Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Ghosh, A. K. , Ramachandhran, V. , Hanra, M. S. and Misra, B. M.(2000) 'SYNTHESIS, CHARACTERIZATION, AND PERFORMANCE OF NITRATED POLYSULFONE MEMBRANES', Journal of Macromolecular Science, Part A, 37: 6, 591 — 608

To link to this Article: DOI: 10.1081/MA-100101111

URL: http://dx.doi.org/10.1081/MA-100101111

J.M.S.—PURE APPL. CHEM., A37(6), pp. 591–608 (2000)

SYNTHESIS, CHARACTERIZATION, AND PERFORMANCE OF NITRATED POLYSULFONE MEMBRANES

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Key Words: Nitrated Polysulfone, Semipermeable Membranes, Separation of Dyes and Electrolytes

ABSTRACT

Wholly aromatic polysulfone was modified by nitration and was investigated as a possible membrane material for separation of inorganic solutes, low molecular weight organic solutes and dyes from aqueous solutions. The nitrated polysulfones were characterized in terms of extent of nitration, percent moisture regain, inherent iscosity, IR spectra, TGA/DTA and DSC data. Membranes were prepared from nitrate polymer and performance characteristics in terms of permeate flux and solute separation are reported. The effects of the casting solution composition and casting condition, effect of feed concentration and separation of different inorganic salts are also included. Separation data for low molecular weight polyethylene glycol (PEG) solutes and dyes are studied. Nitrated polysulfone membranes have been found to give higher separation for polyvalent anionic electrolytes. The stability of membranes in acid and alkaline medium and chlorine tolerance of the membranes are also investigated.

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INTRODUCTION

Semipermeable membranes are widely used as selective barriers in industrial separations and a large number of polymeric and inorganic membranes are developed to suit different operating and selectivity requirements. Polysulfones, polyacrylonitrile and polyvinylediene difluoride (PVDF) are used in ultrafiltration for fractionation and separation of macromolecules and proteins. Polysulfones, being a nonpolar polymer is not considered suitable for synthesizing reverse osmosis (RO)/nanofiltration (NF) membranes which are essentially used for separation of ionic as well as nonionic solutes in aqueous solutions. Ultrafiltration (UF) membranes made from polysulfone are known to be susceptible to protein fouling and modification of polysulfones by hydrophilic substitution is expected to reduce its fouling susceptibility and also make it suitable as a possible RO/NF membrane candidate. A large number of polysulfone composites, either blended or chemically modified are reported for various applications.

For better separation of protein, the hydrophilic vinyl monomers like 2-hydroxy ethyl methacrylate (HEMA), glycidyl methacrylate (GMA) were introduced to hydrophobic poly(arylsulfone) ultrafiltration membrane photochemically by Hideyuki Yamagishi *et al.* [1]. The negatively and positively charged ultrafiltration membranes were prepared from sulfonation of polysulfone and chloromethylation of polysulfone followed by the addition of sufficient triethyl amine respectively by S. Nakao *et al.* [2] for protein separation. Surface modification of polysulfone by propylene oxide has been done by Akon Higuchi *et al.* [3] again for better separation of protein. Carboxylated and sulfonated were used for fractionation of natural and model egg-white protein solution by Neda Ehsani *et al.* [4]. Polysulfone-polyimide (PS-PI) blend membranes were synthesized for gas separation by G. C.Kapantaidakis *et al.* [5]. Development and characterization of crosslinked ionomer membranes based upon sulfinated and sulfonated polysulfone has been done by Jochen Kerres *et al.* [6] for the application of electrodialysis. Nanofiltration membrane suitable for separation of polyvalent electrolyte from sulfonated polycarbonate was reported from our laboratory [7]. This membrane, though stable in acid medium is not however stable in alkaline medium. Nitrated polysulfones are considered as a suitable membrane candidate for RO/NF application from the point of view of balanced polar/nonpolar charactert as well as superior chemical, thermal and oxidation stability. The synthesis, characterization and performance of the nitrated polysulfones are reported in this paper.

EXPERIMENTAL

Materials

Polysulfone (M_w = 30,000) and Polyethylene glycol (M_n = 200, 400, and 600) were obtained from M/s. Aldrich Chemical Company, USA. N,N-Dimethyl acetamide (DMAc) was distilled under reduced pressure. The other organic solvents were purified by the usual distillation method. The other materials were of commercial grade, and used without further purification.

Synthesis of Polymer and Membrane

The nitration has been carried out using concentrated nitric acid (HNO_3). The desired quantity of concentrated HNO_3 was added to a 20% solution of polysulfone in 1,2-dichloro ethane. The reaction was carried out at 55°C temparature. The reaction was allowed to continue for half an hour. The resulting nitrated polysulfone was precipitated in hexane, washed in acetone and vaccum dried.

The membranes were prepared by dissolving a 25% (weight) 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 membranes 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

Nitrated polysulfone sample was characterized in terms of extent of nitration, percent moisture regain, solution viscosity (η_{inh}), IR spectra, TGA/DTA and DSC data. The extent of nitration was estimated from elemental composition analysis and expressed as percentage. The percent moisture regain was calculated from the difference in weight between the exposed polymer sample in 85% relative humidity and the unexposed sample. The inherent viscosity (ηinh) of reacted and unreacted polymer samples were determined in 1,2-Dichloro ethane using falling liquid method with a Ubbelhode viscometer. The IR spectra of reacted and unreacted polymer samples were recorded in film form using a Perkin-Elmer model 577 Spectrometer. The TGA/DTA spectra of samples were recorded in the temperature range of 25°C to 300°C at a heating rate of 10°C/min.,using a Perkin-Elmer Differential Thermal Analyzer. The DSC spectra was recorded using Perkin-Elmer 1b apparatus and the spectra was recorded in N_2 atmosphere at the differential heating rate of 10°C/min. up to 150°C and 2.5°C/min. beyond 150°C.

The membrane samples were tested for solute separation and product permeation rate using a laboratory setup wherein feed water is pumped across a given membrane specimen using a reciprocating pump. The reject and product streams are recycled back to the tank [7].

The analytical method for estimation of PEG is reported in our previous paper [8].

RESULTS AND DISCUSSIONS

Polymer Characterization

The extent of nitration (%), moisture regain (%) and inherent viscosity (η_{inh}) data of polysulfone (PS) and nitrated polysulfone (NPS) are given in Table 1. The extent of nitration data indicate that nitration appears to have taken place on the average of one nitro group ($-NO_2$) per two phenyl group. The moisture regain percentage of NPS sample is found to be slightly higher than that of PS which could be due to the presence of polar nitro group ($-NO_2$). The higher extent of nitration could have improved the percent moisture regain data. The

TABLE 1. Extent of Nitration, Percent Moisture Regain and Inherent Viscosity (η_{inh}) Data for Polysulfone (PS) and Nitrated Polysulfone (NPS)

Polymer	Extent of nitration (%)	Percent moisture regain (%)	Inherent viscosity (η_{inh})
PS	-	1.4	1.224
NPS	5.64	2.9	1.198

extent of nitration was controlled by controlling the reaction time and reactant ratio. Increasing of either of this was found to degrade the polymer resulting in lower inherent viscosity (η_{inh}) data. The inherent viscosity (η_{inh}) data of NPS sample with 5.64% of nitration is found to be slightly less than PS. Nitration of PS is found to improve its solubility and the nitrated derivative is readily soluble in 1,4-Dioxane whereas, PS remains insoluble.

The IR spectra of PS and NPS samples are given in Figure 1. The spectra was recorded within the range of 1600-600 cm^{-1} because the expected changes in the absorption peaks between the two samples fall in this range. From assignment of peaks it can be seen that the characteristic absorption due to substituted phenyl ($-C_6H_4-$), methylene ($-C(CH_3)_2-$) and sulfone ($-SO_2$) groups are present in both the spectra. The nitro group ($-NO_2$) is characterized by two absorption peaks namely, 1515-1560 cm^{-1} and 1345-1385 cm^{-1}. The peak at around 1520 cm^{-1} is observed in NPS sample whereas, the other charecteristic peak at 1345-1385 cm^{-1} is not observed. This could be due to the overlapping with sulfone ($-SO_2-$) absorption peak.

The TGA/DTA spectra of PS and NPS samples are given in Figures 2 and 3. The weight loss for PS was found to be less during the entire heating range as compared to NPS sample. The rate of weight loss for PS sample is also uniform. For NPS sample up to 150°C and beyond 225°C, there is minimum weight loss. The increase in weight loss for NPS sample is in the temperature range of 150-200°C and drastic from 200-225°C. The DTA spectra of PS and NPS samples show an endothermic peak in the temperature range of 100- 125°C. The endothermic for NPS sample is shifted to slightly higher temperature. The endothermic peak is not accompanied by any weight loss for both the samples. Figure 4 gives the DSC spectra of both the samples. The DSC spectra show sharp endothermic peak at 125°C for NPS sample. The endothermic peak is broad and diffused for PS sample. Beyond 150°C, NPS sample shows the stabilished exothermic heat flow whereas PS sample shows a more steep exothermic heat flow.

Membrane Performances

The performance of the membranes from NPS polymer samples has been done in terms of effect of casting solution composition, casting condition and separation behavior for various electrolytes and nonelectrolyte systems. The separation behavior of different electrolytes are studied as a function of feed concentration. The separation of different dye systems and low molecular

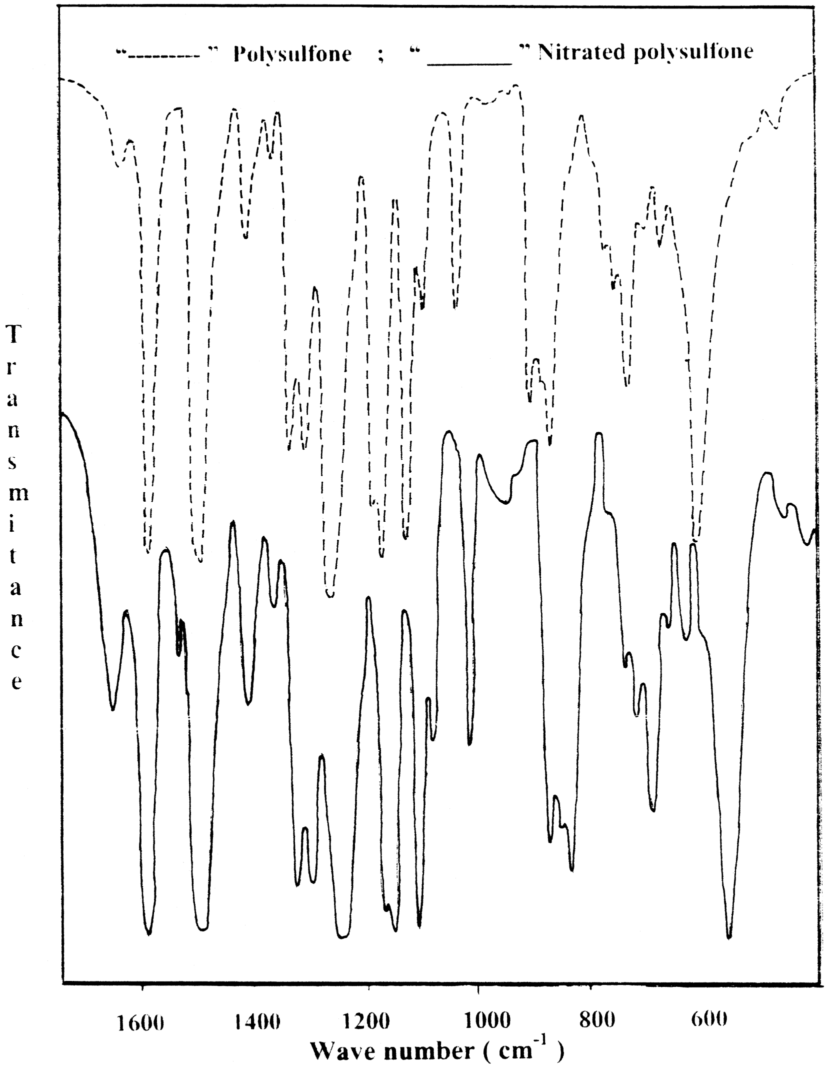

Figure 1. IR Spectra of Polysulfone and Nitrated Polysulfone.

weight polyethylene glycol (PEG) solutes are studied. The stability of the membranes with respect to its separation performance under acidic, alkaline and free chlorine environment are also studied.

Effect of Casting Solution Composition

A comparison of membrane performance in terms of permeate flux and solute separation for 2000 ppm Na_2SO_4 at 7 Kg/cm^2 for four different mem-

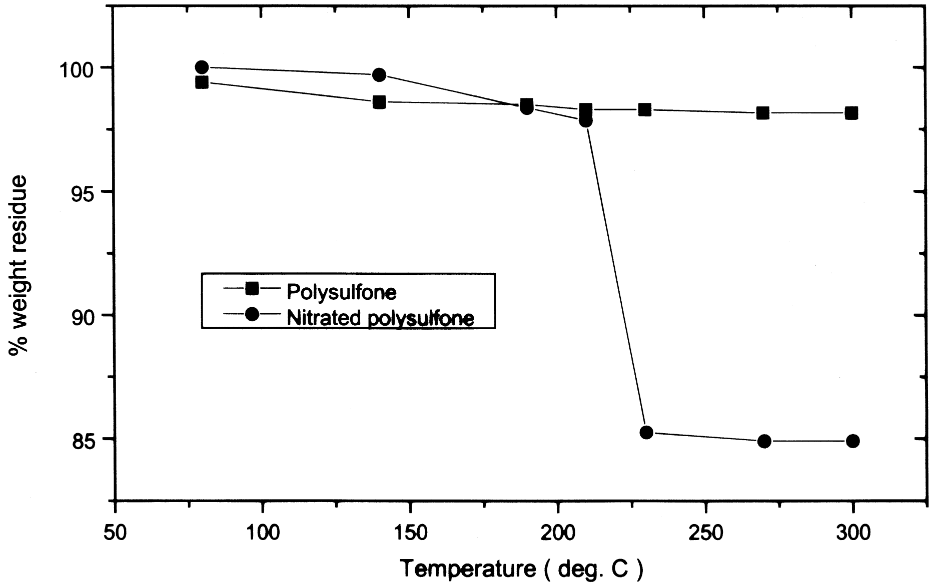

Figure 2. TGA Plot of Polysulfone and Nitrated Polysulfone.

branes (designated as NPS-1, NPS-2, NPS-3, and NPS-4) are given in Table 2. The four membranes are prepared by varying the solvent composition namely, 1,4-Dioxane and N,N-dimethyl acetamide (DMAc). The composition of casting solution are also given in Table 2. The ratio of 1,4-Dioxane to DMAc was reduced from NPS-1 to NPS-4 membrane. It can be seen that the permeate flux and solute separation are significantly affected by solvent composition in casting solution. The permeate flux to be more sensitive than the solute separation. With an increase in the DMAc content in the casting solution the permeate flux improved drastically with loss in solute separation. The separation performance and the permeate flux obtained for NPS membranes is typical of nanofiltration (NF) type of membrane. For a given solute, NF membrane has solute separation less than that of reverse osmosis (RO) membrane but higher than that of ultrafiltration (UF) membrane. The intermediate separation behavior of NF membrane is usually accompanied by much higher permeate flux. The membrane prepared (NPS 4) with higher DMAc concentration in the casting solution show the flux and separation behavior similar to what is observed for NF membranes. The sulfonated polycarbonate (SPC) membranes prepared and reported from our laboratory [7] also showed a comparable separation performance but with lower

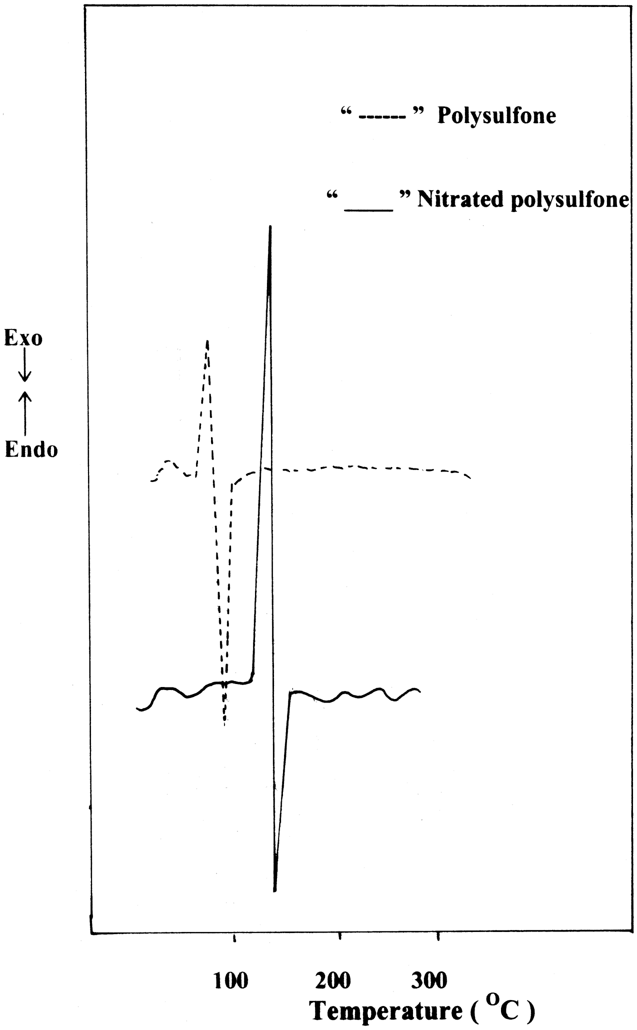

Figure 3. DTA Plot of Polysulfone and Nitrated Polysulfone.

permeate flux. The NPS membranes appear superior to SPC membranes with respect to higher permeate flux.

Effect of Solvent Evaporation Time on the Membrane Performance (NPS-4)

For Na_2SO_4 solution of two different concentration is given in Table 3. The evaporation time is varied from 30 to 120 seconds. As the evaporation time is increased, the permeate flux drastically decreases, whereas the increase in solute separation is marginal. The separation of Na_2SO_4 at two different con-

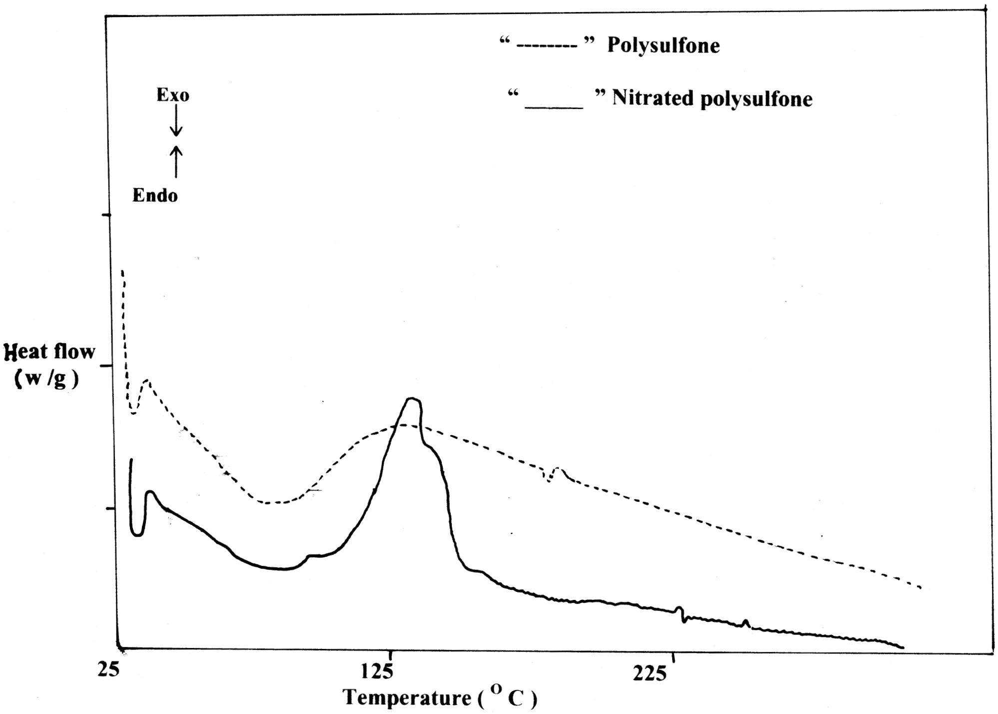

Figure 4. DSC Plot Polysulfone and Nitrated Polysulfone.

centrations as a function of evaporation time indicate that membranes give a higher separation at lower feed concentration.

Effect of Feed Concentration on Membrane Performance

The effect of feed concentration with respect to NaCl, Na_2SO_4 and Na_3PO_4 for NPS-1 membrane is given in Figure 5. It can be seen that membranes give a higher separation for Na_2SO_4 and Na_3PO_4 as compared to NaCl. The separation of Na_3PO_4 is more than that of $Na_2 SO_4$. As the feed concentration increases from 100 ppm to 2000 ppm, the observed solute separation goes through maximum for all the solute systems. The maximum solute separation is observed at a feed concentration of 200 ppm for NaCl whereas maximum separation was observed over a concentration range of 200-500 ppm for Na_2SO_4 and Na_3PO_4. The drop in solute separation beyond 500 ppm is more or less indentical for all solute system.

The maxima in solute separation observed for NPS membranes is similar to what is previously reported for cellulose acetate (CA) [9] and SPC mem-

TABLE 2. Membrane Performances from NPS as a Function of Composition of Casting Solution

Membrane	Composition of casting solutions (w/w %)			Na_2SO_4 (2000ppm)	
	Polymer	1,4 - Dioxane	DMAc	Flux ($l.m^{-2}.d^{-1}$)	% solute separation
NPS-1	19.8	61.5	18.7	341	71.3
NPS-2	20.0	51.7	28.3	585	78.7
NPS-3	20.2	41.8	38.0	2607	75.0
NPS-4	20.4	31.6	48.0	4965	53.0

Evaporation time : 30 sec ; Membrane area : 15.4 cm^2 ; Pressure : 7 Kg / cm^2 ; Temperature : 26°C

TABLE 3. Membrane Performance from NPS-4 (Same Composition of Casting solution) as Function of Time of Evaporation during Casting

Evaporation time (sec)	Na_2SO_4 (200 ppm)		Na_2SO_4 (1000 ppm)	
	Flux ($l.m^{-2}.d^{-1}$)	% solute separation	Flux ($l.m^{-2}.d^{-1}$)	% solute separation
30	5586	81.5	5000	53.0
60	1304	82.5	1240	55.5
90	920	85.0	838	57.0
120	840	88.0	745	58.0

Membrane area : 15.4 cm^2 ; Pressure : 7 Kg / cm^2 ; Temperature : 26°C

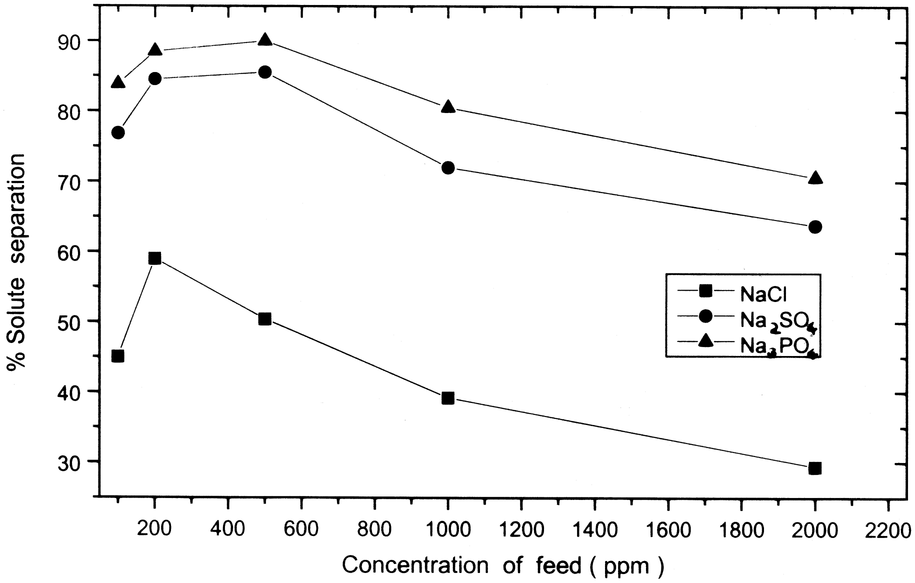

Figure 5. Plot of % Solute Separation as a Function of Concentration of Different Solute Systems for NPS1 Membrane.

brane [7]. It is reported that at higher feed concentration, the salt diffuses through a near neutral membrane whereas at lower feed concentration the action of the fixed charges of the membrane surfaces, to restrict the mobility of the solute ions, comes into play. In the case of CA, the fixed charge could be due to the presence of carboxylic acid group (-CO_2H) and in the case of SPC membranes the fixed charge could be due to the sulfonic acid group (SO_3H). In the case of NPS membranes the surface charge could arise either from the sustituted nitro group (-NO_2) or due to the resonance delocalization of electron density from the para sustituted sulfone group (-SO_2-). The maximum solute separation observed corresponds to 3-4 milli molar/liter of feed concentration.

The action of the fixed charges of the membrane is belived to affect the mobility of the salt ions in the membrane phase [10]. When the external feed concentration becomes comparable tothe fixed charge of the membrane, a Donnan equillibria will exist between the solution and the membrane phase. This Donnan exclusion could help in improving solute separation. When the external solute concentration is in excess of the fixed charge concentration, the sorption of co-ion into the membrane phase is less hindered and this could explain the observed lower separation at higher concentration. But at the lower concentration, the Donnan equllibria may be drastically disturbed to affect enhanced solute concentration in the membrane phase due to reduced coulombic repulsion of the co-ions.

Separations of Different Inorganic Solutes

The performances of four different NPS membranes for different solute systems like $CaCl_2$, Na_3PO_4 and $K_4Fe(CN)_6$ were studied and is given in Table 4. The separation of NaCl is also given for the sake of comparison. It can be seen that the solute separation of $CaCl_2$ is more than that of NaCl but less than the separation of Na_2SO_4 (Table 2). Similarly, the separation of Na_3PO_4 and $K_4Fe(CN)_6$ are higher as compared to Na_2SO_4 for all the membranes. This could be due to the higher charge of the anionic species namely, SO_4^-, PO_4^{-3} and $Fe(CN)_6^{-4}$ compared to Cl^-. The separation of $CaCl_2$ is higher than that of NaCl which may be due to the higher molecular weight of $CaCl_2$. The permeate flux for $K_4Fe(CN)_6$ is higher as compared to others which could be due to the lower osmotic pressure of the feed because of its higher molecular weight and lower feed concentration.

Separation of Low Molecular Weight PEG

The separation data for PEG solutes of low molecular weight for three different membranes (NPS-2, NPS-3 and NPS-4) are given in Figure 6. The separation of PEG increases with increase in the molecular weight from 200 to 600 for all the membrane. The increase in the separation is more for NPS-2 membrane. The separation of Na2SO4 molecular weight = 142.04) is comparable to the separation of PEG (M_n = 400) for all the embranes. The results indicates that the separation of NaCl (molecular weight = 58.45) is lower than PEG (Mn = 200). The comparative separation data between the strong electrolyte of low molecular weights and the neutral PEG solutes highlight the effect of ion-membrane interaction on the separation rather than the solute molecular weight.

Separation of Dyes

Membrane performance (NPS-3) for four different dyes are given in Table 5. It can be seen that the separation of dye does not increase with the increase in the molecular weight and the separation depends more on the molecular structure. The separation of Methyl Red with molecular weight of 269.31 and Bromophenol Blue with molecular weight of 669.98 are higher whereas the

TABLE 4. Membrane Performance for Different Solute Systems

Membrane	NaCl (500 ppm)		$CaCl_2$ (500 ppm)		Na_3PO_4 (500 ppm)		$K_4Fe(CN)_6$ (300 ppm)	
	Flux ($l.m^{-2}.d^{-1}$)	% solute separation	Flux ($l.m^{-2}.d^{-1}$)	% solute separation	Flux ($l.m^{-2}.d^{-1}$)	% solute separation	Flux ($l.m^{-2}.d^{-1}$)	% solute separation
NPS-1	341	50.4	340	58.0	345	88.4	380	94.0
NPS-2	495	46.5	500	52.5	550	81.0	620	90.0
NPS-3	2510	39.0	2550	43.0	2600	78.0	2650	87.0
NPS-4	5050	31.5	5056	35.5	5070	63.0	5120	79.5

Membrane area : 15.4 cm^2 ; Pressure : 7 Kg / cm^2 ; Temperature : 26°C

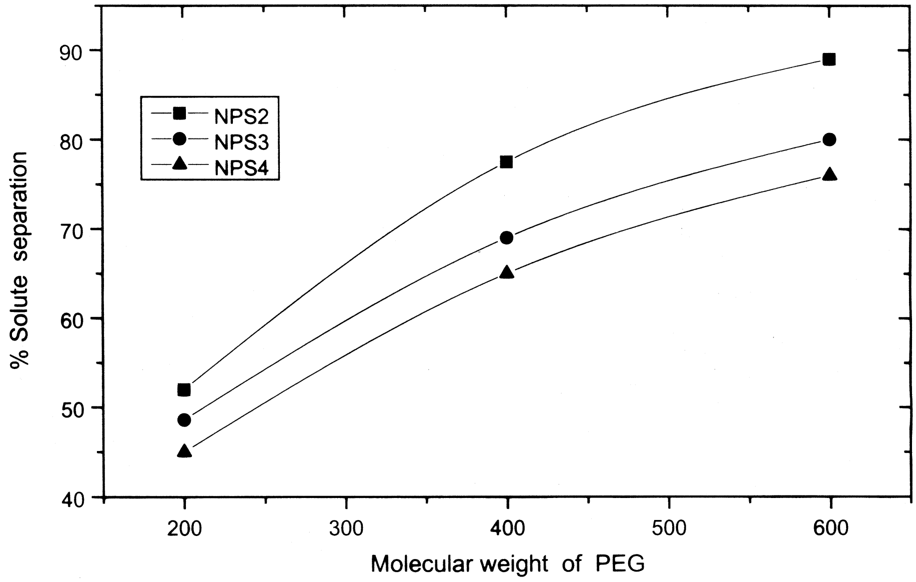

Figure 6. Separation of PEG Solutes as a Function of Molecular Weight.

separation of Methylene Blue with molecular weight of 373.9 and Rhodamine-B with molecular weight of 479.02 are lower. The higher separation for Methyl Red and Bromophenol Blue could be due to the anionic nature of the dye whereas the lower separation for the other two could due to the cationic nature of the dye. The separation of dyes are in general higher than that of PEG solute of comparable molecular weight as well as the inorganic solutes.

TABLE 5. Separation Behavior of Dyes by Nitrated Polysulfone (NPS-3) Membrane

Name of Dye	Mol. Wt.	Flux ($l.m^{-2}d^{-1}$)	% solute separation
Methyl Red	269.31	2700	85.0
Methylene Blue	373.9	2669	63.5
Rhodamine B	479.02	2670	71.0
Bromophenol Blue	669.98	2650	95.5

Concentration of dye in feed : 100 mg/ L ; Pressure : 7 Kg/ cm^2 ; Temperature : 26°C

TABLE 6. Performance of the Membrane (NPS-2) as a Function of Number of Days Exposure in Acid, Alkaline, and Free Chlorinated Demineralized Water

Number of days exposure	0.1 (M) HCl		0.1 (M) NaOH		Chlorine (100 ppm)	
	Flux ($l.m^{-2}.d^{-1}$)	% solute separation	Flux ($l.m^{-2}.d^{-1}$)	% solute separation	Flux ($l.m^{-2}.d^{-1}$)	% solute separation
0	570	74.0	559	76.2	584	72.7
7	535	74.5	524	76.1	587	72.0
14	535	73.2	562	74.9	587	71.7
21	490	76.3	559	74.9	580	72.0
32	490	76.2	560	74.5	580	72.0

Feed : 2000 ppm Na_2SO_4 ; Membrane area : 15.4 cm^2 ; Pressure : 7 Kg / cm^2

Chemical Stability of the Membranes

The chemical stability of the membrane sample (NPS-2) has been evaluated in terms of change in flux and solute separation after regular interval. The membranes are tested using 2000 ppm Na_2SO_4 at 7 Kg/cm^2 pressure. The membranes were exposed to acidic (0.1M HCl), alkaline (0.1M NaOH) and chlorinated (100 ppm free chlorine) demineralized water. The change in the flux and separation data as a function of number of days exposure is given in Table 6. It can be seen that the membranes are fairly stable even after 60 days of exposure in 0.1M HCl, 0.1M NaOH and chlorinated (100 ppm free chlorine) demineralized water.

CONCLUSION

Nitrated polysulfone as used to make semipermeable membranes which show better separation capability for electrolytes as compared to polusulfone membranes. Nitrated polysulfone membranes show higher separation capability for multivalent anionic species in aqueous solution. The separation behaviour of nitrated polysulfone membranes for electrolytes show typical maxima as a function of feed concentration. Nitrated polysulfone membranes show better separation of anionic dye of low molecular weight. Separation data oflow molecular weight PEG and the electrolytes are compared. Nitrated polysulfone membranes show sustained separation behavior up to 32 days of exposure in acid, alkaline and chlorinated demineralized water.

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Received September 1, 1999
Revision received February 1, 2000