

Preparation and Electrochemical Characterization of Sulfonated Polysulfone Cation-Exchange Membranes: Effects of the Solvents on the Degree of Sulfonation

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ABSTRACT: Sulfonated polysulfone cation-exchange membranes with various degrees of sulfonation were prepared by a treatment with chlorosulfonic acid in different solvents of various polarities, and the effect of the solvent polarity on the degree of sulfonation was explored. These membranes were characterized by their ion-exchange capacity, volume fraction of water, and electrochemical properties. The counterion transport numbers, permselectivity, and fixed charge densities of these membranes were estimated from membrane potential data and varied with the degree of sulfonation, concentration,

and external salt concentration. The counterion mobility in the membrane phase was also estimated from membrane conductance measurements. These membranes were found to have good electrochemical properties and are suitable for various types of electromembrane processes. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2344–2351, 2005

Key words: charge transport; functionalization of polymers; membranes; poly(ether sulfones)

INTRODUCTION

Various types of electromembrane processes^{1–6} using ion-exchange membranes (IEMs) have been widely studied in the last decade. Thus, the development of IEMs with excellent electrochemical and mechanical properties is essential to enhancing the process efficiency. Polysulfone (PS) is an important thermoplastic that displays excellent resistance to hydrolysis and oxidation and has good mechanical and thermal stability.^{7,8} Various sulfonation methods for adding sulfonic acid groups to PS are available in heterogeneous or homogeneous media with sulfuric or chlorosulfonic acid. The use of chlorosulfonic acid to produce ionic or polyelectrolyte structures appears to be straightforward. Kerres et al.⁹ reported a quantitative and regio-specific method for adding sulfonate groups to aromatic rings of Udel poly(ether sulfone) via a metalation–sulfonation–oxidation reaction. Meham et al.¹⁰ developed a method for the preparation of sulfonated polysulfone (SPS) with monomer modification with an SO₃ and triethyl phosphate complex. However, this method is relatively inconvenient and expensive. Quentin¹¹ reported that bisphenol A/PS could be sul-

fonated by chlorosulfonic acid to produce a sulfonated arylene ether sulfone. However, we must be concerned with the possibility that the chlorosulfonic acid treatment is capable of cleaving bisphenol A/PS partially at the isopropylidene link or that it might undergo branching and crosslinking reactions by the conversion of the intermediate sulfonic acid group into a partially branched or crosslinked sulfone unit.¹² The extent of these side reactions for the sulfonation of PS mainly depends on the reaction conditions and polarity of the solvents used. Thus, we found it to be necessary to study the extent of sulfonation of PS in different solvents with various polarities.

The sulfonation of PS was carried out with chlorosulfonic acid in different solvents with various dielectric constants to explore the effect of the solvent polarity on the extent of sulfonation. Different membranes of SPS were prepared via dissolution in *N,N*-dimethylacetamide of a known concentration. The electrochemical transport properties of these membranes were analyzed with respect to the extent of sulfonation and the concentration of the membrane casting solution.

EXPERIMENTAL

Materials

Udel PS was used as the starting material and was obtained from Aldrich Chemicals. Chloroform (CHL), dichloromethane (DCM), dichloroethane (DCE), metha-

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nol, chlorosulfonic acid, sodium chloride, sodium hydroxide, and hydrochloric acid (analytical grade reagent) were supplied by S. D. Fine Chemicals (India) and were used without further purification. Distilled water was used in all the experiments.

Preparation of the SPS membranes

PS (Udel 35000; 10 g) was dissolved in 100 mL of different solvents [CHL, dielectric constant at 20° (ϵ) = 4.80; DCM, ϵ = 9.14; and DCE, ϵ = 10.42] separately. Each solution was kept in an ice bath at 0°C. The solvent (50 mL) and 10 mL of chlorosulfonic acid were mixed and added dropwise to the PS solution, with the temperature kept at 0°C. For the different solvents, the rate of the addition time was kept constant. After the complete addition of the mixed solution, the polymer was precipitated in 500 mL of methanol, washed with methanol until it was free of acid, and dried in an oven at 50°C. The yield of the polymer was recorded. The membranes were prepared via the casting of viscous solutions of SPS in *N,N*-dimethylacetamide of known concentrations (the mass fraction was varied between 20 and 40%) onto a clean glass plate, which was latter dried in a vacuum oven at 60°C to remove the residual solvent completely. The membranes were piled out from the glass plate by being dipped in cold water. The details of the different steps involved in the membrane preparation are presented in Figure 1. The membranes were equilibrated in 1M hydrochloric acid and sodium hydroxide alternately and were finally equilibrated in 1M sodium chloride solutions overnight. The membranes were equilibrated in the experimental solution before their evaluation. The different membranes were named SPS/X/Y, where X is the solvent and Y is the mass fraction of SPS in the casting solution.

A CHNS analysis was carried out with a PerkinElmer 2400 CHNS/O analyzer (Wellesley, MA). Fourier transform infrared (FTIR) spectra were recorded with a Spectrum GX Series 49387 (Boston, MA), whereas ¹H-NMR spectra were recorded with a Bruker DPX-200 FT-NMR (200-MHz) instrument (Rheinstetten, Germany).

Ion-exchange capacity (IEC) and volume fraction of water (φ_w)

IEC was determined by the equilibration of the membranes in 1M HCl or 1M NaOH solutions to convert the membranes into the H⁺ or OH⁻ form; they were washed free of excess HCl or NaOH with distilled water and equilibrated in distilled water to remove the last traces of the acid or base. Then, they were equilibrated in 0.1M NaCl for 24 h, and IEC was determined from the increase in the acidity or basicity,

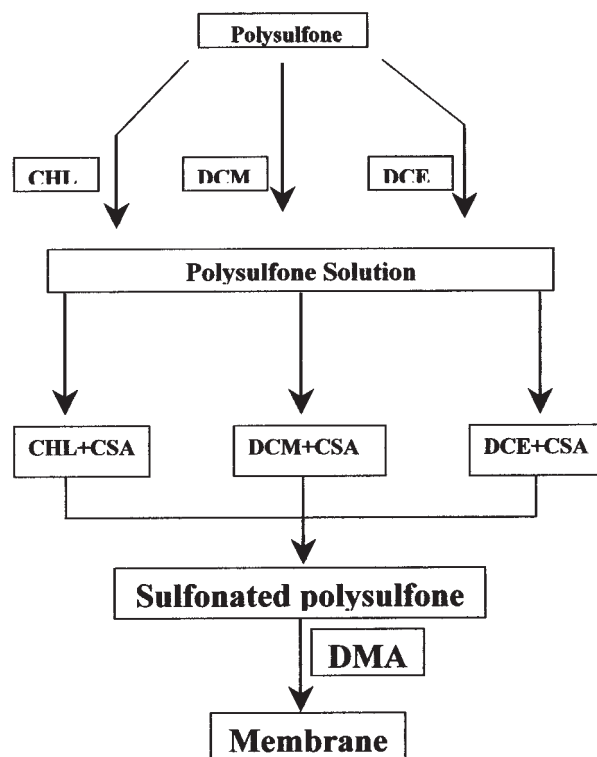


Figure 1 Flow sheet of the different steps involved in membrane preparation (CSA = chlorosulfonic acid, DMA = *N,N*-dimethylacetamide).

which in turn was determined by acid or base titration.

For the measurement of φ_w , a known area of each membrane was immersed in distilled water for 24 h. Then, its surface was wiped, and the wet membrane was weighed. This wet membrane was dried at a fixed temperature of 60°C until a constant weight for the dry membrane was obtained. φ_w was estimated as follows:¹³

$$\varphi_w = \frac{\Delta W/d_w}{\Delta W/d_w + W_d/d_p} \quad (1)$$

where ΔW is the weight difference between the wet and dry membranes, W_d is the weight of dry polymer, and d_w and d_p are the densities of the water and polymer, respectively.

Membrane potential (E^m) and conductance measurements

The experimental cell¹⁴ used for the E^m measurements had two compartments separated by the membrane, which was circular in shape with a 7.0-cm² area. To minimize the effect of the boundary layers on the potential, we vigorously stirred the solutions in both compartments with magnetic stirrers. The potential difference developed across the membrane was re-

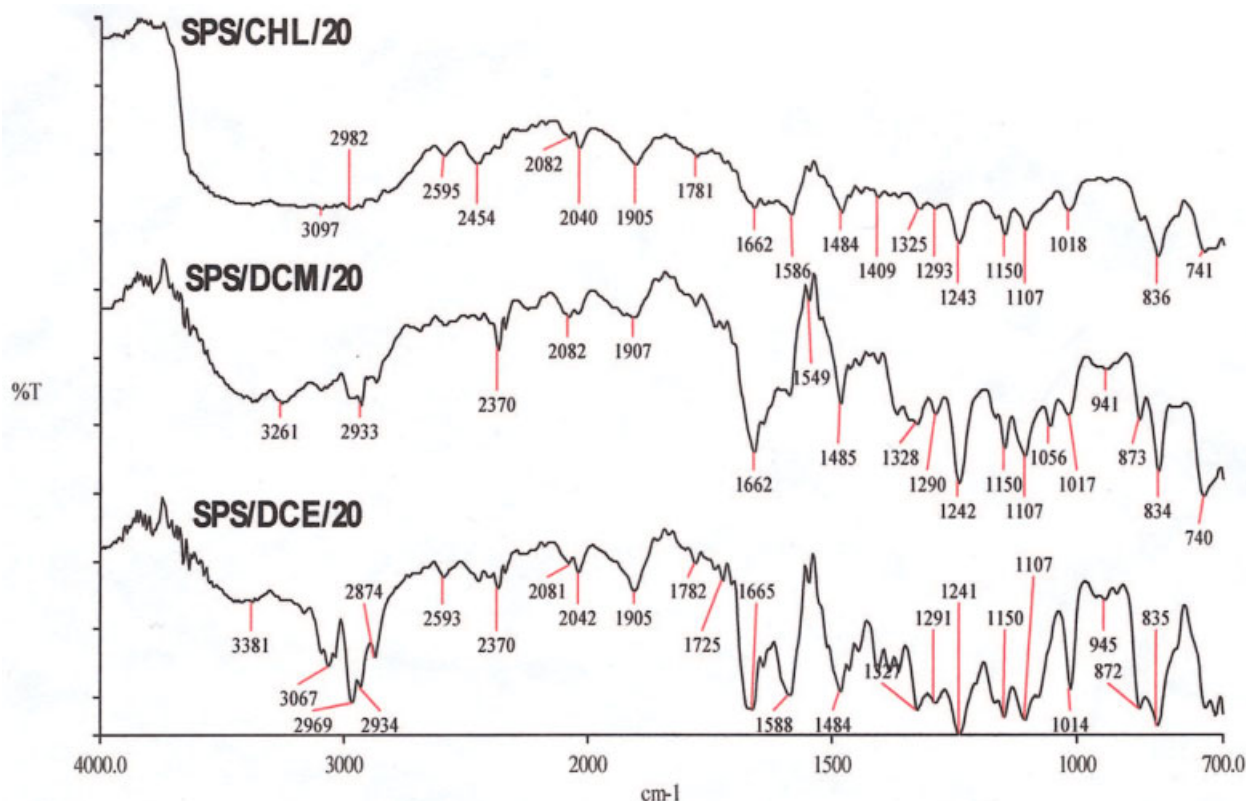


Figure 2 FTIR spectra of SPS membranes sulfonated in different solvents.

corded with a digital multimeter (Systronics, Ahemdabad, India) with saturated calomel electrodes and salt bridges, which were reproducible up to 0.10 mV. For the E^m measurements, the ratio of the salt concentrations on the higher and lower sides (C_1/C_2) was kept constant at 9.0, and $\Delta C/C_s$ was 1.60; C_1 and C_2 were the electrolyte concentrations, ΔC was equal to $C_1 - C_2$, and C_s was equal to $(C_1 + C_2)/2$.

The membrane conductance measurements for the different types of membranes were carried out in aqueous solutions of NaCl with the concentration ranging from 0.005 to 0.040M, with a clip cell as reported earlier.¹⁵ This cell was composed of two black graphite electrodes fixed on Plexiglas plates. The active area of the electrodes and membranes was 1.0 cm². During the experiments, an equilibrated membrane in an experimental solution was sandwiched between both electrodes and was secured in place with a set of screws. The membrane conductance measurements were performed in a potentiostatic two-electrode mode with alternating current. Neither electrodes was in direct contact with the membrane. The membrane resistance (R^m) was estimated by the subtraction of the electrolyte resistance (R_{sol}) without the membrane from the membrane resistance equilibrated in electrolyte solutions (R_{cell} ; $R^m = R_{cell} - R_{sol}$). The membrane conductance was measured with a Century CC601 digital conductivity meter (Chandigarh, India).

The process was repeated until reproducible values (within ± 0.01 mS) were obtained.

RESULTS AND DISCUSSION

Sulfonation study

The sulfonation of PS (Udel) usually occurs at the ortho position of the ether bridge of the bisphenol A portion by electrophilic substitution because of the high electron density (+M effect from the ether bridge and +I effect from the isopropylidene group) at this part of molecule, in contrast to the diarylsulfone portion of the monomer repeating unit, which has a low electron density because of the electron-withdrawing SO₂ group (-I and -M effects).¹⁶ The postsulfonation of the PS was carried out with chlorosulfonic acid in different organic solvents (CHL, DCM, and DCE) separately and was confirmed by FTIR spectra, ¹H-NMR spectra, and CHNS analyses for different membranes. Strong characteristic peaks for FTIR spectra (Fig. 2) at 1030 and 1096 cm⁻¹ were observed for all the sulfonated polymers, and they were assigned to symmetric and asymmetric stretching of the sulfonate group.

The extent of the sulfonation of PS in different solvents was also confirmed by ¹H-NMR spectroscopy and CHNS analysis. In the ¹H-NMR spectra, the presence of a sulfonic group caused a significant down-

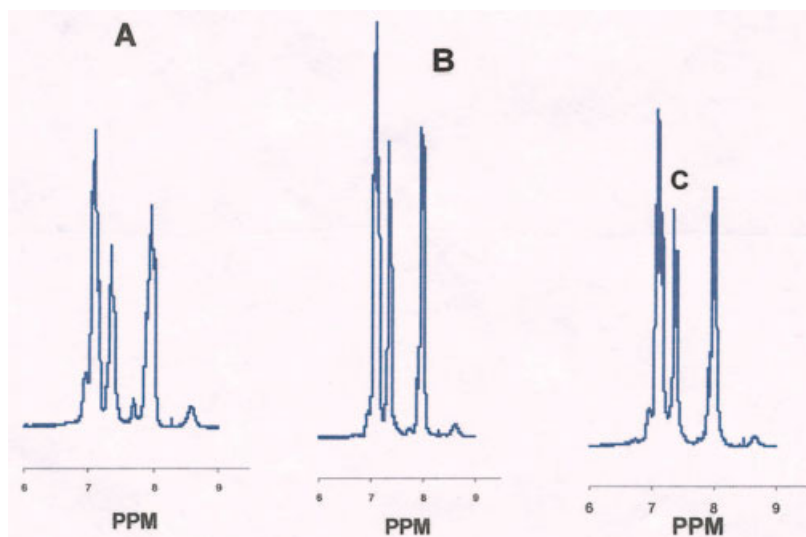


Figure 3 ^1H -NMR spectra of SPS sulfonated in different solvents: (A) CHL, (B) DCM, and (C) DCE.

field shift from 7.24 to 8.31 ppm of the hydrogen located in the ortho position at the aromatic ring, as shown in Figure 3. By evaluating the ratios of the peak area of the signal corresponding to the hydrogen atoms located next to the sulfonic acid groups (H_E) and the peak areas of the signals corresponding to the other aromatic hydrogen atoms ($H_{A,A',B,B',C,D}$), where n is the number of H_E hydrogen atoms and $8 - 2n$ is the number of residual hydrogen atoms ($H_{A,A',B,B',C,D}$), we estimated the degree of sulfonation [x (mol %)] of PS prepared in different solvents with the following mathematical expressions:¹⁷

$$\frac{n}{(8 - 2n)} = \frac{AH_E}{\sum AH_{A,A',B,B',C,D}} \quad (2)$$

$$z = \frac{AH_E}{\sum AH_{A,A',B,B',C,D}} \quad (3)$$

$$x = \frac{8z}{(1 + 2z)} \times 100 \quad (4)$$

where AH_E is the integral of H_E and $\sum AH_{A,A',B,B',C,D}$ is the integral of $H_{A,A',B,B',C,D}$. The x values for PS in different solvents were obtained from ^1H -NMR mea-

surements and are presented in Table I. CHNS analysis data are also presented in Table I. From the percentage of sulfur in the polymer matrix, the extent of sulfonation was found to be higher in DCE. However, according to the ^1H -NMR spectra, the integration values for the H_E proton present in the polymer matrix sulfonated in the DCE solvent were lower than the integration values for the H_E proton present in the polymer matrix sulfonated in the DCM and CHL solvents. This clearly indicated that there might be crosslinking or chain degradation in a high-dielectric-constant solvent. CHL (which had a low dielectric constant) may have solvated the electrophile and polymer matrix poorly; this resulted in a lower rate of sulfonation in comparison with that of DCM and DCE, in which higher x values were obtained.⁷

During sulfonation, the active species is the electrophile (SO_3). The reactivity of the electrophile mainly depends on the solvents because different solvents have different dielectric constants¹⁸ and hence exhibit various extents of solvation of the electrophile and polymer matrix.¹⁹ In the solvation process, the solvent molecules are attached to the active species and polymer matrix with different types of forces, such as electrostatic attraction, dipole moments, and hydro-

TABLE I
Physicochemical Properties of Different Membranes Prepared in Various Solvents

Membrane property	SPS/CHL/20	SPS/DCM/20	SPS/DCE/20
Extent of sulfonation by ^1H -NMR	11.20	26.88	4.12
SO_3H group by titration (mol %)	12.95	23.44	3.27
S (%) by CHN analysis	1.13	1.60	2.68
IEC (mequiv/g)	1.13	1.06	0.43
Volume fraction of water	0.05	0.07	0.05

TABLE II
Electrochemical Properties of Membranes Prepared in Different Solvents in Equilibration with NaCl Solutions with a 0.05 M NaCl Mean Concentration

Membrane	κ^m (mS)	$\omega_+ \times 10^{-12}$ (mol cm ² J ⁻¹ s ⁻¹)	E^m (mV)	t_i^m	P_s	X (mol dm ⁻³)
SPSCHL	1.00	0.355	52.8	0.969	0.949	0.302
SPSDCM	0.42	0.423	37.4	0.832	0.726	0.106
SPSDCE	0.83	0.151	22.5	0.600	0.510	0.059

phobic–hydrophobic interaction. The electrophile will exhibit high solvation in solvents with considerably high dielectric constants. In this study, the solvation of the polymer matrix also played a major role. Poly(ether sulfone) (the dielectric constants at 60 and 10⁶ Hz were 3.14 and 3.26, respectively) had a lower dielectric constant than any of the solvents. The polymer matrix may have shown a lower extent of solvation in the solvent with a lower dielectric constant. Because of the low solvation of the polymer matrix, a lower extent of sulfonation was observed in the solvent with a low dielectric constant. However, the reverse order was observed for the sulfonation of PS in solvents with high dielectric values. FTIR, ¹H-NMR, and CHNS studies also supported a higher extent of sulfonation of PS in a solvent with a relatively high dielectric constant. Despite the higher extent of sulfonation of PS in a solvent with a high dielectric constant, these membranes exhibited lower concentrations of exchangeable sulfonic acid groups. This may be because chlorosulfonic acid, which was capable of cleaving the bisphenol A/PS partially at the isopropylidene link, caused branching and crosslinking reactions by converting the intermediate sulfonic groups into partially branched or crosslinked sulfone units.

IECs of different membranes are also presented in Table I. In all these membranes, IECs arose because of the introduction of sulfonic acid group by the sulfonation of the PS matrix. In general, increasing the fixed ion or functional group concentration led to an increased ion exchange capacity. The IEC values followed the trend SPS/CHL/20 > SPS/DCM/20 > SPS/DCE/20 for the different membranes. This trend also supported the previous explanation of the higher extent of sulfonation but lower concentration of exchangeable functional groups. Furthermore, the addition of functional groups to the polymeric matrix increased its hydrophilic nature. The φ_w values for different types of membranes, estimated by eq. (1), are also summarized in Table I, and they follow a trend similar to that of the IEC and X values.

Variation of the membrane electrochemical properties for the different types of solvents used for sulfonation

Different types of membranes, with a 20% (w/v) weight fraction of SPS in *N,N*-dimethylacetamide,

were prepared, and their electrochemical characterizations were carried out in equilibration with 0.05M NaCl solutions through the measurement of E^m and the membrane conductance. When electrolyte solutions of unequal concentrations are separated by a membrane, an electrical potential difference develops across the membrane because of the tendency of oppositely charged ions to move with different mobilities. For the same electrolyte concentrations, the magnitude of E^m depends on the nature and concentration of the charged functional group in the membrane matrix.²⁰ E^m data were recorded for SPS/CHL/20, SPS/DCM/20, and SPS/DCE/20 membranes separately in equilibration with NaCl solutions (mean concentration = 0.05M, $C_1/C_2 = 9$), and they are presented in Table II. The counterion transport number in the membrane phase (t_i^m) was estimated from E^m data with the TMS approach:²¹

$$E_m = (2t_i^m - 1) \frac{RT}{F} \ln \frac{a_1}{a_2} \quad (5)$$

where a_1 and a_2 are the activities of the electrolyte solutions contacting through the membranes, F is the Faraday constant, T is the absolute temperature, and R is the gas constant. t_i^m values for different types of membranes are presented in Table II. These data reveal that all the membranes behaved as strong cation-selective membranes, whereas their cation selectivity markedly deteriorated when a solvent with a high dielectric constant was used for the sulfonation of PS. An ion-selective membrane is endowed with permselectivity (P_s), which measures the extent to which counterion migration is facilitated by it. P_s is defined as follows:²²

$$P_s = \frac{(t_i^m - t_i)}{(1 - t_i)} \quad (6)$$

where t_i denotes the counterion transport number in the solution phase. The P_s values (Table II) followed a trend similar to that of the t_i^m values. The membrane exhibited ion selectivity because of the charge due to the functional group that the membrane matrix carried. The fixed charge density (X) on the membrane matrix can be expressed in terms of P_s :¹⁴

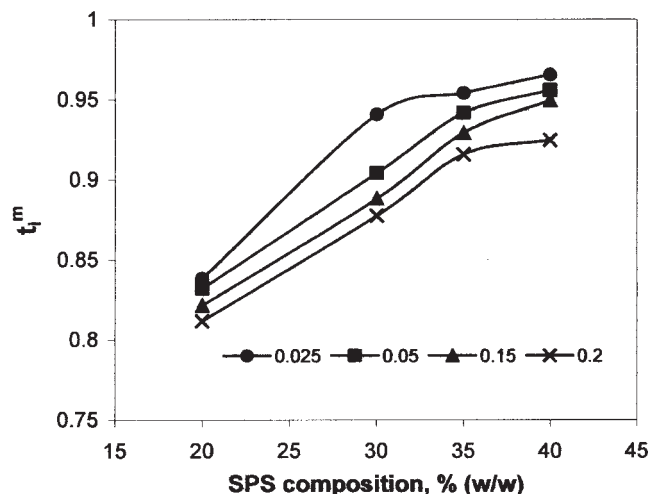


Figure 4 Variation of t_i^m with the concentration of SPS in *N,N*-dimethylacetamide in equilibration with NaCl solutions of different mean concentrations.

$$X = \frac{2CP_s}{\sqrt{1 - P_s^2}} \quad (7)$$

where C is the mean concentration of the NaCl solution (0.05M). A fixed charge in the membrane matrix arose because of the sulfonic acid group, which was introduced by the sulfonation of PS. The P_s and X values for the different membranes followed the trend SPS/CHL/20 > SPS/DCM/20 > SPS/DCE/20 and additionally supported the conclusion made on the basis of the x determinations from FTIR and $^1\text{H-NMR}$ studies or from IEC values.

The membrane conductance values and X values were used to obtain further information on the charged nature of the membranes and counterion mobility in the membrane matrix. The effective membrane resistance, determined experimentally, may in principle be used for the estimation of the membrane specific conductivity (κ^m). κ^m is given by the following relation:

$$\kappa^m = \frac{l}{AR} \quad (8)$$

where l is the thickness of the wet membrane, A is its area, and R is its resistance. The κ^m values for different membranes are presented in Table II, and they increased with an increase in the dielectric constant of the solvent in which the sulfonation of PS was carried out, even though the SPS concentration in all these membranes was 20% (w/v). If we assume the establishment of Donnan equilibria at the membrane surfaces, a negligible effect of mass flow across the ion-selective membranes, and an external salt concentration much less than the charge density, κ^m is

attributable to the mobile counterion equivalent of the charge and can be expressed in terms of the counterion mobility in the membrane phase (ω_+) in the following manner:²³

$$\kappa^m = F^2 X \omega_+ \quad (9)$$

The ω_+ values, estimated from eq. (9), are presented in Table II. The reduction of the ω_+ values for different membranes was observed along with other membrane electrochemical transport properties when a solvent with a high dielectric constant was used for the sulfonation of PS. The results indicated that the greater the sulfonation extent was, the better the possible SPS cation-exchange membranes were when the sulfonation of PS was carried out in a solvent with a low polarity. For solvents with a high polarity or a high dielectric constant, X of PS was less because of some side reactions or crosslinking of the sulfonic acid groups in the polymeric matrix. This resulted in a lesser number of exchangeable sulfonic acid groups, which were responsible for the electrochemical transport properties of the cation-exchange membranes.

Variation of the membrane electrochemical properties with the concentration of SPS in the membrane casting solution

Different SPS/DCM membranes with various SPS concentrations (20–40% w/w) in *N,N*-dimethylacetamide were prepared, and their electrochemical characterizations were carried out in NaCl solutions with mean concentrations ranging from 0.025 to 0.200M. From the E^m values, t_i^m , P_s , and X values were estimated with eqs. (5), (6), and (7), respectively, and are presented in Figures 4–6 versus the SPS concentration

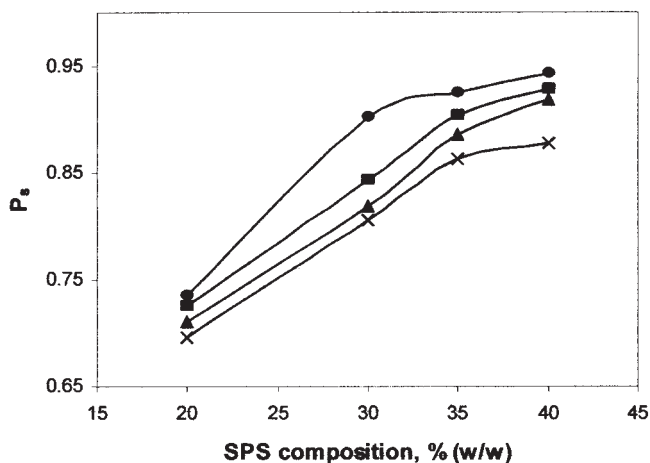


Figure 5 Dependence of P_s on the SPS concentration in *N,N*-dimethylacetamide in equilibration with NaCl solutions of different mean concentrations (see Fig. 4 for the symbols).

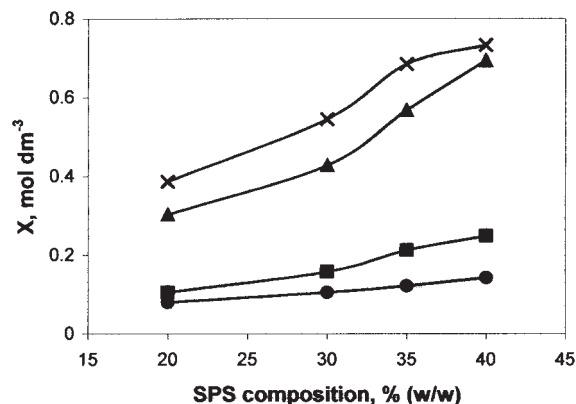


Figure 6 Variation of X with the SPS concentration in N,N -dimethylacetamide in equilibration with NaCl solutions of different mean concentrations (see Fig. 4 for the symbols).

for different NaCl solutions. All these electrochemical transport properties increased initially with the concentration of SPS, and after 35% (w/w), they tended to attain the limiting values. Furthermore, in NaCl solutions with higher concentrations, they exhibited better electrochemical properties than those at lower concentrations. These data reveal that the membranes behaved as good cation-exchange membranes, whereas their cation selectivity markedly increased with the SPS concentration in the casting solution. An increase in the cation selectivity may be attributed to enhanced Donnan exclusion due to a higher concentration of functional groups with a high SPS concentration. An increase in the SPS concentration beyond 35% (w/w) led to the formation of quite dense membranes, which may have restricted a further increase in the ion transport, and thus the electrochemical transport properties of the membranes tended toward a limiting point. The values of φ_w presented in Table III also suggest a reduction in the void volume in the membrane phase with an increase in the SPS concentration. No increase in IEC was observed for SPS concentrations higher than 35% (w/w). This also indicated that with a further increase in the SPS concentration, the concentration of exchangeable functional groups in the membrane matrix remained the same. We obtained further information regarding ionic migration from the κ^m and ω_+ values across the membranes.

TABLE III
 φ_w and IEC for Membranes with Various Weight Percentages of P5 Prepared in DCM

Membrane	φ_w	IEC (mequiv/g)
SPS/DCM/40	0.0730	1.1092
SPS/DCM/35	0.0337	1.1392
SPS/DCM/30	0.0754	1.1574
SPS/DCM/20	0.0723	1.0594

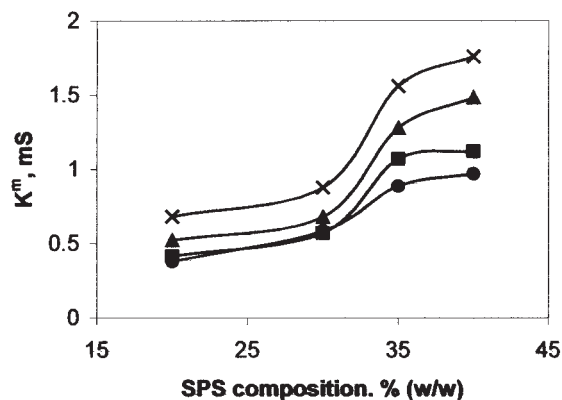


Figure 7 Variation of κ^m with the SPS concentration in N,N -dimethylacetamide in equilibration with NaCl solutions of different mean concentrations (see Fig. 4 for the symbols).

The κ^m and ω_+ values for different SPS/DCM membranes in equilibration with NaCl solutions with various concentrations are presented in Figures 7 and 8, respectively. κ^m increased with the external salt concentration, and this supported the idea that κ^m in the relevant salt concentration range should be proportional to the external salt concentration. Furthermore, κ^m and ω_+ increased slowly at first (between 20 and 30% w/w) and then steeply (between 30 and 35% w/w) with the concentration of SPS/DCM in N,N -dimethylacetamide and attained a limiting value at 35% (w/w). These variations may be explained in terms of two factors, the structural retardation of ion movement by the enhanced water structure in the membranes and the relaxation effect arising from the electrostatic interaction of the counterions with the membrane matrix. Here *structural retardation* means that water in the membrane, especially when the wa-

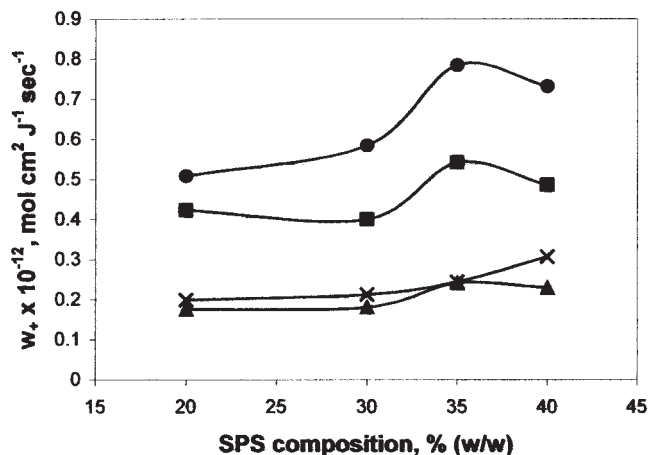


Figure 8 Variation of ω_+ with the SPS concentration in N,N -dimethylacetamide in equilibration with NaCl solutions of different mean concentrations (see Fig. 4 for the symbols).

ter content is low, becomes sticky to ions and, therefore, leads to lower conductivity or mobility. The relaxation effect due to the electrostatic interaction of the counterions will be proportional to the concentration of charged functional groups or X in the membrane matrix. Figure 6 shows that X increased with the concentration of SPS/DCM and attained a limiting value beyond its 35% (w/w) concentration. Thus, the two factors were separately or jointly responsible for the observed variations of κ^m and ω_+ .

CONCLUSIONS

The sulfonation of PS was carried out with chlorosulfonic acid and different solvents with various dielectric constants. FTIR, $^1\text{H-NMR}$, and CHNS studies supported higher x values of PS in a solvent with a relatively high dielectric constant. Despite the higher x values of PS in a solvent with a high dielectric constant, those membranes exhibited lower concentrations of exchangeable sulfonic acid groups. This may be because chlorosulfonic acid is capable of cleaving the bisphenol A/PS partially at the isopropylidene link and, moreover, causes branching and crosslinking reactions by converting the intermediate sulfonic groups into partially branched or crosslinked sulfone unit. E^m and membrane conductance studies suggested that the electrochemical transport properties of the different membranes followed this trend: SPS/CHL/20 > SPS/DCM/20 > SPS/DCE/20. Thus, the membrane for which sulfonation was carried out in a solvent with a relatively low dielectric constant exhibited better electrochemical properties than the other. The variations of the membrane properties were also observed with the concentration of SPS in the membrane casting solution for SPS/DCM membranes. The membranes' electrochemical transport properties increased with the SPS concentration up to 35% (w/w), and beyond this, they attained limiting values. These variations were attributed to the structural retardation of the ion movement by the enhanced water structure in the membranes and the relaxation effect arising from the electrostatic interaction of the counterions with the membrane matrix. Because of their excellent electrochemical transport properties, SPS cation-ex-

change membranes are suitable for various types of electromembrane applications.

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