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SYNTHESIS, CHARACTERIZATION, AND PERFORMANCE OF SULFONATED POLYETHERSULFONE NANOFILTRATION MEMBRANES

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ABSTRACT

TGA/DTA data. Membranes were prepared from sulfonated polymer and performance characteristics in terms of permeate flux and solute separation are reported. The effects of the casting solution composition on performance of both PES & SPES membranes, effect of feed concentration and separation of different inorganic salts are also included. Separation of multivalent cation (Ca^{2+}) was studied in presence of PAA of different concentration and as a function of pH.

Key Words: Sulfonated polyethersulfone; Nanofiltration membranes; Separation of electrolytes

INTRODUCTION

Polyethersulfone is an excellent polymeric candidate for membrane application with very good mechanical, biological, chemical, and thermal stability. The hydrophobic nature of this polymer makes it suitable

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for synthesizing porous membranes for use in ultrafiltration (UF) and microfiltration (MF) application [1]. Hydrophilicity of polyethersulfone can be introduced through chemical modifications. Vinyl monomers like 2-hydroxy ethyl methacrylate (HEMA), glycidyl methacrylate (GMA) and methacrylic acid (MA) were introduced photochemically on the surface of polyethersulfone ultrafiltration membranes by Hideyuki Yamagishi et al. [2, 3] for reducing the nonselective adsorption of proteins. Asymmetric polyether sulfone (PES) ultrafiltration (UF) membranes were prepared and modified by electron irradiation in various environments with different doses and by subsequent grafting with hydrophilic monomers like acrylic acid and acrylamide and the changes in their transport and surface characteristics were studied by Keszler et al. [4]. Naik et al. [5] reported on the synthesis and the characterization of amination on the main chains of a copolymer of polyethersulfone (PES) and polyether ethersulfone (PEES) by nitrating the hydroquinone unit of the repeat unit followed by amination but have not mentioned anything about membrane application. Esser and Parsons have reported [6] synthesis of PES/PEES polymers with pendent carboxyl groups and these functional groups can be used as potential grafting sites for grafting of crystalline oligomers but have not mentioned anything about membrane. Chitosan modified sulfonated polyethersulfone as a support for affinity separations was used by Elias Klein et al. [7]. ATR-FTIR spectroscopic studies of the structure and permeability of sulfonated polyethersulfone membranes have been reported by M.R. Pereira et al. [8]. By introducing charged groups on a hydrophobic membrane, nanofiltration membranes with desired anionic and cationic selectivity could be synthesized. Though chemical modification of polysulfone group of polymers is extensively discussed, detailed membrane preparation particularly of nanofiltration type from the derivatives of polysulfones is not discussed.

Negatively charged membranes selectively separate the multivalent anions in presence of multivalent cations. It is possible to separate multivalent cations by negatively charged membranes (NF/UF) if these ions could be bound in relatively large hydrophilic macromolecular ligands. It was reported that the relatively low molecular weight ligands such as ethylene diamine tetra acetic acid (EDTA) [9] and macromolecular ligands such as polyvinyl alcohol [10], polyamine [11], polyvinyl pyrrolidone [10], polyacrylic acid [10] can be used for complexation of metal ions to improve their selectivity.

In this study, sulfonated polyethersulfone (SPES) was synthesized and used to prepare nanofiltration (NF) type of membranes with anionic selectivity. The possibility of improving cationic selectivity by complexation nanofiltration is also looked into. The synthesis, characterization, performance and selectivity towards multivalent cations and anions are reported in this paper.

EXPERIMENTAL

Materials

Polyether sulfone (PES, $M_w = 132{,}000$, $M_n = 94{,}000$), in powder form was obtained from M/s. Gharda Chemical Company, India. Polyacrylic acid (PAA, $M_n = 2000$) was procured from M/s. Aldrich Chemical Company, USA. N,N-Dimethyl acetamide (DMAc) was distilled under reduced pressure. The other organic solvents were purified by usual distillation method. The other materials were of laboratory grade and used without further purification.

Synthesis of Polymer and Membrane

The sulfonation has been carried out using chlorosulfonic acid ($HClSO_3$) [12]. The desired quantity of $HClSO_3$ was added to a 20% solution of PES in dichloromethane. The reaction was carried out at −10°C temperature. The polymer was precipitated in hexane and washed repeatedly with acetone. The resulting sulfonated polyethersulfone (SPES) was neutralised with sodium methoxide/methanol solution to produce sodium salt first and then equillibriated with HCl to make sulfonic acid form. The resulting polymer was vaccum dried for 8 hours.

The membranes were prepared by dissolving 20% (w/w) polymer in different proportions of mixed solvent of 1,4-dioxane and DMAc. The clear solution was filtered and spread over a clean glass plate using a glass tube. The thickness of the membrane was controlled with the help of side runner tapes. After a predetermined time of solvent evaporation in a dehumidified room (20°C, 40% R.H.), the nascent film was gelled in demineralized water at ambient condition.

Characterization of Polymer and Membrane

SPES sample was characterized in terms of ion exchange capacity, percent moisture regain, inherent viscocity, IR spectra and TGA/DTA data. The ion exchange capacity was determined by the method of Fisher and Kunin [13] and expressed as m.eq./gm. The percent moisture regain was calculated from the difference in weight between the exposed polymer sample in 85% RH and the unexposed sample. The inherent viscosities of the reacted and the unreacted samples were determined in chloroform using falling liquid using Ubbelohde viscometer. The IR spectra of the reacted and the unreacted polymer samples were recorded in transparent film form using a Perkin-Elmer model 577 Spectrometer. The TGA and the DTA spectra of samples

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were recorded in the temperature range of 25°C to 400°C at a heating rate of 10°C/min using a Perkin-Elmer Differential Thermal Analyzer.

The membrane samples were characterized in terms of solute separation and product permeation rate using a constant recirculation type test cell wherein feed solution is pumped across a given membrane specimen (area 14.5 cm^2) at a flow rate of 3 $L.m^{-1}$ using a reciprocating pump. The desired pressure was set using a back pressure regulating valve. The reject and the permeate stream were recycled back to the tank to maintain the feed concentration. Solution containing PAA and metal ions (Ca^{2+}) was mixed and left standing overnight at room temperature to complete complexation. The pH of the feed solution was adjusted by adding a small amount of HCl or NaOH.

All electrolytes in feed and permeate samples were analysed by conductance measurements. Sodium chloride in presence of sodium sulfate was estimated by chloride titration using standard silver nitrate solution and potassium chromate indicator. Calcium chloride in presence of PAA was analyzed by atomic absorption spectrophotometer.

RESULTS AND DISCUSSIONS

Polymer Characterization

Ion exchange capacity (IEC), percent moisture regain and inherent viscosity data of polyethersulfone (PES) and sulfonated polyethersulfone (SPES) are given in Table 1. The inherent viscosity datum of SPES sample is found to be less than that of PES sample. The inherent viscosity of SPES sample was found to be low possibly due to degradation of PES during sulfonation with $HClSO_3$. Sulfonation of PES improves it's solubility in general and it readily dissolves in 1,4-dioxane giving thermodynamically more stable casting solution of slightly less viscosity as compared to PES sample. The percent moisture regain of SPES sample is found to be slightly higher than that of PES sample which is due to the presence of polar sulfonic acid group ($-SO_3H$). The ion exchange capacity of the sulfonated polymer is low because of the low reactivity of the aromatic rings directly attached to the

Table 1. Inherent Viscosity, Percent Moisture Regain, and Ion Exchange Capacity Data for PES and SPES

Polymer	Inherent Viscosity (η_{inh}) (dl/gm)	Percent Moisture Regain (%)	Ion Exchange Capacity (m.eq/gm)
PES	1.312	2.08	–
SPES	1.289	2.95	0.64

sulfone groups which acts as sink for the electron density from the aromatic rings. The degree of substitution (DS) could be related to ion exchange capacity (IEC) by the following relations

$$\mathrm{DS} = 232.\mathrm{IEC}/(1000 - 80.\mathrm{IEC}) \qquad (1)$$

where 232 is the M_W of one repeat unit of PES and 80 is the M_W of SO_3 group. A value of 0.64 m.eq/gm of IEC works out to a DS of 0.156 which works out to substitution of one SO_3 groups per every 6.4 repeat units of PES.

The IR spectra of PES and SPES samples are given in Fig. 1. It can be seen that IR spectra are similar for both the polymers except the presence of peaks at around $1160\,\mathrm{cm}^{-1}$ and $1024\,\mathrm{cm}^{-1}$ which are present in SPES polymer. The absorption peak at $1160\,\mathrm{cm}^{-1}$ is due to antisymmetric O=S=O stretching of the sulfonate group and at $1024\,\mathrm{cm}^{-1}$ is due to symmetric O=S=O stretching of the sulfonate group. The TGA and the DTA spectra are given in Fig. 2 and 3. For PES polymer up to 150°C, there is no weight loss, beyond 150°C to 250°C the weight loss is marginal. For the SPES polymer there is a gradual weight loss up to 150°C, beyond 150°C–250°C, the weight loss is more and the overall weight loss is around 8%. Accounting for the loss of moisture, the net loss in weight at around 250°C for SPES sample works out to 5.05% which accounts for a DS of 0.117. This closely matches the DS figure worked out from the ion exchange capacity data. The DTA spectra of both PES and SPES polymers are nearly identical. Both polymers show two exothermic peaks. In addition, the SPES polymer shows two endothermic peaks at around 75°C and 100°C which indicates the loss of absorbed moisture in the polymer. It is expected that the glass transition temperature (T_g) of the substituted polymer sample will be higher than that of the unsubstituted polymer. The reported T_g value of PES sample is 230°C and the T_g of SPES sample is expected to be higher than this. However, no attempt has been made to quantitatively measure and compare the T_g values of both the polymers.

Membrane Performance

The performance evaluation of the membranes from SPES polymer samples has been done in terms of effect of casting solution composition, casting condition, a separation behavior for various electrolytes. The separation of different electrolytes is studied as a function of feed concentration. Separation behavior of mixed electrolyte systems is also studied. Separation of multivalent cation (Ca^{2+}) is studied in presence of polyacrylic acid (PAA, molecular weight -2000) of different concentrations and as a function of pH.

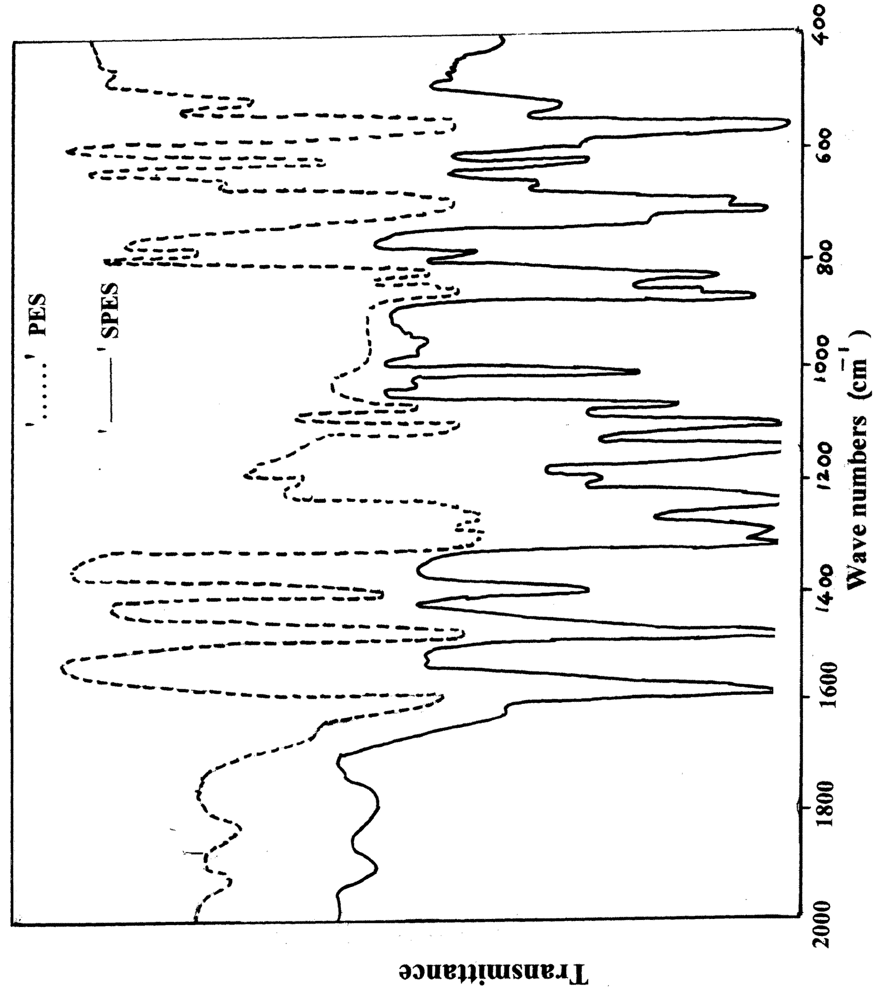

Figure 1. IR spectra of PES and SPES polymers.

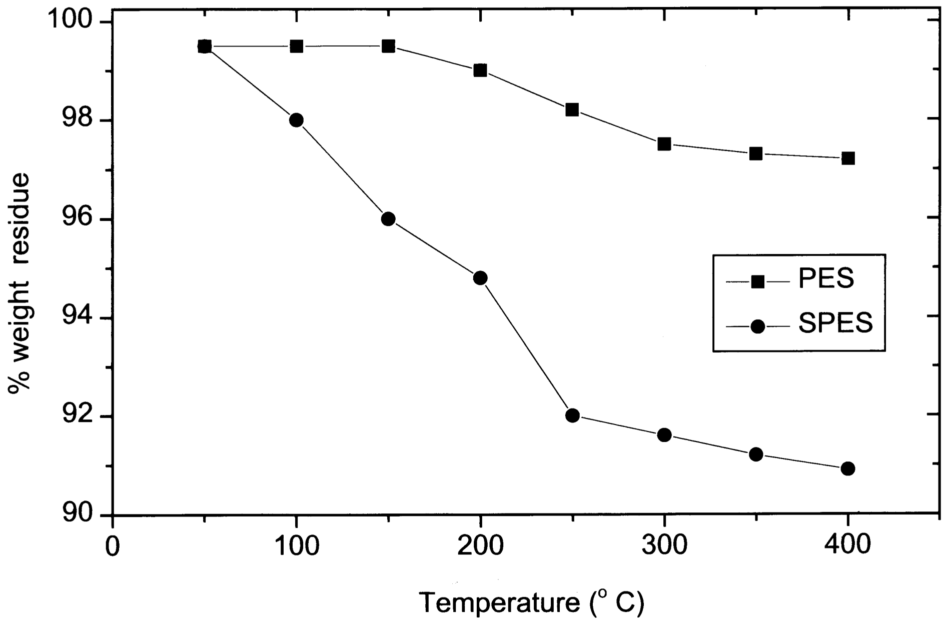

Figure 2. TGA plot of PES and SPES polymers.

Effect of Casting Composition

A comparison of membrane performance from substituted, as well as unsubstituted polymer, in terms of permeate flux and solute separation for 2000 ppm sodium sulfate at 1 MPa for four different membranes (designated as PES-1, PES-2, SPES-1 and SPES-2) is given in Table 2. The membrane from unsubstituted polymer was made from the same solvent and polymer composition for the sake of comparison with the membrane from substituted polymer. The composition of casting solution is also given in Table 2. The introduction of a SO_3H group in the polymer increases not only the hydrophilicity but also the solubility towards polar solvent. As hydrophilicity increases, the membranes have a tendency to attract more water which is reflected in higher permeate flux. Higher solubility of the SPES polymers in the same solvents used in casting solution, changes the structure of the casting solution significantly as compared to unsubstituted polymers resulting in formation of a large number of smaller macromolecular aggregates. The effect of the casting solution viscosity and the polymer solubility in the solvent system on the membrane performance is extensively studied for cellulose acetate and aromatic polyamide membranes [14]. During gelling, this results in a tighter structure with a large number of small pores for SPES membranes which is both reflected in a better solute separation and a higher permeate flux. DMAc, as well as a mixture of

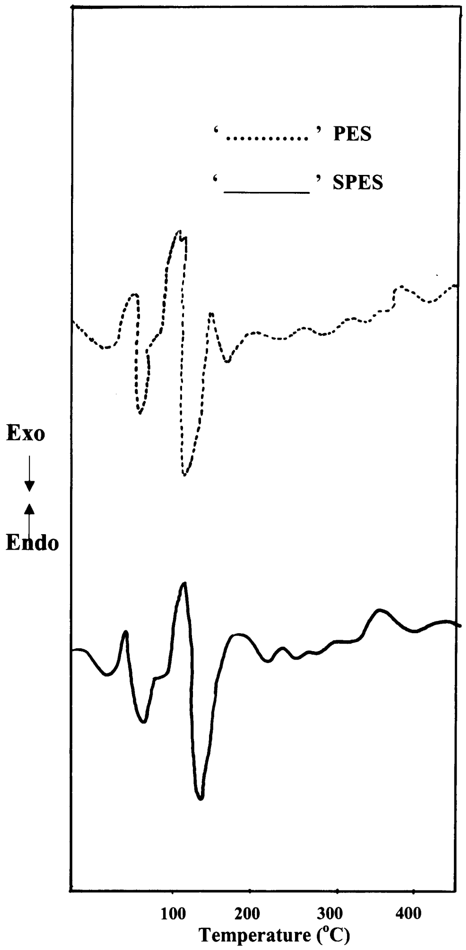

Figure 3. DTA plot of PES and SPES Polymers.

Table 2. Membrane Performances from PES and SPES as a Function of Composition of Casting Solution

	Composition of Casting Solutions (w/w %)			Na_2SO_4 (2000 ppm)	
Membrane	Polymer	1,4 - Dioxane	DMAc	Flux ($L.m^{-2}.h^{-1}$)	% Solute Separation
PES-1	20.2	41.8	38.0	7.05	67.2
SPES-1	20.2	41.8	38.0	27.13	84.6
PES-2	20.4	31.6	48.0	18.5	54.3
SPES-2	20.4	31.6	48.0	58.2	68.4

Evaporation time: 90 seconds; Membrane area: 15.4 cm^2; Pressure: 1 MPa; Temperature: 25 °C.

DMAc and 1,4-dioxane, are found to be good solvents for PES, as well as SPES. SPES dissolves faster in both the solvent systems giving a relatively more stable casting solution, whereas PES dissolves slowly giving a less stable casting solution.

The viscosity of the casting solutions PES-1, SPES-1, PES-2, and SPES-2 along with their coagulation time are given in Table 3. The coagulation time was measured by the time taken for a membrane of area 10 cm × 10 cm × 200 μ to become a completely opaque film subsequent to spreading on a smooth clean glass plate and immersing in a gelling bath which contained demineralized water maintained at room temperature. The increased solubility of SPES in the solvent system is reflected in the lower solution viscosity and higher coagulation time as compared to the PES sample. The ratio of 1,4-dioxane/DMAc was reduced from PES-1, SPES-1 to PES-2, SPES-2. It can be seen that the permeate flux and the solute separation are significantly affected by solvent compositions in casting solutions. The SPES membrane shows better performance than the corresponding PES membranes in terms of higher permeate flux and solute separation. With an increase in the DMAc content in the casting solution the permeate flux improves drastically with a loss in solute separation. The addition of 1,4-dioxane as a cosolvent cum additive helps in the densification of the layer exposed to the ambient atmosphere as a result of relative volatility of 1,4-dioxane. The observed higher solute separation and lower permeate flux in the case of PES-1 and SPES-1 as compared to PES-2 and SPES-2 could be explained as due to the presence of higher 1,4-dioxane in the casting solutions. In addition, the pore blocking by the small degraded SPES during the process of coagulation could also have contributed to the higher observed performance in case of SPES membranes. The solute separation and the permeate flux obtained for SPES membranes are typical for nanofiltration (NF) type of membranes. The sulfonated polycarbonate (SPC) membranes [15] and the nitrated polysulfone (NPS) membranes [16] prepared and reported from our laboratory earlier also showed a comparable separation performance under the identical casting conditions. The SPES membrane appears superior to SPC membrane but inferior to NPS membranes in terms

Table 3. Viscosity Data and Coagulation Time for PES and SPES Casting Solutions

Membrane	Viscosity (Centi Poise)	Coagulation Time (Secs)
PES-1	15840	11
SPES-1	13780	14
PES-2	14432	9
SPES-2	12579	12

Evaporation time: 90 seconds; Membrane area: 100 cm^2.

of higher permeate flux and solute separation. The reason why SPES membrane showed moderate performance between SPC and NPS membrane could be explained as follows. The slightly better membrane performance of SPES over SPC membrane could be due to a slightly higher degree of sulfonation in the former case, as well as its higher solubility characteristics with chosen solvent system which is identical in both the cases. Similarly, the lower performance observed in SPES membrane over NPS membrane could be due to the case with which substitution could be carried out in the PS polymer backbone due to the presence of an aromatic ring farther away from the resonating sulfone groups.

SEM photographs of either surface of PES-2 and SPES-2 membranes are shown in Fig. 4 to 7. It can be seen that both the surfaces of the membranes show differential pore structure indicating the asymmetric nature of the membranes. The surface in contact with the glass plate show large symmetrical void structure whereas the air exposed surface shows a relatively smooth structure. The surface of the SPES-2 membrane appears to be relatively smoother with fewer number of voids as compared to PES-2 membranes.

Effect of Solvent Evaporation Time on the Membrane Performance (SPES-1)

The membrane (SPES-1) performances for Na_2SO_4 solution (500 ppm) are given in Table 4. The evaporation time varied from 30 to 120 seconds. As the

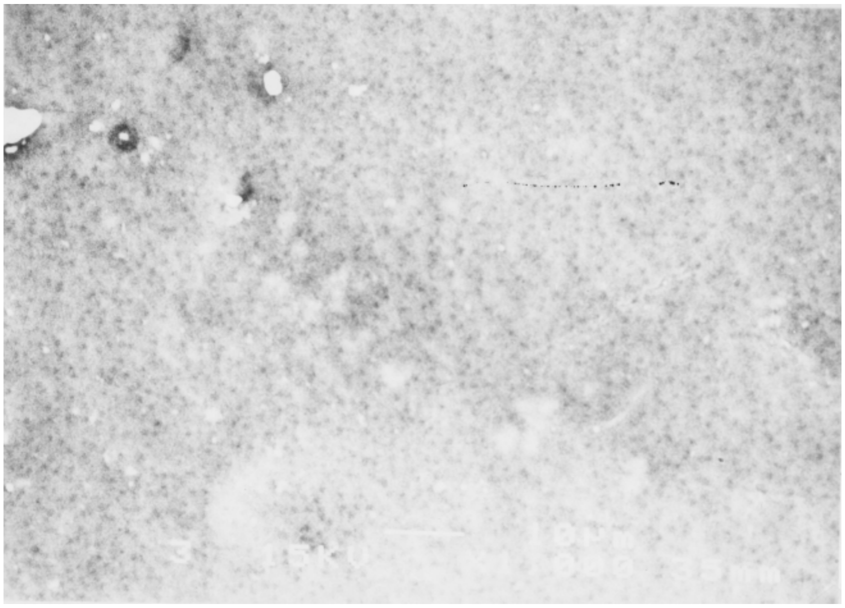

Figure 4. SEM Photograph for skin surface of PES-2 membrane.

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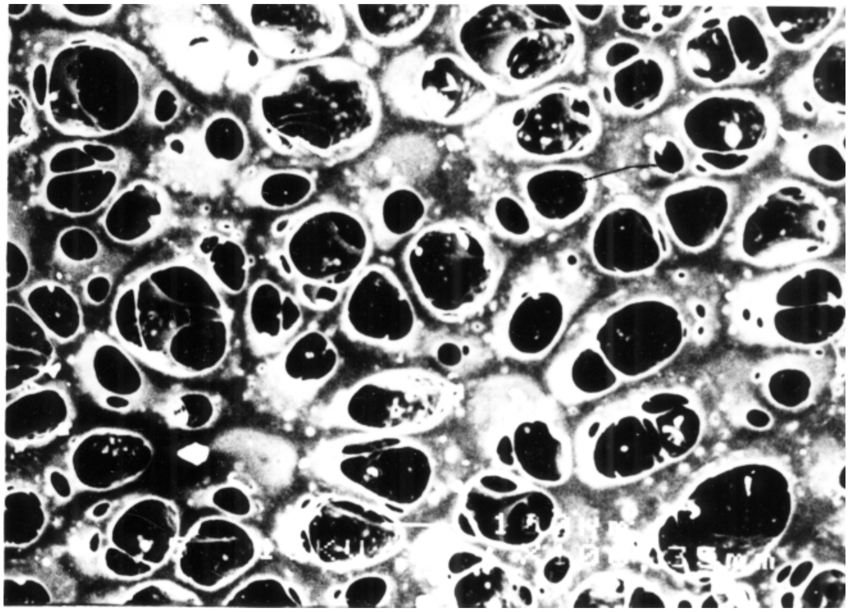

Figure 5. SEM photograph for back surface of PES-2 membrane.

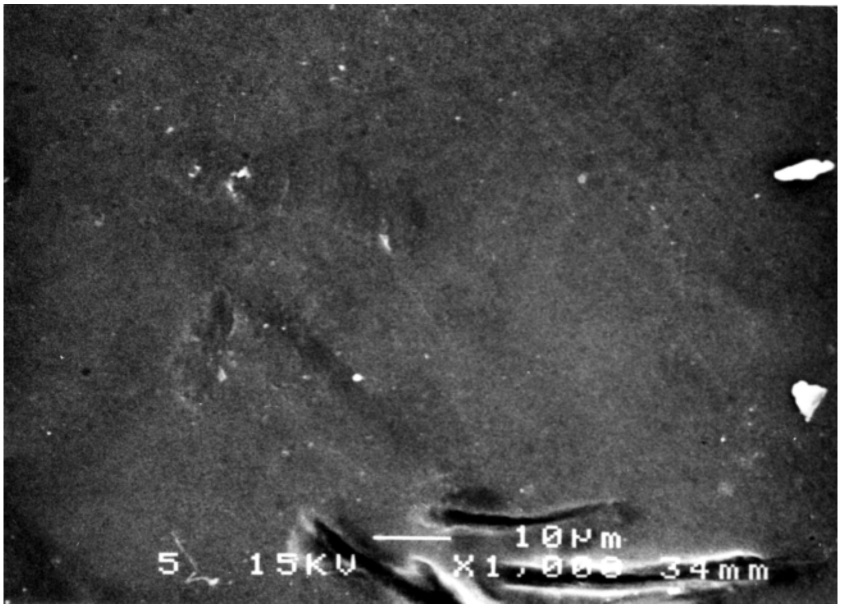

Figure 6. SEM photograph for skin surface of SPES-2 membrane.

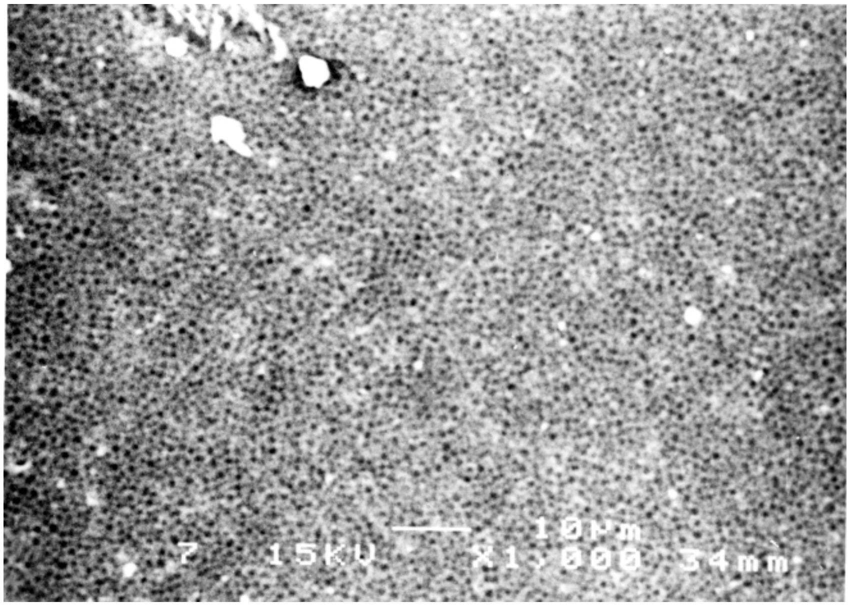

Figure 7. SEM photograph for back surface of SPES-2 membrane.

evaporation time is increased, the permeate flux drastically decreased and the solute separation increased. More volatile solvent among two solvents, namely, 1,4-dioxane, is expected to evaporate out with time, leaving behind a more dense polymer network in membranes which is reflected in performance.

Separation of Different Inorganic Solutes

The performance of the SPES-1 membrane for different solutes, namely, NaCl, $CaCl_2$, Na_2SO_4, $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ are studied and given in Table 5. The order of solute separation was $K_4Fe(CN)_6 >$

Table 4. Membrane Performance from SPES-1 (Same Composition of Casting Solution) as a Function of Time of Evaporation During Casting

	Na_2SO_4 (500 ppm)	
Evaporation Time (sec)	Flux ($Lm^{-2}.h^{-1}$)	% Solute Separation
30	203.54	34.5
60	94.53	73.5
90	31.42	94.0
120	19.7	96.5

Membrane area: 15.4 cm^2; Pressure: 1 MPa; Temperature: 25 °C.

Table 5. Membrane Performances (SPES-1) for Different Solute Systems

Solute	Flux ($L.m^{-2}.h^{-1}$)	% Solute Separation
NaCl	28.1	44.4
$CaCl_2$	28.4	42.0
Na_2SO_4	28.5	91.6
$K_3Fe(CN)_6$	29.1	95.8
$K_4Fe(CN)_6$	29.3	97.9

Membrane area: 15.4 cm^2; Pressure: 1 Mpa; Temperature: 25 °C; Feed concentration: 1000 ppm.

Table 6. Diffusion Coefficient Data and Hydrodynamic Radii of Different Ions in Water

Ion	Diffusion Coefficient (10^{-9} cm^2/sec)	Hydrodynamic Radii (A)
Na^+	1.33	1.64
K^+	1.96	1.115
Ca^{2+}	0.92	2.37
Cl^-	2.03	1.076
$SO_4{}^{2-}$	1.605	2.05

Temperature: 25 °C.

$K_3Fe(CN)_6 > Na_2SO_4 > NaCl > CaCl_2$. It can be seen that the solute separation increases with an increase in the valency of the anions present in the electrolytes. The separation of $CaCl_2$ is marginally less than that of NaCl, which may be due to the presence of a higher valancy cation in $CaCl_2$. The permeate fluxes for $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ are higher as compared to others which could be due to the lower osmotic pressure of the feed due to their higher molecular weights. The self diffusion coefficent data in water, as well as the hydrodynamic radii of ions, are given in Table 6.

Effect of Feed Concentration on Membrane Performance

The effect of feed concentration with respect to different electrolytes, namely, K_2SO_4, $K_3Fe(CN)_6$, and $K_4Fe(CN)_6$ for the SPES-1 membrane is given in Fig. 8. It can be seen that membranes give a higher separation for $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ as compared to K_2SO_4. As the feed concentration increases from 100–2000 ppm, the observed solute separation goes through the maximum for all the solute systems. The maximum solute separation is observed at a feed concentration of around 300–500 ppm for K_2SO_4, whereas maximum separation is observed over a concentration range

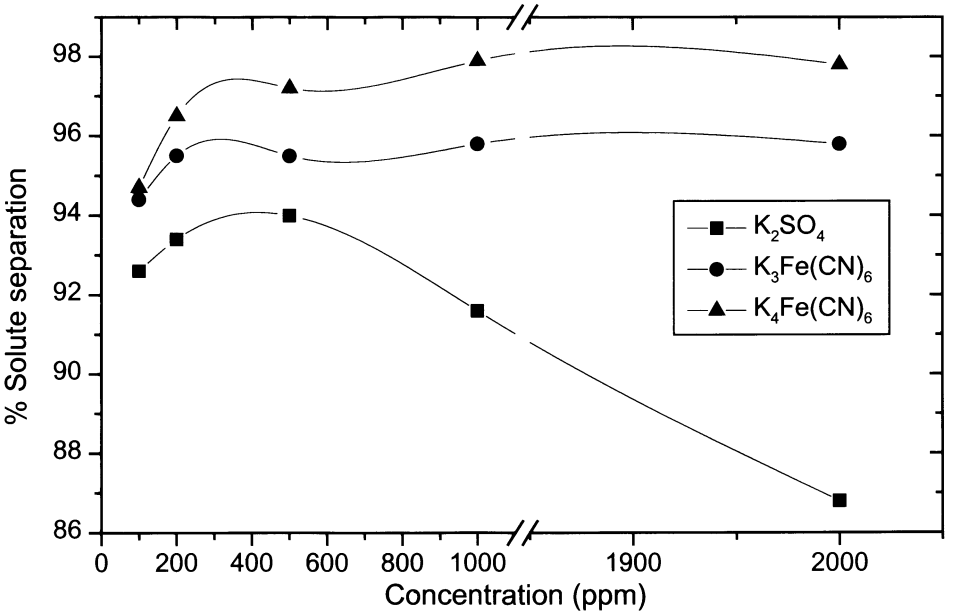

Figure 8. Plot of % solute separation as a function of concentration of different solute systems for SPES-1 membrane.

of 1000–1500 ppm for $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$. The drop-in solute separation is observed at a lower concentration, as well as a higher concentration, particularly for lower anionic valence solutes, namely, K_2SO_4 and $K_3Fe(CN)_6$. In the case of $K_4Fe(CN)_6$, the separation is found to be asymptotic.

The maxima in solute separation observed for SPES membranes are similar to what is previously reported for SPC [11] and NPS membrane [12]. When the external solute concentration becomes comparable to the fixed charge density of the membrane a Donnan exclusion of solute ions in the membrane phase could result causing maxima in solute separation. The decline in solute separation with an increase in concentration is understandable due to the higher concentration gradient across the membrane contributing to higher diffusive permeability of solute ions across the membrane. At very low feed concentrations, the solute separation declines, possibly due to osmotic swelling of polymer matrix containing ionogenic groups as a result of concentration gradient between external solution and the solution within the pores arising out of fixed coions and mobile counterions. This osmotic swelling could result in leakage of solute ions through enhanced membrane pores. With increase in feed concentration in the dilute range, the osmotic swelling may decline contributing to pore shrinkage resulting in higher observed solute separation.

These two opposing trends possibly meet to provide the observed maxima in solute separation.

Effect of Polyacrylic Acid on Separation

Separation of $CaCl_2$ in the presence of PAA has been studied. PAA is a water soluble polymer and known to complex divalent metal ions. Since the separation of divalent cationic solutes is lower as compared to divalent anionic solutes, the effect of complexation of divalent metal ions on their possible improvement in separation is studied. A known amount of PAA is equilibrated with varying concentrations of $CaCl_2$ and separation of $CaCl_2$ is found and presented in Fig. 9. Separation of $CaCl_2$ in the absence of PAA is also given in the same figure for the sake of comparison. It is well known that when an electrolyte permeates through a semipermeable membranes, the permeation of positive and negative ions, though independent of each other are regulated by the electroneutrality criteria. The less permeable ion is expected to hinder the transport of more easily permeable ion of opposite charge. The calcium ion in presence of PAA is analysed in the feed and permeate sample and as such the reported solute separation refers to separation of Ca^{2+} ions through the membranes. In Fig. 9–11, the feed concentration refers to concentration of Ca^{2+} ions in the solutions. It can be seen that the presence of PAA improves $CaCl_2$ separation at all concentrations

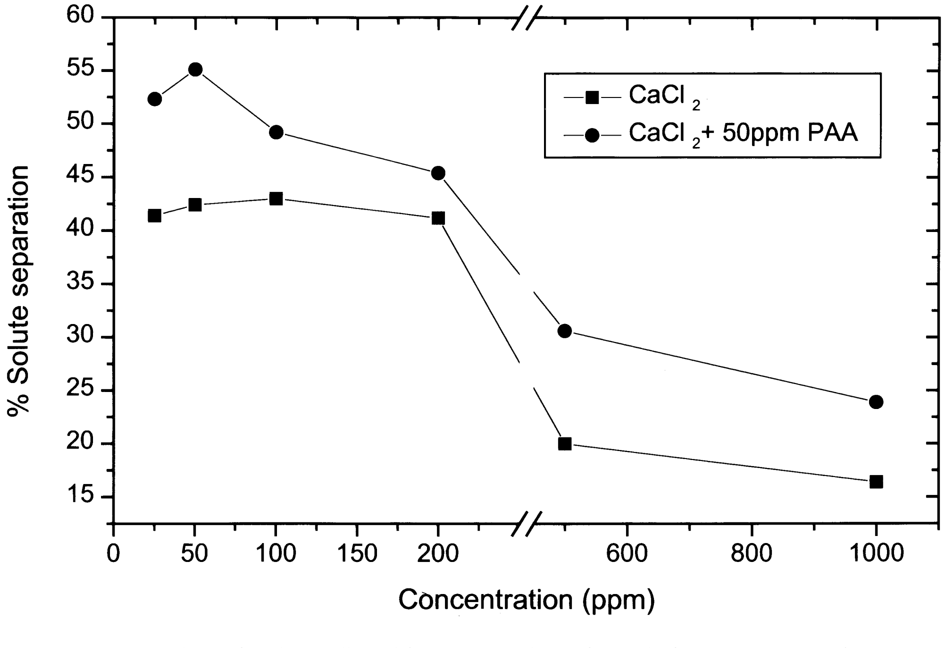

Figure 9. Effect of polyacrylic acid on separation of $CaCl_2$ for SPES-1 membrane.

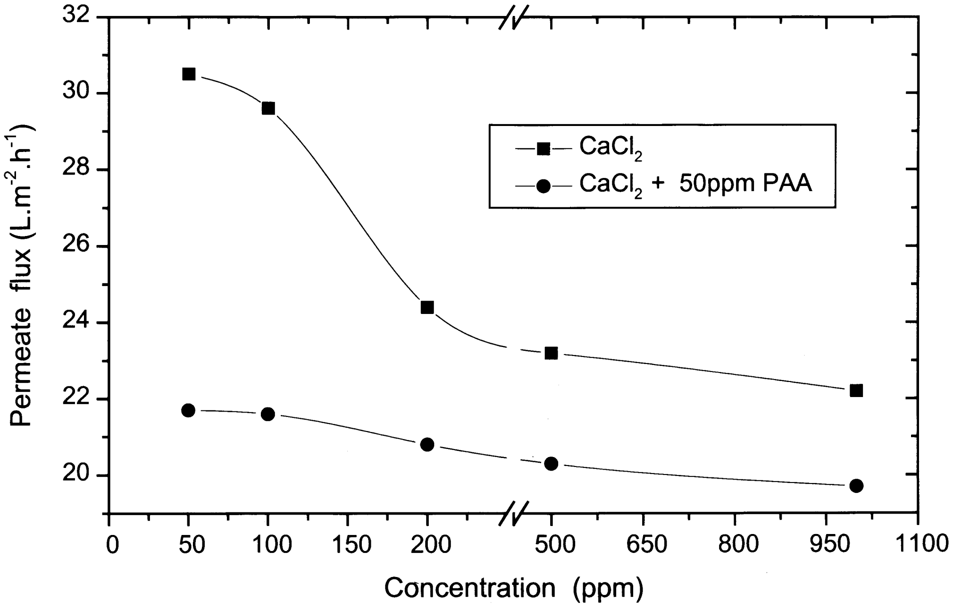

Figure 10. Effect of polyacrylic acid on permeate flux during seperation of $CaCl_2$ for SPES-1 membrane.

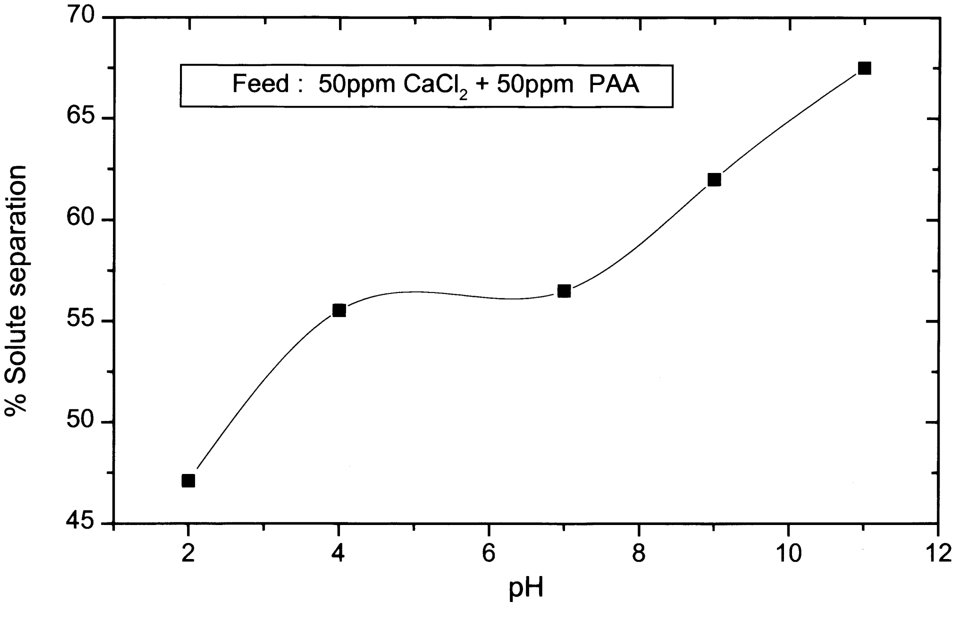

Figure 11. Plot of % solute seperation of $CaCl_2$ in presence of PAA as a function of pH for SPES-1 membrane.

studied and separation of complexed Ca^{2+} ions follows the same trend as observed for uncomplexed $CaCl_2$ systems. Maximum separation is observed when the metal ion concentration is the same as that of polyacrylic acid. With an increase in metal ion concentration, the separation decreases but it is more than uncomplexed $CaCl_2$ system. The permeate flux is also plotted in Fig. 10, and it is found that the complexed $CaCl_2$ system has a lower permeate flux. The molecular weight of PAA is important in achieving higher separation of complexed metal ions. Near total separation of Cu^{2+} and Zn^{2+} ions is reported [17] in the presence of a very high molecular weight PAA (molecular weight-90,000). The moderate separation observed for the complexed $CaCl_2$ system could be partly due to the lower molecular weight of the complexing agent used as higher molecular weight complexing agent could lead to membrane fouling and consequent low permeate flux. The pH of the feed system is another important aspect to be considered while studying the effect of complexation. Separation of complexed Ca^{2+} ions as a function of pH of the feed system is given in Fig. 11. Higher pH leads to near total ionization of carboxylic acid groups and the polymer assumes a rigid structure due to repulsion of carboxylate ions which will result in better separation of complexing agent. It is expected that the separation of complexed metal ion will be maximum at the pH, when the stability constant of the metal complex is maximum.

CONCLUSION

Sulfonated polyethersulfone semipermeable membranes show better performance (flux as well as solute separation) for electrolytes as compared to polyethersulfone membranes under identical conditions. Sulfonated polyethersulfone membranes show higher separation capability for multivalent anionic species in aqueous solution. The separation behaviour of sulfonated polyethersulfone membranes for electrolytes shows typical maximum as a function of feed concentration. Sulfonated polyethersulfone membranes show improved separation of multivalent cations after complexation with polyacrylic acid. Alkaline pH is preferable for getting higher separation of divalent cationic solute systems when used in conjunction with polyacrylic acid.

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