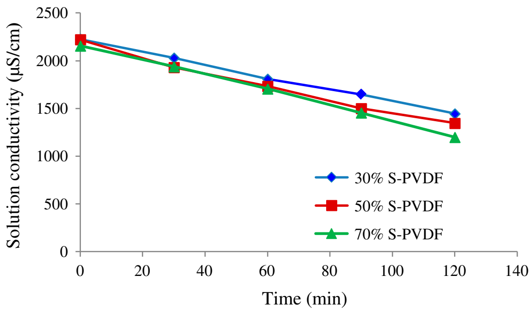

Fig. 4. Conductivity of diluate solution for binary cations in different membranes by ED test.

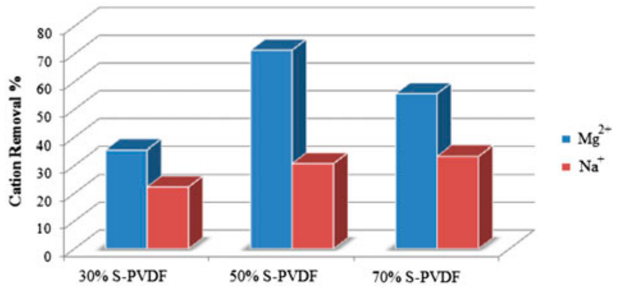

Fig. 5. Cation removal percentage for different membranes.

Table 4
Cation selectivity for different membranes

Membrane	S-PVDF 30%	S-PVDF 50%	S-PVDF 70%
P_{Na}^{Mg}	1.74	3.41	2.01

overcoming an energy barrier caused by the necessity of partial dehydration of ions. The effective parameter for this barrier breakage is the hydration energy of cations. This can be expressed by the ratio of hydrated-ion-hop/not-hydrated-ion-hop, which is equal to 0.10 and 5.65 for Na^+ and Mg^{2+}, respectively. Thus, Mg^{2+} cations intend to jump inside the membrane in their hydrated state and therefore a hydrophilic surface provides more diffusion of Mg^{2+} than of Na^+. Furthermore, Van der Bruggen et al. [19] described the effect of cation entrapment in anionic membrane due to their charge.

With increase in S-PVDF, the surface hydrophilicity and water uptake will increase thus providing more diffusion of bivalent cation. However, the more sulfonic groups are present in the structure, the more bivalent electrically movement is hindered. So, when S-PVDF reaches to 70%, the effect of charge interaction will decrease the role of hydrophilicity and selectivity will decrease.

4. Conclusion

A novel composite membrane was synthesized based on PVDF blended with sulfonated PVDF. The effect of a different percentage of S-PVDF in the PVDF matrix was evaluated by different characterization methods. It was concluded that with an increase in the S-PVDF fraction, the permselectivity will decrease, while the IEC and membrane conductivities improve and this will cause a trade-off in salt removal performance. Seventy per cent S-PVDF gave the best salt removal, with results even better than that of a commercial membrane. The composite membranes show a good selectivity for bivalent cations and the 50% S-PVDF membrane gave the best selectivity up to 3.4. This result was explained by diffusion phenomena of cations through the membranes and it was concluded that a trade-off exists between water affinities of the membrane and electrical entrapment of the higher charged cations due to S-PVDF increase in membrane.

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