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Dependence of Performance of Poly(Sulfone-co-Amide) Membranes on Compositional Variation of Casting Solution and Coagulation Media—Development of Reverse Osmosis and Nano Filtration Membranes

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ABSTRACT

Poly(sulfone-co-amide) polymer was synthesized by a low temperature solution polycondensation technique from benzene 1,3 dicarboxylic acid chloride (isophthaloyl chloride), benzene 1,4 dicarboxylic acid chloride [terephthaloyl chloride (TPC)], and *bis*[4-amino phenyl] sulfone, i.e., (4,4′-diamino diphenyl sulfone) as monomers using *N*,*N* dimethyl acetamide (DMAc) as solvent cum acid acceptor. Casting solutions using various combinations of DMAc and acetone as solvent and LiCl and

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$LiNO_3$ as additives were prepared. Wet phase inversion membranes were prepared from them at ambient temperature (25°C) using demineralized water (DMW) or aqueous sodium dodecyl sulfate (SDS) as coagulation media. Solute rejections of the membranes increased and solvent flux decreased with increasing proportion of acetone and decreasing DMAc content in the casting solution. Use of 1% and 2% aqueous SDS solution as gelling media improved the flux of the membranes significantly. Evaporation of solvent at room temperature prior to gelling, in certain cases, led to high solute rejecting membranes. By the proper combination of casting solution composition, evaporation time, and gelling medium, it was possible to make a range of NF membranes and also high solute rejecting brackish water RO membranes from the single polymer. More importantly, use of a significant amount of acetone in the casting solution enabled us to make high solute rejecting integrally skinned asymmetric membranes simply by evaporation of solvent followed by coagulation in a proper medium, all at ambient temperature. The membranes do not need any other treatment before use.

Key Words: Poly(sulfone-co-amide) membranes; Reverse osmosis; Nanofiltration; Coagulation media; Donnan exclusion.

INTRODUCTION

Phase inversion technique is a widely used method to prepare integrally skinned semipermeable membranes from synthetic polymers.[1–5] A casting solution consisting of a homogeneous mixture of polymer and nonsolvent additive in an appropriate solvent is cast on a plane surface and then immersed in a coagulation bath where phase separation takes place due to diffusive action of solvent of the polymer solution into the coagulation bath and the nonsolvent of the latter into the polymer solution. The solidified phase inversion membrane that results is a porous asymmetric structure with a morphology and structure that are governed by the polymer solution composition (concentration of solvent and additive), thermodynamics of membrane casting conditions, and the type of coagulation bath.

Performance of a membrane from a given polymer depends on various factors. Kesting suggested that the surface tension of casting solution has a significant effect on resulting membranes.[6] Khulbe et al. found that membrane performance is affected by the boiling point of solvent.[7] Hamza et al. have investigated how performance of membranes could be varied by adjusting the composition of its solvent system.[8] They found that there is an increase in nodule size of membrane due to an increase in polymer solvent interaction. Tsai et al. have also tried to improve the performance of membranes by adjusting the composition of casting solution.[9] Several researchers studied the effect of solvent power in shaping the membrane performance.[1,10]

In addition to the composition of the casting solution, the coagulation medium also has a tremendous effect on the performance of the resulting membranes. Chuan et al. investigated the effect of *N*,*N* dimethylacetamide (DMAc) in an aqueous coagulation bath on membrane performance.[11] Wang et al. studied the effect of the addition of nonsolvent in the casting solution and coagulation of the membranes in a bath of ethanol.[12] Yao et al. studied the effect of coagulation conditions on the structure and properties of aliphatic polyamide membranes.[13] Tweddle and Sourirajan used a water–ethanol mixture as gelation media.[14] Frommer used various aqueous electrolyte solutions and studied the rate of water penetration and the rate of solvent outflow and correlated it to the observed membrane performance.[15] Okada and Matsuura used aqueous solutions of sodium chloride as gelation media to study the effect of change in water activity on the pattern formation at the surface of cellulose acetate membranes prepared by phase inversion technique.[16] Various other investigators researched the effect of casting solution composition and the type of gelation media on the formation of phase inversion membranes.[17,18]

Synthetic polyamide types of polymers have been extensively researched as candidates for semipermeable membranes for application in reverse osmosis (RO), nanofiltration (NF), and ultrafiltration (UF) based separations. Aromatic polyamide types of polymers having the requisite balance of hydrophilic and hydrophobic moieties are suitable for RO and NF applications.[19] Some such candidates with excellent membrane properties have been reported on earlier from our laboratory.[20,21] However, the steps for polymer synthesis are lengthy since some of the monomers are not available commercially and have to be synthesized before polymer synthesis. We developed a polymer of this class, the poly(sulfone-co-amide), using commercially available monomers, which has not been widely studied or reported. This polymer is also significantly different from the polysulfone (PSf) or polyether sulfone (PESf) polymers. The latter two polymers, being hydrophobic, are not suitable for RO or NF applications without further modifications by suitable chemical reactions like sulfonation. The unmodified PSf or PESf are mainly used for UF applications. Introduction of amide functionality in the present work is supposed to improve the hydrophilicity of the polymer, making them more suitable for NF and RO applications. In the present work, we synthesized the poly(sulfone-co-amide) polymer and tried to make membranes of different types, such as high solute rejecting RO and NF membranes, with a wide range of performance by using various combinations of casting solution composition, evaporation period, and coagulation media in addition to other membrane casting conditions. To our knowledge, polyamide types of polymers are generally made by high temperature solvent evaporation of nascent membranes. We developed a procedure to make phase inversion membranes from one such polyamide class of polymers by a two-step process: evaporation and gelling, all at ambient temperature (25°C).

EXPERIMENTAL

Materials

Monomers 4,4′-diamino diphenyl sulphone, isophthaloyl chloride, and terephthaloyl chloride (TPC) were purchased from Aldrich Chemical Co. (Mumbai, India) and used for polymerization after purification by double recrystallization. *N*,*N* dimethyl acetamide, LiCl, and $LiNO_3$ were of reagent grade and used without further purification.

Polymer Synthesis

Poly(sulfone-co-amide) was synthesized by low temperature solution polycondensation technique of 4,4′-diamino diphenyl sulfone (DADPS), isophthaloyl chloride (IPC), and TPC using DMAc as solvent. Monomers were used in the ratio of DADPS : IPC : TPC :: 50 : 15 : 35 (mol/mol). Dimethyl acetamide also acts as acid acceptor by complexing with the by-product HCl, thereby, enhancing the rate of the reaction. The polymer was precipitated in the size of small globules (so that handling of the polymer is easy) by pouring the reaction liquor drop wise in a bath of demineralized water (DMW). Care was taken to ensure that all solvents leached out of the polymer by keeping it in demineralized water for several days and changing the water frequently. The polymer was then vacuum dried, using a water bath for heating, before being used for membrane making. The scheme of polymer synthesis is presented in Fig. 1.

Preparation of Casting Solution

Casting solutions of different compositions were prepared from the polymer using a mixture of DMAc and acetone in different proportions and a mixture of LiCl and $LiNO_3$ as nonsolvent additives. They were mixed to form a homogeneous solution, which was then used for preparation of membranes, after ensuring that there was no trapped air bubble left in the viscous dope.

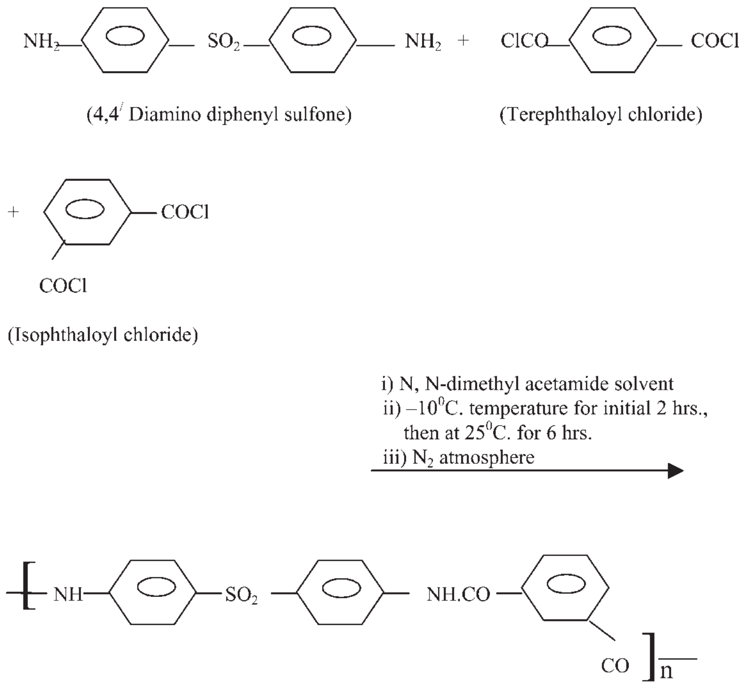

Figure 1. Scheme of poly(sulfone-co-amide) synthesis.

Casting of Membrane

The casting solution was spread to a uniform thickness by a smooth roller on a plane glass plate. The cast thickness of the membrane was kept 100 microns. The cast solution was kept exposed for certain predetermined period to allow partial evaporation of volatile solvent, essentially from the top surface of the cast film, before being immersed in a coagulation bath. It was kept immersed in the coagulation bath for 3–4 hr, then removed and kept in a DM water bath for another 2 hr before being used for testing.

Evaluation of Membrane Performance

Membranes were cut in circular shape and tested in a test cell having an effective area of 15.5 cm^2. Single solute aqueous solutions of 2000 ppm NaCl, $CaCl_2$, and Na_2SO_4 were used as feed. The applied pressure was 10–15 kg/cm^2 for NF membranes and 30 kg/cm^2 for RO membranes.

Concentrations of solutes in feed and permeate were determined from their conductivity values. Percentage solute rejection (%SR) was calculated from the values of feed and permeate concentration using the following relation

$$\%\mathrm{SR} = \frac{\text{Concentration of feed} - \text{Concentration of permeate}}{\text{Concentration of feed}} \times 100$$

The permeate flux was measured and expressed in units of liter/m^2/day (L m^{-2} d^{-1}).

RESULTS AND DISCUSSION

Casting Solution Compositions

Casting solutions containing the polymer, a mixture of DMAc, and acetone as solvent and LiCl and $LiNO_3$ as additives were used for studies in this series. The compositions used are presented in Table 1. The polymer swells in acetone but does not dissolve in it. It, however, becomes soluble in a mixture of acetone and DMAc. So, instead of an established practice of using only DMAc or other strong solvents, like *N*-methyl pyrrolidone or dimethyl formamide, a mixture of acetone and DMAc was tried as solvent. A solvent mixture containing DMAc and acetone in the DMAc : acetone ratio (vol/vol) of 100 : 0, 90 : 10, 80 : 20, 60 : 40, 50 : 50, 40 : 60, 30 : 70, 25 : 75, and 20 : 80 were used to prepare dope solutions. Dope composition containing more than 80% (vol/vol) acetone was not suitable for membrane making. In all the compositions, a mixture of LiCl and $LiNO_3$ (1 : 1 wt/wt) was taken as

Table 1. Casting solution composition of poly(sulfone-co-amide) polymer.

Composition number	Polymer weight (g)	DMAc : acetone (vol/vol)	LiCl (g)	$LiNO_3$ (g)
1	10	10 : 0	2.5	2.5
2	10	9 : 1	2.5	2.5
3	10	8 : 2	2.5	2.5
4	10	6 : 4	2.5	2.5
5	10	5 : 5	2.5	2.5
6	10	4 : 6	2.5	2.5
7	10	3 : 7	2.5	2.5
8	10	2.5 : 7.5	2.5	2.5
9	10	2 : 8	2.5	2.5

nonsolvent additive. The amount of additive used was 50% of the weight of the polymer present in the dope.

Solubility Parameters of Polymer and Solvents

The Gibbs free energy associated with the dissolution of the polymer in a solvent can be represented in a simplified relation as

$$\Delta G = V_{\mathrm{m}}[(\delta_{\mathrm{sp}})_{\mathrm{pol}} - (\delta_{\mathrm{sp}})_{\mathrm{solvent}}]^2 \varphi_1 \varphi_2 - T\Delta S \tag{1}$$

where φ_1 and φ_2 are volume fractions of polymer and solvent, respectively, δ_{sp} is the solubility parameter, and V_{m} is the molar volume of polymer solution.

In the mixture of solvents, the cohesive energies are assumed to be additive when normalized for volume fraction of the constituents present and the solubility parameter is calculated using the following:

$$\delta = \sum_i \varphi_i \delta_i \tag{2}$$

φ_i is the volume fraction of species i and δ_i is the solubility parameter of the species i.

The solubility parameter difference between the polymer (P) and the solvent (S) is given by

$$\Delta\delta_{\mathrm{P-S}} = \sqrt{(\delta_{\mathrm{d,p}} - \delta_{\mathrm{d,s}})^2 + (\delta_{\mathrm{p,p}} - \delta_{\mathrm{p,s}})^2 + (\delta_{\mathrm{h,p}} - \delta_{\mathrm{h,s}})^2} \tag{3}$$

The solubility parameters of the polymer were calculated using group contributions of the constituent functional groups in the polymer[22] and the similar values of the solvent were calculated using values from other work.[23] The values are presented in Table 2.

Effect of Variation of Casting Solution Composition and Gelling Media

Effect of Variation of Casting Solution Composition

Table 2 summarizes the composition of solvents used for making the casting solution and their solubility parameters. In the whole series of compositions, the polymer concentration and the additive concentration were kept constant; only the solvent composition was varied.

Table 2. Solubility parameter values of polymer and solvent and their differences.

Composition number	Volume fraction of DMAc	Volume fraction of acetone	δ_p $(J/cm^3)^{1/2}$	δ_h $(J/cm^3)^{1/2}$	δ_d $(J/cm^3)^{1/2}$	δ_{sp} $(J/cm^3)^{1/2}$	$\Delta\delta_{P-S}$ $(J/cm^3)^{1/2}$
1	1 (only DMAc)	0	11.5	10.2	16.8	22.7	8.21
2	9/10	1/10	11.39	9.88	16.67	22.47	8.45
3	8/10	2/10	11.28	9.56	16.54	22.18	8.7
4	6/10	4/10	11.06	8.92	16.28	21.61	9.22
5	5/10	5/10	10.95	8.6	16.15	21.32	9.49
6	4/10	6/10	10.84	8.28	16.02	21.04	9.76
7	3/10	7/10	10.73	7.96	15.89	20.76	10.04
8	2.5/10	7.5/10	10.68	7.8	15.83	20.62	10.18
9	2/10	8/10	10.62	7.64	15.76	20.48	10.33
Acetone			10.4	7	15.5	20.1	10.91
Polymer			7.5	16.79	19.06	26.39	—

As can be seen from the table, δ_{sp} values of DMAc, acetone, and polymer are 22.7, 20.1, and 26.39 $(J/cm^3)^{1/2}$, respectively. Since the value for DMAc is closer to that of the polymer than the value of acetone to the polymer, it is evident from Eq. (1) that DMAc is a better solvent for the polymer than acetone. As acetone component increases in the solvent system, the δ_{sp} of the solvent mixture becomes less than that of DMAc, but more than that of acetone. This implies that the solvent power of the mixture of acetone and DMAc is less than that of pure DMAc but more than that of acetone.

The compatibility of the polymer and solvent is better represented by the values of $\Delta\delta_{P-S}$. The $\Delta\delta_{P-S}$ value involving only DMAc as solvent is the lowest and it increases as the acetone component is increased. This indicates that DMAc is most compatible and the strongest solvent for the polymer than any combination of acetone and DMAc. However, stronger solvents may not always be helpful, as it will take the casting solution farther away from the phase boundary, which will not be a helpful factor, especially for membranes made by phase inversion technique.

The performances of membranes made from these compositions are presented in Table 3. These results are for membranes made without evaporation of solvents. These membranes were made by spreading the dope on a plane glass plate to a predetermined thickness and then immediately putting them in the coagulation bath. The results show that for a given gelling medium, the solute rejection of membranes increases regularly with increasing fraction of acetone and decreasing fraction of DMAc in the casting solution. The solute rejections of all the solutes studied are minimum when membranes were made using casting solution having only DMAc as solvent (composition number 1 of Table 2). It increases regularly and is maximum with the casting solution having highest acetone to DMAc ratio. Correspondingly, the solvent flux goes on decreasing as the acetone to DMAc ratio increases and is minimum with the casting solution having the highest acetone to DMAc ratio.

The $\Delta\delta_{P-S}$ values increase as the acetone concentration increases in the casting solution. Because of this, it is easier to make membranes by phase inversion technique from casting solution having higher acetone concentration, since it is closer to the phase boundary than solutions having lesser acetone concentration. The presence of acetone serves two purposes. It helps in bringing the casting solution closer to the phase boundary by reducing the solvent power, which is still sufficient to hold the polymer and additive in a stable solution, and making the process of phase inversion easier. Second, it being a volatile solvent comes in handy during the fabrication of membranes. This second effect will be clearer in the case of results presented in Table 4, where membranes have been made by evaporation of solvent. When acetone is present in substantial proportions, such as in compositions 7, 8, and 9, membranes

Table 3. Effect of casting solution composition and coagulation media on membrane performance (membranes made without evaporation of solvents).

		Coagulation media					
		DMW		1% SDS		2% SDS	
Composition	Solute species	%SR	Flux ($L\,m^{-2}\,d^{-1}$)	%SR	Flux ($L\,m^{-2}\,d^{-1}$)	%SR	Flux ($L\,m^{-2}\,d^{-1}$)
1	NaCl	10	1856	8.5	2600	Negligible	3408
	Na_2SO_4	21.1	1728	12.25	2260	6.3	3120
	$CaCl_2$	6.8	1700	5.1	2200	Negligible	2976
2	NaCl	12.5	1715	8.6	2400	Negligible	3168
	Na_2SO_4	26.53	1540	17.7	2160	6.4	2840
	$CaCl_2$	8.6	1416	5.8	2100	Negligible	2788
3	NaCl	15.2	1256	12.2	2300	4.8	2890
	Na_2SO_4	35.71	1152	21.5	1990	8.9	2688
	$CaCl_2$	10.23	1010	6.8	1810	Negligible	2584
4	NaCl	17.5	820	13.92	1780	6.6	2650
	Na_2SO_4	40.7	760	29.42	1684	12.5	2580
	$CaCl_2$	11.27	710	8.91	1620	Negligible	2520

5	NaCl	18.81	740	16.66	1620	11.6	2488
	Na_2SO_4	42.56	682	35.56	1572	20.36	2020
	$CaCl_2$	12.31	608	10.92	1542	6.4	2050
6	NaCl	21.1	660	19.1	1588	17.55	2240
	Na_2SO_4	46.12	581	42.5	1510	38.75	2016
	$CaCl_2$	14.12	498	12.1	1476	8.5	1860
7	NaCl	—	—	38.5	1240	36.25	1460
	Na_2SO_4	90	204	89.9	1108	87.2	1370
	$CaCl_2$	—	—	18.8	1080	17.3	1320
8	NaCl	—	—	47.3 (58.8)[a]	1008 (1360)[a]	43.4 (53.33)[a]	1272 (1520)[a]
	Na_2SO_4	92	200	92.59	960	89.62	1156
	$CaCl_2$	—	—	24.9	880	23.3	1060
9	NaCl	87.78	103	57.6	376		484

Note: (i) Applied pressure 10 kg/cm^2; (ii) Feed system—2000 ppm single solute.

[a] Tested at 15 kg/cm^2 pressure.

Table 4. Effect of solvent evaporation time on performance of membranes made using different casting solution compositions.

		Evaporation time (sec)									
		Nil		25		45		60		75	
Composition number	Feed type	%SR	Flux ($L\,m^{-2}d^{-1}$)	%SR	Flux ($L\,m^{-2}d^{-1}$)	%SR	Flux ($L\,m^{-2}d^{-1}$)	%SR	Flux ($L\,m^{-2}d^{-1}$)	%SR	Flux ($LM^{-2}D^{-1}$)
6	NaCl	17.55	2240	22.6	1622	24.4	1210		—		—
	Na_2SO_4	38.75	2016	57.5	1410	67.5	1130				
	$CaCl_2$	8.5	1860	9.6	1348	10.5	960				
7	NaCl	36.25	1460	46.25	1113	52.2	884		—		—
	Na_2SO_4	87.2	1370	90.4	994	90.2	756				
	$CaCl_2$	17.4	1320	27.05	946	34.06	708				
8	NaCl	43.4	1272	69.22	740	86.09	1689^a	90.29	1344^a	93.41	1056^a
	Na_2SO_4	89.62	1156	92.1	710	96.5	1588^a	97.76	1256^a	98.9	964^a
	$CaCl_2$	23.3	1060	44.3	688	82.36	1562^a	87.8	1212^a	92.8	924^a
9	NaCl	50	484	92.94	908^a	97.64	600^a	98.18	517^a	98.4	395^a
	Na_2SO_4	—	—	98.7	864^a	99.2	582^a	99.42	472^a	99.5	344^a
	$CaCl_2$	—	—	90.4	820^a	97.8	544^a	98.32	416^a	98.8	324^a

Note: Feed—2000 ppm single solute.

[a] Tested at 30 kg/cm^2, others tested at 10 kg/cm^2 pressure.

can be prepared by evaporation of acetone at ambient temperature (see Table 4), just like it is done in the case of cellulose acetate RO membranes containing acetone as a major solvent. However, it may be interesting to note that even in the case of the membranes shown in Table 3, which were not subjected to solvent evaporation prior to their coagulation, there is also a regular increase in solute rejection and an accompanying decrease in solvent flux with an increase in acetone amount in the solvent.

Generally, it is observed that stronger solvents yield high solute rejecting low flux membranes. However, deviation from this has been observed in some cases[12] when the system is multicomponent and the membrane making process is not a simple case of high temperature evaporation of the solvent. In the present case, a multicomponent casting solution with a mixture of additives and solvents makes the system so complex to be simplified. All of these factors along with the casting technique are believed to play a role in this type of trend of membrane performance.

Effect of Coagulation Media

As the cast polymer film is immersed in a gelling bath, exchange of solvent (of the nascent film) and nonsolvent (water) takes place at the film–gelation medium interface. Solvent and additive diffuse out of the membrane and, simultaneously, nonsolvent (water), from the gelation bath, enters into the membrane. As a result, nonsolvent to solvent ratio increases in the top surface of the membrane setting up a thermodynamic instability where the solvent can no longer hold the polymer in stable solution. This induces the process of precipitation of the polymer, initially at the top surface of the membrane. The process of precipitation continues with time and propagates deep into the membrane matrix. The overall membrane performance depends on the relative rates of counter transports of solvent and solutes into and out of the membranes that result in the final membrane structure. In addition to the solvent movement, it is reported[1] that polymer in the bulk of cast membrane keeps moving toward the interface during the gelation, which continues until it gets precipitated. The more time it takes for polymer precipitation, the longer the polymer moves from the bulk of nascent membrane to the interface (Fig. 2) and the higher its concentration becomes at the interface. This results in a denser polymer layer at the interface. Hence, a slower process of gelling results in low flux membranes.

The 1% and 2% concentration of sodium dodecyl sulfate (SDS) in water is higher than its critical micellar concentration (CMC). So at these concentrations, SDS molecules, after getting saturated in the aqueous solutions, remain in micellar form in the gelling media (see Fig. 2). These micelles have a greater capacity to accommodate solvents and solutes.

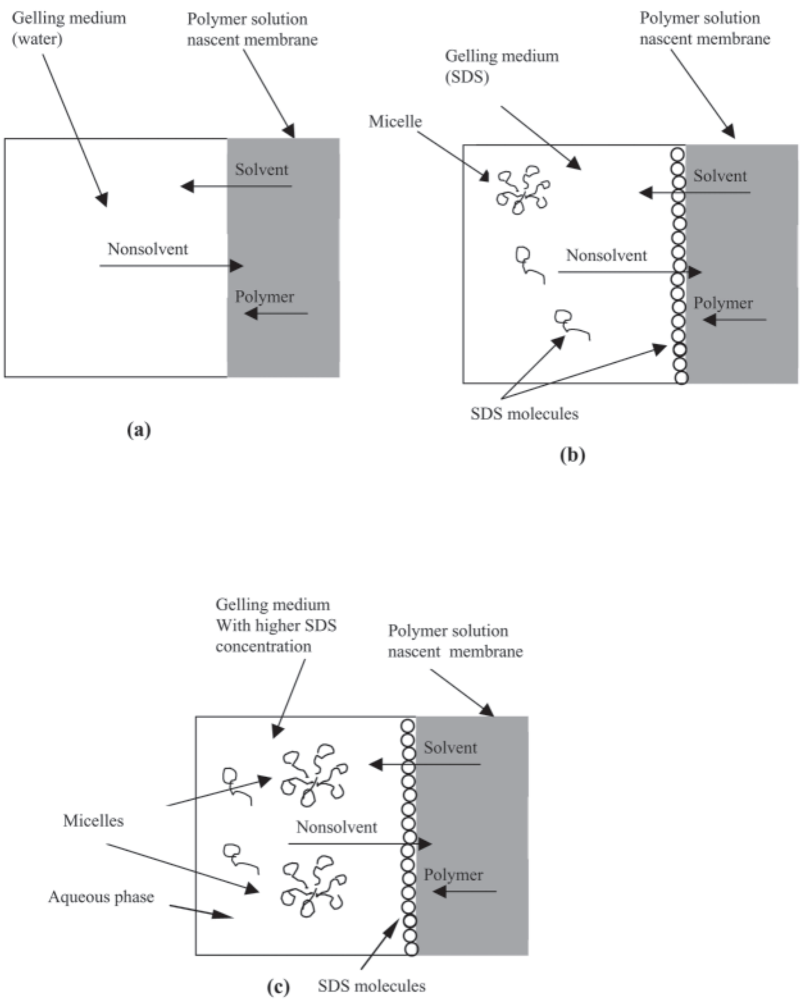

Figure 2. Schematic diagrams of exchange between solvent and nonsolvent at the interface of gelation medium and polymer solution. (a) Pure water as gelation medium, (b and c) aqueous SDS with extensive micellar network as gelling media.[24]

The solvent molecules, therefore, after leaching out of the membrane, get enveloped inside the micelles. This results in a further driving force for solvent to leach out at a faster rate. This leads to faster precipitation and, consequently, a less dense (more porous) polymer layer at the top surface of the membrane. This explains the higher flux and lower rejection of the membrane gelled in

SDS bath as compared to DM water bath. The increase of SDS concentration to 2% still increases the solvent flux of these membranes with a corresponding decrease in solute rejection, indicating that the presence of more micellar structure in the gelling bath enhances the process of gelling, resulting in a less dense skin layer of the membrane. Alsari et al.[24] reported a similar effect of SDS gelling medium in the context of formation of PES membranes.

This aspect, which may be more complex than has been assumed here, is the subject of further investigations and future communications, where studies will deal with the morphological changes associated with the experimental conditions, such as casting solution composition, coagulation media, and also solvent evaporation period (discussed in a subsequent section). That will lead one to a better understanding of the individual effect as well as the combined effect of all these factors.

Effect of Evaporation Period

After casting of the membrane on a plane surface to uniform thickness and before immersing it in the gelling bath, the membrane was kept exposed for certain period to allow partial evaporation of solvents from its top surface. The results of these membranes are presented in Table 4. It can be seen that in case of composition 6, with 60% acetone and 40% DMAc, there is not much improvement of solute rejection even up to 45 sec of evaporation. In the case of composition 7, with 70% acetone and 30% DMAc, the increase in solute rejection with evaporation time is more than the earlier one. However, with composition 8, where the solvent is 75% acetone and 25% DMAc, the increase in solute rejection (and the accompanying decrease in solvent flux) with evaporation period is rapid. In the case of composition 9, containing 80% acetone and 20% DMAc, the solvent flux at 10 $\mathrm{kg/cm^2}$ pressure is much lower with an improved solute rejection. In fact beyond a 25-sec evaporation period, high solute rejecting, tighter RO membranes are formed.

During the evaporation period, acetone evaporates from the top surface of the membrane since this is the volatile component of the solvent system. This results in a top surface depleted of solvent, which cannot hold the polymer in a homogeneous mixture. This thermodynamic instability causes a thin layer of tiny polymer aggregates to separate out of the solution. This initiates the formation of skin layer of the membrane at the top. Since in the case of composition 6, acetone concentration is not much for evaporation and formation of skin layer, there is not much improvement in solute rejection with evaporation. As acetone fraction in the casting solution increases, there is rapid improvement of solute rejection with evaporation time. This indicates the formation of high rejecting skin layer in the membrane top surface.

Our observation of the effect of coagulation medium, as well as solvent evaporation, gives some interesting results. Where densification by rapid solvent evaporation leads to tighter (low solvent flux, high solute rejecting) membranes, rapid coagulation in aqueous SDS leads to membranes with improved solvent flux. Effect of solvent evaporation has been extensively studied in context with cellulose acetate membranes containing acetone as a major solvent[19] and we believe our present situation may not be much different from those cellulose acetate membranes as far as the effect of solvent evaporation on membrane performance is concerned. However, in contrast, faster precipitation by SDS coagulation bath improves the flux of the membranes. This apparent anomaly is not fully understood and needs further investigation.

Selectivity Pattern

Three single solute aqueous feed systems of NaCl, $CaCl_2$ and Na_2SO_4 were used to study the rejection behavior of the membranes. It can be observed (see Table 3) that irrespective of the nature of the coagulation media, the rejection of Na_2SO_4 is significantly higher than that of NaCl, which, in turn, is higher than the $CaCl_2$ rejection for most of the membranes. This type of pattern indicates the charged nature of the membranes. If we look at the structure of the polymer, we can see that one of the end groups of the polymer is $-COCl$, which, in aqueous medium, will remain as $-COOH$. This will impart a partial ion exchange character to the membrane with a fixed negative charge ($-COO^-$) on its surface and also on the pore walls and a mobile H^+ as counter ion. Due to this, there will be high rejection of negatively charged co-ion $SO_4{}^{2-}$ because of Donnan exclusion. The doubly charged counter ion Ca^{2+} shows a very low rejection since its passage will be facilitated through the negatively charged membrane. The passage of the univalent counter ion Na^+ will be less than the bivalent Ca^{2+} ion, which is reflected in the higher Na^+ rejection than the Ca^{2+} ion rejection. This results in the high rejection of Na_2SO_4 and poor rejection of $CaCl_2$ with an intermediate NaCl rejection.

Though the rejection of Na_2SO_4 is always the highest of the three, the gap between the rejections of NaCl and $CaCl_2$ becomes closer for high rejecting membranes, especially with those of compositions 8 and 9. The high solute rejection and low solvent flux of these membranes indicate that they have smaller pores as compared to other membranes. In fact, in some of the highly rejecting membranes the rejection of $CaCl_2$ is some times more than NaCl rejection (Fig. 3). Two mutually opposing factors are believed to be responsible for this type of behavior. The smaller pore size of these membranes retards the passage of Ca^{2+} ion and, at the same time, the surface

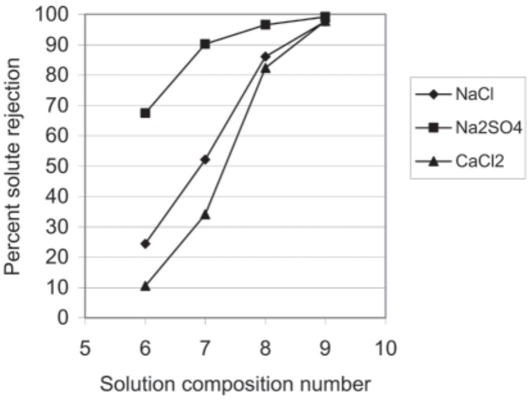

Figure 3. Trend of %SR of three solutes using membranes cast by dopes having different casting solution compositions; 6, 7, 8, and 9 (from experimental data at 45 sec evaporation time and 2% SDS gelling media; membranes of composition 8 and 9 tested at 30 kg/cm^2, others tested at 10 kg/cm^2 applied pressure).

negative charge helps the passage of Ca^{2+} ions. The narrowing of the gap between NaCl and $CaCl_2$ rejections, consequent to the increase of $CaCl_2$ separation, indicates that the pore size factor plays a dominant role in this zone than the Donnan exclusion factor for the overall rejection of the salts. Similar results due to the end and stray carboxylic groups of nitrocellulose membranes have also been reported elsewhere.[25,26]

NF and RO Membranes

With the increase in acetone fraction in the solvent used in casting solution, the solute rejection properties of the membranes are seen to improve. Simultaneously, using aqueous SDS as a gelling medium, the flux of these membranes is seen to increase significantly. NF membranes with a wide range of performance are prepared by a combination of these two factors using solvent evaporation as a tool. The rejection of NaCl ranged from 20% to 45% at 10 kg/cm^2 pressure associated with high solvent flux. In some of the cases, up to 60% NaCl rejecting membranes could be obtained with good solvent flux when tested at 15 kg/cm^2 applied pressure. All of the membranes had high solute rejection for Na_2SO_4, ranging up to greater than 90% and high solvent flux at 10 kg/cm^2 applied pressure. The performance of some of our NF membranes compare very closely to the corresponding data available in published research and also to those of commercial membranes.[27–30] Table 5

Table 5. Solute rejections of poly(sulfone-co-amide) NF membranes compared to other reported NF membranes.

Solute type	Membrane				
	PSAm	NF-40	XP-45	NTR-7450	Desal-5
NaCl	47	45	50	51	47
$CaCl_2$	24.9	—	—	—	—
$MgCl_2$	—	—	83	13	—
Na_2SO_4	92.5	—	97.5	92	—
$MgSO_4$	—	—	—	32	—

Note: PSAm, Poly(sulfone-co-amide); feed 2000 ppm, pressure applied 10 kg/cm^2; NF-40: feed 2000 ppm, pressure applied 20 kg/cm^2; Desal-5: feed 1000 ppm, pressure applied 10 kg/cm^2; NTR-7450: feed 5000 ppm, pressure applied 10 kg/cm^2.

shows the comparative data of our membranes vs. the nanofiltration membranes reported elsewhere.

Similarly, using solvent evaporation as a tool in addition to a proper casting solution composition and using appropriate coagulation baths, RO membranes with very high solute rejection and good solvent flux have also been made.

CONCLUSIONS

In this work, we synthesized poly(sulfone-co-amide) polymer by subzero temperature solution polycondensation technique for the purpose of making nanofiltration and reverse osmosis membranes. In principle, the polymer can also be suitable for other membrane applications, such as ultrafiltration.

It was demonstrated that casting solutions can be prepared by using a mixture of high volatile acetone and high boiling DMAc as solvent. It has also been shown how the change of casting solution composition, only in terms of change in the composition of solvent system, has a tremendous effect on the performance of the resulting membranes.

In addition to the casting solution composition, the effect of gelling medium as well as solvent evaporation prior to gelling, was investigated and discussed in this article. A proper combination of all of these three parameters enabled us to prepare tailor-made RO and NF membranes from a single polymer. The use of aqueous SDS as a gelling medium significantly improves the solvent flux of the membranes.

From the rejection behavior of these membranes toward NaCl, $CaCl_2$ and Na_2SO_4, single solute aqueous feed solutions, it was established that the membrane has surface negative charge, resulting in Donnan type of exclusion of solutes for NF membranes. The Donnan exclusion effect is, however, superseded by the rejection due to possibly smaller pore size in the case of high rejecting RO membranes.

A striking feature of this work is the simplicity of preparation of these membranes. The use of a significant portion of acetone as solvent in the casting solution enables us to prepare membranes by evaporation of the volatile component of the solvent at room temperature (25°C), followed by gelling. There is no need of any further pretreatment of the membranes before they are ready to be used.

The polymer seems to be an excellent candidate for RO and NF applications, especially for the latter, owing to its charged properties. Couple this to the fact that it responds significantly to the variations in thermodynamic parameters like casting solution composition, solvent evaporation, and gelling media, and the claim is more justified.

Further works in this area will focus on better understanding of the mechanisms and effects of the experimental parameters with particular emphasis on changes in morphology associated with these factors. Wider applicability in various feed concentration regimes for different feeds, including complex feed systems containing a mixture of solutes in aqueous medium having different ionic strength of water, will be investigated. The possibility of modification to introduce charged groups to the polymer might make it a still better candidate for NF applications. The aim is to attain an excellent polymer candidate for making commercial grade, charged NF membranes.

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