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Separation Behavior of Composite Polyamide Membranes from Mixed Amines: Effects of Interfacial Reaction Condition and Chemical Post-Treatment

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Abstract: Composite polyamide membranes are prepared using in-situ interfacial polymerization using mixed amine system comprising 1,4-phenylene diamine and pipperazine. Separation performance of the membranes are studied as a function of the concentration of amine and acid chloride, the concentration ratio of the amines, nature of the acid chloride, and the presence of surfactant and acid acceptor in the aqueous reagent. The effect of esterification and hydrazide reactions involving residual carboxylic acid groups in the polymeric membranes on the co-polymeric composite membrane performance is also studied. The membrane performance can be tailored easily by conversion of the residual reactive functional groups in post-treatment.

Keywords: Composite membranes, interfacial polymerizations, polyamide, separation

INTRODUCTION

Composite membranes have gained much importance in the membrane technology because of their ability to have the properties of two different membranes together with improved separation performance. Thin film composite (TFC) membranes are the most preferred RO and NF membranes to date because of the combination of excellent permeability

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and selectivity in the same membrane. Composite polyamide membrane development has been well documented in the literature for the last three decades. Peterson (1) gave a detailed review of composite Reverse Osmosis (RO) and Nanofiltration (NF) membranes. There are several patents explaining different methods and systems used to make commercially successful TFC membranes (2–9). After successful preparation of fully aromatic polyamide TFC membrane by Cadotte (2), most of the research was directed towards improvements in performance of polyamide composite membranes for aqueous applications in terms of increasing membrane productivity and selectivity by changing new monomeric systems or adding extra additives or by surface treatments (10–18). For example, Kenichi and Tomaschke (10) have prepared new composite RO membranes based on m-phenylene diamine and 1, 2, 3, 4-cyclopentane tetra carboxylic acid polyamide. These membranes exhibited the solute rejection of more than 99% and high flux. In the same line, the TFC membranes prepared from m-phenylene diamine and biphenyl acid chlorides like 3,4′,5-biphenyl triacyl chloride (BTRC) and 3,3′,5,5′-biphenyl tetraacyl chloride (BTEC) exhibit higher salt rejection compared with that prepared from trimesoyl chloride (TMC) at the expense of some flux (11). Similarly, the TFC membranes with enhanced performance were prepared using different amines with fixed acid chloride. For example, Z. Yong et al. (12) reported the preparation of high flux TFC membrane from *m*-phenylenediamine and *m*-phenylenediamine-5-sulfonic acid and trimesoyl chloride (TMC). The influence of the diamine structure on the nanofiltration performance, surface morphology, and the surface charge of the composite polyamide membranes was reported by S. Verı́ssimo et al. (13). Novel polyamide RO composite membranes were manufactured by Ahmed et al. (14) using mixed amines of pipperazine and 3,5-diaminobenzoic acid which give about 92.0% salt rejection. Addition of extra additives to the amine solution can produce high-flux reverse osmosis membranes with good rejection. For example, adding dimethyl sulfoxide (DMSO) to the aqueous amine solution improves water flux by formation of a thinner and rough polyamide film (15). Sodium hydroxide, sodium tertiary phosphate, dimethyl piperazine, triethylamine (TEA), and other acylation catalysts accelerate the MPD–TMC reaction by removing hydrogen halides formed during amide bond formation (1). Recently it has been reported that on addition of triethyl amine (TEA) and organic acids like camphor sulfonic acid (CSA) in an aqueous solution of MPD, pure water permeability dramatically increases, salt rejection is practically unchanged, the contact angle is slightly reduced, and roughness is significantly reduced in TFC membranes (16). The surface modification was performed to hydrophilize the surface of TFC membrane to enhance the flux is also studied in detail (17,18).

However, TFC membranes using 1,4-phenylene diamine or paraphenylene diamine (PPDA) is not very widely studied though it is advantageous over commonly used 1,3-phenylene diamine or metaphenylene diamine (MPDA). PPDA gives more stable aqueous solution (does not oxidize or change color in the presence of air and light) and it is easy to purify by simple recrystallization from benzene unlike MPDA. Because of the presence of the amine group in 1 and 4 position of the benzene ring in PPDA, it forms less cross-linked structure in reaction with acid chloride than that of MPDA where the amine groups are in 1 and 3 positions of the benzene ring. So salt separation achieved with PPDA based membranes could be not as high as MPDA based membranes. But brackish water RO membranes and NF membranes can be very easily prepared using PPDA as amine. Pipperazine (Pip) is another amine compound where secondary amine (–NH–) groups present in 1 and 4 position and is very commonly used to make composite NF membrane. The performance optimization by use of mixed amines like PPDA and Pip (primary amine and secondary amine containing compound) in interfacial polymerization and subsequent conversion of the residual reactive functional groups in post-treatment is not widely reported.

In this work, we systematically study the performance of composite co-polyamide membranes derived from mixed monomeric amines (comprising anhydrous pipperazine and 1,4-phenylene diamine) under varying preparation conditions (reaction time for individual amine and their concentration ratio, nature of the acid chloride, and nature of the additives used in the aqueous reagent) with respect to different electrolytes (sodium chloride, magnesium sulphate, and calcium chloride). Finally, we evaluate the impact of possible chemical post-treatment reactions (acid, alkali treatments, and esterification reactions) involving residual acid groups on the performance of composite co-polyamide membranes derived from mixed monomeric amines.

EXPERIMENTAL

Materials

Polysulfone (PS, $M_n = 37,000$) in powder form was obtained from M/s. Gharda Chemicals, India. The reagent grade solvent used for making membranes is N-methyl pyrrolidone (NMP) and is procured from M/s. Sisco Research Laboratories, India. 1,4-phenylene diamine or paraphenylene diamine (PPDA) and anhydrous pipperazine (Pip) are obtained from M/s. Fluka. PPDA is purified by recrystallisation using benzene. Pipperazine is used as received. 1,3-benzene dicarbonyl chloride or isophthaloyl chloride (IPC), 1,4-benzene dicarbonyl chloride or terephthaloyl chloride (TPC), and 1,3,5-benzene tricarbonyl chloride or trimesoyl chloride (TMC) of M/s. Aldrich, USA make is used. Polyethylene glycol ($M_n = 200$) liquid is obtained from M/s. E. Merck, India. Sodium lauryl sulphate (SLS) is used as surfactant and trisodium phosphate (TSP; Na_3PO_4) is used as acid acceptor and both are procured locally.

Membrane Preparation and Testing

Membrane preparation is done in two stages. In the first stage the base membrane is cast. In the second stage this base membrane is coated with thin film of polyamide so as to obtain a composite membrane. In an airtight glass bottle, 22 gm of PS is taken and then 78 gm of the NMP is added. The solution is kept agitated for several hours for complete dissolution. The solution is homogenized and kept overnight for deaeration. The dope solution thus obtained is spread over a nonwoven polyester spun bonded fabric support (Viledon grade H1006 obtained from M/s. Freudenberg Nonwovens India Pvt. Ltd.) using a knife edge. The size of the membrane prepared is typically of 15 cm length and 6 cm width. The thickness of the membrane is controlled by varying the thickness of adhesive tapes at the sides of the glass plate. The thickness of a single adhesive tape used is 50 μm. This thickness was measured using a micrometer with a screw gauge. The membranes were made in the environment of controlled temperature (typically 22°C) and humidity (typically 40% RH). The membrane, after casting, is immersed in a gelling bath, which is generally demineralized water, maintained at a known temperature. The membrane, obtained after gelling is repeatedly washed with demineralized water and wet stored. These membranes are inspected for pinholes and good areas are chosen for subsequent composite membrane preparation.

The support membrane is subjected to in situ interfacial polymerization reaction. The wet water saturated support membrane is pressed between a pair of filter papers to remove surface droplets of water and is immersed subsequently in a solution of amine (mixed monomeric amines wherever applicable) of known concentration for 2 minutes, then positioned vertically to drain the excess reagent till the surface looked free of amine solution and subsequently immersed in hexane solution of acid chlorides of known concentration for a specified time. The composite polyamide or co-polyamide (depending on pure amine or mixed amines used) membranes obtained are dried under an infra red (IR) light for 10 minutes or till the surface of the composite membranes looked completely dry.

The composite membranes are subjected to post-treatment in order to study the change in separation performance. Post-treatment of composite co-polyamide membranes is done by keeping the membrane inside acid, alkali, and alcohol solution separately for a predetermined time. Among acids, inorganic acids like hydrofluoric acid (HF), hydrochloric acid (HCl) with organic acid like sulphamic acid (NH_2SO_3H) are used for treatment. Among alkali, sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) are used. The membranes are treated with different alcohols (in presence of very small amount of sulphuric acid $\sim$ 2% of alcohol weight which act as catalyst in esterification reaction) in order to convert the free acid group to an ester.

The TFC membranes are first characterized in terms of pure water permeability (PWP), then later characterized in terms of fractional rejection of the solute. The characterization data are collected in a tangential flow type test cell offering a membrane area of $15.4\,cm^2$ at 225 psig (1551 kPa) pressure. The feed water is pumped across a given specimen using a reciprocating pump. The schematic details of the experimental set up is given elsewhere (19). The solute separation data are collected at 225 psig pressure at a feed concentration of 2000 ppm. Flux is calculated by taking the average of three readings taken for three membrane samples prepared separately. The flux values obtained as milli liter/minute (mL/min.) are reported as $L\ m^{-2}\,d^{-1}$. Salt rejection (S.R) by each membrane was determined according to $S.R = 1 - C_p/C_f$, where C_f and C_p are the salt concentrations of feed and permeate solutions. The specific conductance of feed and permeate samples are measured using a standard laboratory conductivity meter. Subsequently, salt concentration is calculated from a calibration plot of measured specific conductance versus concentration of pure salt solution. The concentration of PEG-200 in feed and permeate sample is determined from the total organic carbon analysis (TOC).

RESULTS AND DISCUSSIONS

Effect of Reaction Conditions on Separation Performance of Composite Membranes

Concentration of both the reagents (amine and acid chloride), the time of dipping in either solution particularly in organic medium (reaction time), the presence of additive in either solution are important parameters which influence the separation behavior of composite membranes. At first the effects of some of these parameters are varied for a single amine system and subsequently for mixed amine systems to study the separation behavior of composite membranes.

Varying Reaction Time and Concentration of the Amines

The optimization of reaction time and concentration of individual amine (PPDA, Pip) to get better performance composite membranes by interfacial polymerization reaction are studied. The composite membrane performance in terms of PWP and NaCl rejection as a function of reaction time (time in organic solution) is given in Fig. 1. Amine and TMC concentrations used are 2.0% (w/v) in water and 0.3% (w/v) in hexane respectively. There is some minimum time needed to complete the polymer formation over support to get the composite membrane which can show the separation of salt close to saturation value (highest separation achieved). For the PPDA based composite membrane, the time is around 30 second whereas for the Pip based membrane it is 60 second. In polycondensation reaction, the concentration of both the reactants and time are two variables which directly influence the reaction rate and the degree of polymerization. The amine group present in PPDA is a primary amine whereas that in Pip is a secondary amine and as the reactivity of the primary amine is more than in the secondary one, the reaction could have been faster in PPDA than Pip. So for a same reactant concentration, Pip takes more time to form a polymer of sufficiently high molecular

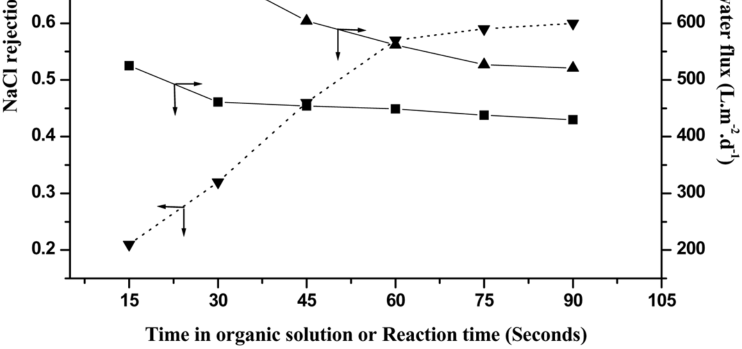

Figure 1. Separation performance of composite membranes as a function of time in organic solution (reaction time).

weight to show enough mechanical strength and reproducible salt rejection than PPDA.

The performance of the composite membranes as a function of concentration of amine with respect to NaCl and $MgSO_4$ feed solutions are given in Table 1. It can be seen from the table that for a fixed acid chloride concentration, an increase in diamine concentration from 1.0% to 3.0% reduces the product flux and the solute separation reaches an optimum and declines marginally for both the amines. It is reported (1) that the interfacial reaction occurs in the organic layer, particularly when monomeric diamines are used. As the concentration of diamines increase, it is expected that higher quantities of diamines are partitioned across the interface into the organic layer with the possibility of forming thicker barrier, which could account for the reduced permeate flux. But once a layer of polyamide formed over the support membrane, it acts as a barrier for PPDA to diffuse through it and then come in contact with TMC in hexane. The reaction terminates after sometime irrespective of amine concentration. So, flux reduction due to change of amine concentration from 1.0% to 2.0% amine is higher than that of change from 2.0% to 3.0% amine concentration.

The effect of mixed amines concentration in the aqueous reagent with fixed acid chloride concentration on the performance of copolyamide RO membrane is studied. PPDA and Pip are mixed in varying ratios keeping the total amine concentration constant. TMC of 0.3% (w/v) is used as the acid chloride in these experiments. It can be seen from Fig. 2 that by increasing the ratio of phenylene diamine the solute separation increases. The separation data obtained for $MgSO_4$ and $CaCl_2$ are also given for the co-polyamide membranes obtained. The membranes show comparable separation for NaCl and $CaCl_2$ with a relatively higher separation of

Table 1. Separation performance of composite membranes as a function of concentration of amine

Concentration of amine (% w/v)	PPDA			Pip		
	PWP ($L \cdot m^{-2} \cdot d^{-1}$)	NaCl rejection	$MgSO_4$ rejection	PWP ($L \cdot m^{-2} \cdot d^{-1}$)	NaCl rejection	$MgSO_4$ rejection
1.5	592	0.81	0.9	742	0.39	0.76
2	449	0.95	0.98	562	0.57	0.89
3	419	0.93	0.98	498	0.55	0.89

Concentration of TMC: 0.3% (w/v).
Time in hexane-TMC solution: 60 seconds.

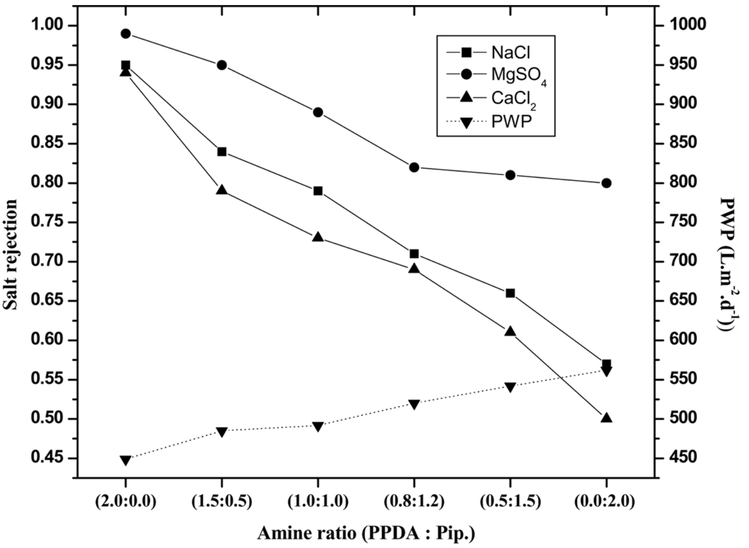

Figure 2. Separation performance of co-polymeric composite membranes as a function of concentration ratio of PPDA and piperazine.

$MgSO_4$ in all the cases. The higher level of $MgSO_4$ rejection observed is due to the negative surface charge of the membranes which repels the divalent sulphate ions strongly than monovalent ions. The residual unreacted acid chloride group gets hydrolysed to free carboxylic acid group in contact with aqueous solution and it tend to give anionic nature to the polyamide barrier layer. With increase in piperazine concentration in mixed amine, the separation of NaCl and $CaCl_2$ decreases but $MgSO_4$ separation almost reached saturation at 60% of piperazine.

Varying Concentration of Acid Chlorides for Two Different Amines

The performance of the composite membranes as a function of concentration of TMC with respect to NaCl and $MgSO_4$ feed solutions are given in Table 2. For a given diamine concentration, increase in diacid chloride concentration similarly reduces the permeate flux with simultaneous improvement in solute separation. Given that the diacid chloride partition coefficient into the aqueous layer is relatively unfavorable, it is expected that larger quantities of acid chlorides compete in reaction, possibly forming a thicker barrier with higher crosslinking, particularly in this case. A comparison between 1,4-phenylene diamine and piperazine reveal that the piperazine system gives lower solute separation although

Table 2. Separation performance of composite membranes as a function of concentration of acid chloride

Concentration of TMC (% w/v)	PPDA			Pip		
	PWP ($L \cdot m^{-2} \cdot d^{-1}$)	NaCl rejection	$MgSO_4$ rejection	PWP ($L \cdot m^{-2} \cdot d^{-1}$)	NaCl rejection	$MgSO_4$ rejection
0.1	664	0.79	0.9	858	0.21	0.46
0.2	507	0.91	0.95	666	0.41	0.67
0.3	449	0.93	0.98	562	0.57	0.89

Concentration of Amine: 2.0% (w/v).
Time in hexane-TMC solution: 60 seconds.

the permeate flux is better. This could be due to the possible more open structure formed because of the secondary amine group being present in the pipperazine ring as compared to the presence of the primary amine group attached with the benzene ring in PPDA. The performance of the composite membranes as a function of different acid chloride with respect to NaCl and $MgSO_4$ feed solutions are given in Table 3. Use of diacid chlorides in place of trifunctional acid chlorides drastically reduce the solute separation with higher permeate flux. It is observed that a relatively better performance is obtained in the case of the piperazine system with difunctional amines, particularly, with metasubstituted acid chlorides. This could be possibly due to the inability of the third functional group participating in the reaction. Hence, after thin film formation, the extra acid chloride group turns to carboxylic acid group on hydrolysis

Table 3. Separation performance of composite membranes formed using different acid chloride

Acid chloride	PPDA			Pip		
	PWP ($L \cdot m^{-2} \cdot d^{-1}$)	NaCl rejection	$MgSO_4$ rejection	PWP ($L \cdot m^{-2} \cdot d^{-1}$)	NaCl rejection	$MgSO_4$ rejection
IPC	596	0.57	0.74	670	0.43	0.68
TPC	809	0.45	0.62	1034	0.21	0.49
TMC	449	0.93	0.98	562	0.57	0.89

Concentration of Amine: 2.0% (w/v).
Concentration of Acid chloride: 0.3% (w/v).

which makes TMC-piperazine based membrane more anionic and it gives better $MgSO_4$ separation.

Varying Amine Ratio in Presence of Surfactant and Acid Acceptors

The changes in composite membrane performance due to presence of surfactant (sodium lauryl sulfate) and acid acceptor (trisodium phosphate) in the aqueous mixed amines is given in Figure 3. These data represent changes in pure water flux and salt rejection (NaCl and $MgSO_4$) relative to the membrane formed without surfactant and acid acceptor. The actual flux and solute separation data are given in Table 4. PPDA and Pip are mixed in varying ratios keeping the total amine concentration constant with TMC of 0.3% (w/v) is used. The surfactant is expected to facilitate penetration of aqueous reagent into the pores of the support membrane simultaneously preventing partitioning of acid chloride in the aqueous phase. It can be seen that the presence of surfactant tends to improve the product flux with a slight decline in solute separation. It is noted that with higher pipperazine content in aqueous reagent the extent of increase in sulphate rejection over chloride rejection is relatively higher, indicating the need for surfactants in pipperazine systems to get

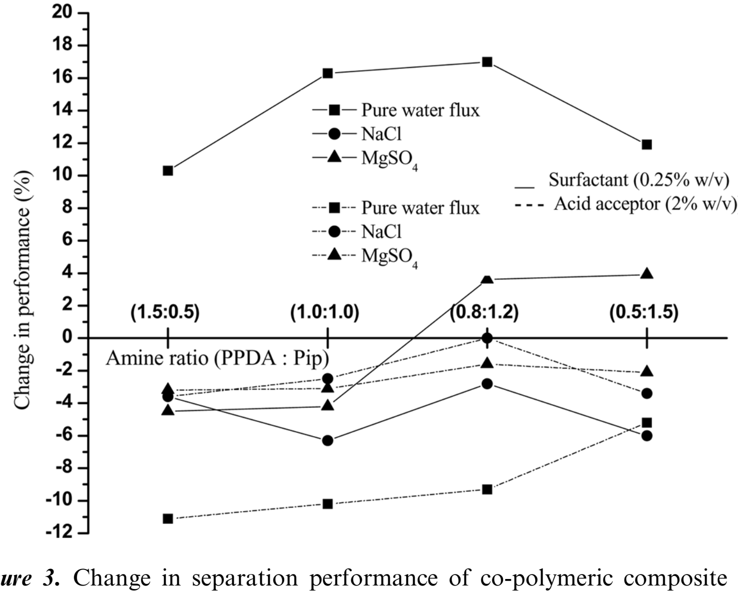

Figure 3. Change in separation performance of co-polymeric composite membranes in presence of surfactant and acid acceptor on varies concentration ratio of PPDA and piperazine.

Table 4. Separation performance of composite polyamide membranes in presence of surfactant and acid acceptor on varies concentration ratio of PPDA and piperazine

Amine composition (PPDA:Pip.) (wt. in gm/100mL solution)	Without any additive			With surfactant, SLS			With acid acceptor, TSP		
	PWP ($L \cdot m^{-2} \cdot d^{-1}$)	NaCl rejection	$MgSO_4$ rejection	PWP ($L \cdot m^{-2} \cdot d^{-1}$)	NaCl rejection	$MgSO_4$ rejection	PWP ($L \cdot m^{-2} \cdot d^{-1}$)	NaCl rejection	$MgSO_4$ rejection
1.5:0.5	485	0.84	0.95	535	0.81	0.91	431	0.81	0.92
1.0:1.0	492	0.79	0.89	572	0.74	0.85	442	0.77	0.86
0.8:1.2	520	0.71	0.82	608	0.69	0.85	472	0.71	0.81
1.5:0.5	542	0.66	0.81	608	0.62	0.84	514	0.64	0.79

Concentration of TMC: 0.3% (w/v).

improved flux and higher anionic character. It is reported that acid acceptors like sodium hydroxide, sodium tertiary phosphate, dimethyl piperazine, triethylamine (TEA) etc. accelerate the metaphenylene diamine (MPD)–trimesoyl chloride (TMC) reaction by removing hydrogen halides formed during amide bond formation (1). But presence of trisodium phosphate is found to reduce both the product flux and solute separation for all the membranes tested. With increase in piperazine concentration in aqueous reagent, the percent reduction of product flux is noticeable (from −11.5% to −5.2%). May be lower concentration of acid acceptor is needed to get better membrane performance.

Effect of Chemical Post-Treatment on Separation Performance of Composite Co-Polymer Membranes

The effect of posttreatment of composite co-polyamide membranes on separation performance is studied by subjecting the membranes to possible secondary reactions involving the free acid group. The separation characteristics are evaluated using electrolyte solution of NaCl and neutral polyethylene glycol (PEG-200). PEG is used to evaluate the separation capability of composite membranes for organic solutes like polysaccharides, sucrose, urea etc.

Acid and Alkali Treatment

In this experiment, the contact time is 5 minutes after which the membranes are thoroughly washed and tested. The effect of different acid and alkali treatment on the membrane performance is given in Table 5. It is generally observed that the permeate flux improves to varying extent depending upon the nature of acid or the alkali. The solute separation declines to different extents accordingly. The flux improvement could be due to the removal of oligomers or low molecular weight polyamide polymers formed during interfacial polycondensation reaction and sits in the polysulfone pores. Hydrofluoric acid, sulphamic acid, and sodium carbonate are found to give enhanced water flux without much loss in solute separation. Sulphamic acid has been found to give nearly 20% increases in flux. Sodium hydroxide and hydrochloric acid are found to reduce the solute separation. Maybe in the presence of sodium hydroxide and hydrochloric acid, along with the removal of oligomers or low molecular weight polyamide polymers from polysulfone support, some of the actual barrier layer high molecular weight polymer gets hydrolyzed.

Table 5. Separation performance of composite membranes formed on post-treatment of acid and alkali

Amine composition (PPDA:Pip) (wt. in gm/100mL solution)	Post treatment reagent	Performance		
		PWP ($L \cdot m^{-2} \cdot d^{-1}$)	NaCl rejection	PEG-200 rejection
1.5:0.5	Nil	485	0.84	0.885
	10% (v/v) HF	534	0.83	0.878
	0.1 (M) HCl	579	0.79	0.850
	0.2% (w/v) NH_2SO_3H	585	0.82	0.866
	0.25% (w/v) NaOH	529	0.76	0.804
	0.25% (w/v) Na_2CO_3	531	0.82	0.863
1.0:1.0	Nil	492	0.79	0.850
	10% (v/v) HF	537	0.77	0.832
	0.1 (M) HCl	585	0.73	0.804
	0.2% (w/v) NH_2SO_3H	576	0.78	0.841
	0.25% (w/v) NaOH	537	0.72	0.771
	0.25% (w/v) Na_2CO_3	532	0.75	0.804
0.5:1.5	Nil	542	0.66	0.735
	10% (v/v) HF	574	0.64	0.714
	0.1 (M) HCl	602	0.60	0.667
	0.2% (w/v) NH_2SO_3H	608	0.68	0.721
	0.25% (w/v) NaOH	579	0.61	0.670
	0.25% (w/v) Na_2CO_3	567	0.62	0.692

Concentration of TMC: 0.3% (w/v).

Different Alcohol Treatments

A contact time of 3 minutes is employed in this experiment. The effect of posttreatment of composite co-polyamide membranes on separation performance is studied by subjecting the membranes to possible secondary reactions involving the free acid group so as to decrease the anionic character and convert to neutral membrane and thereby increase the solute separation for PEG. The free acid groups are converted to ester groups on treatment with different alcohols. The results are given in Table 6. Small quantities of sulphuric acid are added to accelerate the esterification reaction. It can be seen that the decline in flux is marginal whereas the improvement in the solute separation is significant. The increase in separation is more noticeable for PEG-200. The increase is more for membranes prepared with a higher pipperazine content. This is perhaps due to easy penetration of alcohols in the relatively more porous membranes obtained with higher pipperazine contents. A contact

Table 6. Separation performance of composite membranes formed on post-treatment of alcohol

Amine composition (PPDA:Pip) (wt. in gm/100mL solution)	Post treatment reagent	Performance		
		PWP ($L \cdot m^{-2} \cdot d^{-1}$)	NaCl rejection	PEG-200 rejection
1.5:0.5	Nil	485	0.84	0.885
	MeOH + H_2SO_4	467	0.87	0.925
	EtOH + H_2SO_4	432	0.92	0.980
	Isopropanol + H_2SO_4	309	0.85	0.885
1.0:1.0	Nil	492	0.79	0.850
	MeOH + H_2SO_4	473	0.81	0.883
	EtOH + H_2SO_4	431	0.85	0.931
	Isopropanol + H_2SO_4	311	0.8	0.861
0.8:1.2	Nil	520	0.71	0.766
	MeOH + H_2SO_4	492	0.75	0.829
	EtOH + H_2SO_4	451	0.83	0.887
	Isopropanol + H_2SO_4	322	0.73	0.789
0.5:1.5	Nil	542	0.66	0.735
	MeOH + H_2SO_4	511	0.68	0.795
	EtOH + $H_2 SO_4$	467	0.82	0.913
	Isopropanol + H_2SO_4	332	0.72	0.812

Concentration of TMC: 0.3% (w/v).

time of 3 minutes was employed in these experiments. When methanol, ethanol, and isopropanol were treated, only ethanol gave a better performance. In the case of isopropanol, the flux declined substantially. A similar trend was noticed for all the membranes tested.

CONCLUSIONS

Composite polyamide membranes with varied separation characterictics are prepared using a mixture of paraphenylene diamines and pipperazines by in situ interfacial polymerization over polysulfone macroporous membranes under different reaction and postreaction conditions.

To get optimum membrane performance, reaction time and concentration of the reactants needs, to be optimized. For the secondary amine, it takes more time to give optimum performance than the primary amine containing compound. Pipperazine based membranes showed an enhanced performance for divalent salts like magnesium sulfate over monovalent salt sodium chloride. Aromatic triacid chlorides give more cross-linked and negatively charged composite membrane than corresponding diacid chlorides. Separation performance in terms of water permeation and salt separation can be easily tailored using mixed primary and secondary amine compounds. Acid and alkali treatment improves the permeate flux to a varying extent with decrease in solute rejection but alcohol treatment gives just the opposite trend for permeate flux and solute rejection. So, a combined posttreatment of acid/alkali and alcohol treatment is needed to get the best performing membrane.

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