



Research Paper

Performance and Structure of Thin Film Composite Reverse Osmosis Membranes Prepared by Interfacial Polymerization in the Presence of Acid Acceptor

Jaydevsinh M. Gohil^{1,2,*}, Akkihebbal K. Suresh^{1,*}¹ Department of Chemical Engineering, Indian Institute of Technology Bombay, Mumbai-400076 India,² Present address: School for Advanced Research in Polymers - Advanced Polymer Design & Development Research Laboratory (SARP-APDDRL), Central Institute of Plastics Engineering & Technology (CIPET), Bengaluru-560058, Karnataka, India.

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Highlights

- Facilitation of IP by capturing byproduct hydrochloric acid to get consistency membranes.
- Additive acid acceptor employed during IP for improving TFC membrane performance.
- Membrane formed in presence of AA exhibited more water flux, SAD and hydrophilicity.
- Membrane showed lower crosslink density and thickness when inorganic AA used.
- Use of TEACSA along with DMSO and silica nanoparticles improved water flux and salt rejection.

Abstract

During interfacial polymerization (IP) reaction between m-phenylenediamine (MPDA) and trimesoyl chloride (TMC), a by-product, i.e. hydrochloric acid can produce. This produced acid diffuses back in aqueous phase and protonates MPDA and reduces its reactivity that results in lowering of polymer yield and performance of membrane. Further, for getting consistency in reverse osmosis membranes formation, different acid acceptors (AAs) can investigate in the IP to form polyamide-made barrier layer formation. The main objective was to scavenge hydrochloric acid produced during IP and to fabricate membrane having high flux and salt rejection ability. AAs (of varying concentrations) tested were triethylamine-campohorsulfonic acid (TEACSA), triphenyl phosphate (TPP), sodium hydroxide (SH) and trisodium phosphate (TSP) for studying structure and performance of membranes. The membrane samples were then characterized using surface profilometer, scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy, atomic force microscopy (AFM), and contact angle goniometer. Results indicated that the addition of organic AA improves water permeability of the membranes without sacrificing salt rejection. The optimum membranes were prepared with AA concentrations of 3.4, 0.15, 0.02 and 0.19 wt.% for TEACSA, TPP, SH and TSP respectively. Membranes produced in presence of AA had higher surface area difference, hydrophilicity and water flux. Additionally, compare to inorganic AAs, the use of organic AA produced membrane with thicker polyamide layer and higher cross-link density. These induced changes in the physicochemical features of the prepared membranes also signified the role of the AA in scavenging the hydrochloric acid to forestall the formation of amine salts during IP for polyamide nanocomposite membrane formation.

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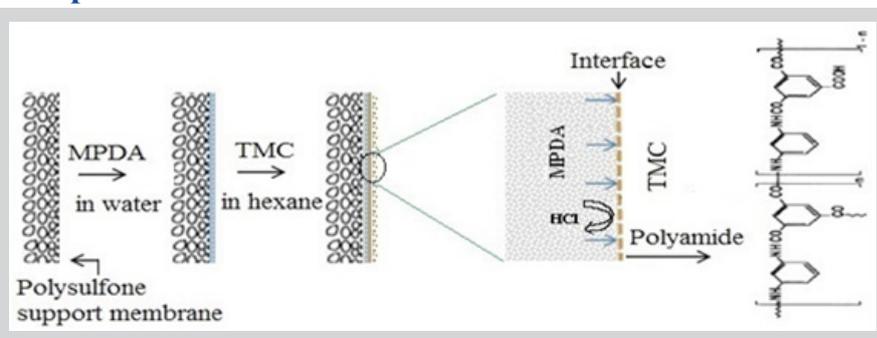
1. Introduction

In the 1970s, Cadotte and their team prepared a composite membrane that made of a thin layer of polyamide (PA) formed in situ by condensation polymerization between branched polyethyleneimine and 2,4-diisocyanate on a porous polysulfone substrate membrane [1]. Since then the interfacial polymerization (IP) reaction route has become popular technique for PA based thin film composite (TFC) membrane formation as it offers a good selectivity and high performance combined with simplicity and reproducibility. Today

in-situ IP reaction between m-phenylenediamine (MPDA) and trimesoyl chloride (TMC) or their modified forms are widely used to produce aromatic PA-TFC membranes for removal of dissolved salt ions from water for potable water [2, 3].

Specifically the desalination performance of the aromatic PA-TFC membrane is the combined functions of the monomers chemistry, their concentrations and the resulting structural characteristics. Structural

Graphical abstract



* Corresponding author at: Phone: +91 (22) 25767240, fax: +91-22-2572 6895 (A.K. Suresh); Phone: +91 (80) 28366454, fax: +91-22-2572 6895 (J.M. Gohil)
 E-mail address: aksuresh@iitb.ac.in (A.K. Suresh); jay21480@yahoo.co.in (J.M. Gohil)

properties such as morphology cross-link density and thickness of the IP films are the inherent properties of the membrane besides their hydrophilicity, surface charge and chemical composition. The relation between the active layer's structure, surface morphology and roughness have been reported for nanofiltration (NF) and reverse osmosis (RO) membranes [4]. A PA film formation by IP is kinetically diffusion controlled reaction and self-limiting in nature. The organic-soluble monomer (e.g., acid chloride) is not soluble in IP film and excludes from the PA film. The water-soluble monomer (e.g., amine) diffuses through a PA film and reacts immediately with the acid chloride at the polymer/organic interface. In order to tailor the IP film, a number of feasibilities of IP reaction have made to model the structural properties. One such effort included the inclusion of the different additives in aqueous amine or in organic acid chloride solution during IP for membranes preparation. Various additives that are reported to are the polar and apolar solvents, surfactants, metal/metal oxide nanoparticles and the catalysts [3, 5, 6], which influence the physicochemical properties of the composite membranes. Based on function and mechanism of their action, additives can categorize in two classes: those, without entrapping into the PA matrix modify alter properties of the IP film, and those, which by retaining inside the PA matrix change the physicochemical properties of IP film. The first category of the additive directly or indirectly influences inherent physiognomies of PA barrier layer by accelerating the kinetics of IP reaction and thereby improves water flux and salt removal potential of TFC membrane. The use of a polar solvent like dimethyl sulfoxide (DMSO) in the aqueous phase assists the diffusion of water molecules along with aqueous phase monomer through the IP films and plays a favorable role in increasing the water flux without substantial loss of salt rejection of the resulting membrane [7, 8]. Similar DMSO, acetone can also play the significant function in lessening the solubility difference between two immiscible solutions. Kong et al. [9] prepared TFC NF membranes by adding co-solvent (acetone) into the organic phase to control thickness of active layer having nanopores. Mansourpanah et al. [10] added surfactants such as cationic cetyltrimethylammonium bromide and non-ionic Triton X-100 in an organic phase to modify the PA layer characteristics. Their results showed superior overall membrane performance and produced the membranes with the thicker PA layer due to increase in diffusion of amine monomer to the organic phase. The second class of additives, such as nanoparticles, metal salts, metal oxides and catalysts have entrapped within the PA matrix, either physically or chemically. For instance, inclusion of the nanoparticles (zeolite, silica, TiO₂) to prepare TFC nanomembranes offered promising performance and improved hydrophilicity, morphology and antifouling fouling properties [5].

Despite the use of different additives in a TFC membrane formation, the possibility of hydrochloric acid neutralization can only achieve by addition of AA catalyst. Reaction kinetics of the IP between MPDA and TMC reveals the generation by-product hydrochloric acid (Figure 1) and reduction in pH of the reaction medium as IP reaction progress [11]. This produced acid diffuses back in an aqueous medium and protonates MPDA and reduces its reactivity that results in lowering of polymer yield and performance of membrane. Additionally, for getting reproducible and consistence results with better performance of TFC membrane, the organic AA (catalyst) like triethylamine (TEA) has used for preventing the protonation of amine. As well, to achieve the synergistic effect, AA also employed in combination with the other additives to get multifunctional PA membranes. In case of poly(piperazine amide) based TFC NF membrane preparation, for instance, a series of AAs frequently used are triethylamine, sodium hydroxide, trisodium phosphate, and N,N-dimethyl piperazine [12-16]. Apart from this, Jayarani and Kulkarni [17] employed a catalyst tetrabutylammonium bromide in aqueous phase monomer to modify the morphology of the TFC poly(ester amide)-based membrane. Typically, the concentrations of the AA varies from 0.1 to 1% (w/v) [18]. Presence of this additive smoothed IP reaction. Study showed that the addition of the AA like TEA in the aqueous medium increases the membrane thickness, whereas the pore radius remains unaffected [13]. Although literature reported the use of AAs for preparation of aromatic PA-TFC reverse osmosis (RO) membrane [19-22], a systematic study has not found that describes the influences of the AA on performance of membranes and their structural properties.

This study describes the influence of AAs as a catalyst during IP and resultant TFC membranes' performance and properties. Different acid acceptors have added to aqueous amine or organic acid chloride solution to prevent amine salt formation during the IP reaction. Membranes characteristic properties such as thickness, surface roughness and surface area difference (SAD), surface morphology, contact angle, elemental compositions and cross-link density were determined to correlate their performance and structure. Analysis of results showed changes in the aforementioned physicochemical structures and improvement in water flux and the salt rejection almost attained >98%, for membranes prepared in presence of TEACSA without any other additives.

2. Experimental

2.1. Materials

The polysulfone (PSF) membrane substrate was purchased from Dow Chemicals, USA. Monomers MPDA and TMC were obtained from Sigma-Aldrich Co., USA. The solvents hexane, dichloromethane and chloroform, and TEA, sodium carbonate, sodium hydroxide (SH), triphenyl phosphate (TPP) and trisodium phosphate (TSP) were bought from Merck & Co., USA. While D(+)-10-camphorsulfonic acid (CSA) was acquired from Spectrochem Pvt. Ltd., India.

2.2. Membrane preparation

Fresh MPDA solution in Milli-Q water and TMC solution in hexane were prepared to fabricate TFC membranes (Figure 1). Weighed AA, such as SH, TSP or triethylamine camphorsulfonic acid (TEACSA) salt was dissolved in aqueous MPDA solution, whereas TPP was added in hexane solution of TMC. The concentration of the monomers and AAs used for TFC membranes preparation is represented in Table 1. For membrane preparation, first aqueous MPDA solution was contacted with the PSF base support membrane for 3 min, followed by superficial drying, and contacted with TMC solution prepared in hexane for 50-60 s to form an IP film [23]. After removing excess TMC solution from the surface, membrane was dried in oven at 80 °C for 5 min and subsequently washed with 0.2 (w/v%) sodium carbonate solution at 50 °C. Finally, membranes were washed using distilled water, and stored in an airtight container for performance testing and characterization.

2.3. Membrane characterization

Thickness of isolated PA thin films deposited on glass slide were measured using surface profiler (Dektak 150 Stylus Profiler, Veeco Instruments Inc., USA) as described in [24]. Initially a polyester non-woven fabric was peeled off from PSF membrane, a PA coated PSF membrane then laid onto glass slide in such a way so PA face to the glass surface. The upper PSF layer then removed by dripping solvent dichloromethane and chloroform from the burette. After drying, the PA film remained intact onto glass surface. Small vertical features (vertical height) were measured as a stylus moved in contact with surface across the surface of the glass slide to polyamide thin film with total scan length of about 1000-2000 μm. A diamond stylus (12.1 μm diameter) was moved across in contact with surface of glass slide to thin film at 9.8066×10⁻⁶ N force. Height deviation of the vertical stylus was measured as function scan length.

Table 1
Compositions of aqueous and organic phase monomers used for membrane preparation by IP.

Membrane	Aqueous phase			Organic phase TMC (w/v%)
	MPDA (wt.%) ^a	AA (wt.%)	pK _a of AA	
TFC0	2.25	-	-	0.125
TFCSH	2.25	Sodium hydroxide (0.02)	13.8	0.125
TFCTSP	2.25	TSP (0.19)	11.8	0.125
TFCTC	2.25	TEACSA salts (3.4)	10.8 [25]	0.125
TFCTPP	2.25	TPP ^b (0.11)	10 [26]	0.125

^a pK_a value of MPDA is 5.11 [27]

^b TPP was added in TMC solution in hexane.

Surface morphology of membranes was evaluated by field emission gun-scanning electron microscopy (FEG-SEM) (JEOL, JSM-7600F). A 10 nm layer of platinum was applied by sputter coating (JFC-1800) on the dried membrane to avoid charging. SEM images were taken at accelerating voltage of 10 kV. An Energy-dispersive X-ray spectroscopy (EDAX) was used to analyze C, N and O contents in isolated polyamide thin films.

For measurement of roughness factors of PA surface, membranes were characterized by Atomic force microscopy (AFM) in tapping mode using Nanoscope IV scanning probe microscopy equipped with 6642J scanner (Digital Instruments Multimode, Singapore). Collected AFM images were analyzed to determine roughness factors in terms of rms (root mean square) roughness (R_q) and surface area difference (SAD).

The dried membrane samples were attached to the glass slide; and surface

hydrophilicity of PA membrane was determined by measurement of contact angle of water droplets using Contact angle goniometer (DIGIDROP, GBX Instruments DS Model, France).

2.4. Desalination performance

Feed solution containing 2000 ppm NaCl was pumped at 1.5 MPa (225 psi) through cross flow permeation cell (Sterlitech Corporation, USA) equipped with flat sheet membrane having active area of 42 cm². Water permeate was collected after 1 h to evaluate the flux (J , lm²d⁻¹) and the rejection (R , %). The salt content in the permeate (C_p) and the feed (C_f) were determined by measuring conductivity (Conductivity meter Orion 145A+) and the actual NaCl content was calculated from the standard calibration curve. Finally, the rejection (R , %) and water permeability (P , m/Pa s) were estimated using formula (1) and (2) respectively.

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (1)$$

$$P = \frac{J_v}{A \cdot t \cdot \Delta P} \quad (2)$$

where, J_v is the water flux (m³), t is permeation time (s), A membrane area (m²) and ΔP is transmembrane pressure (Pa).

3. Results and discussion

Membrane performance and AAs optimization

In general, the performance of TFC-RO membrane depends upon the characteristics of thin film formed by IP. The parameters that affect the kinetics of IP can also affect the properties of the PA film formed. In the beginning of IP, the fresh MPDA aqueous solution was alkaline (pH >8). In the companion study of reaction kinetics of IP showed that as the IP reaction advanced, diamine concentration decreased which led continuous drop in pH of reaction medium [11]. This decrease in pH also attributed by the release of hydrochloric acid as a by-product during the IP as shown in Figure 1 [28].

In the presence of a strong acid like hydrochloric acid, MPDA gets protonated easily and lost reactivity for further reaction with acyl halide. Hence, the formation rate of PA barrier layer turns out to be slow, which results in drop of polymer yield.

Presence of an AA is necessary to prepare best PA composite membrane. Usually AAs stronger than MPDA (e.g., $pK_{a(AA)} > pK_{a(MPDA)}$) could prevent amine salt formation by reaction with hydrochloric acid. As seen from the Table 1, pKa values of various AAs selected in this study is greater than hydrochloric acid (pKa -8) so AAs expected to abstract proton from the hydrochloric acid to form corresponding conjugate acid and thereby minimize the protonation of MPDA. IP reaction scheme for PA membrane formation is shown in Figure 2. Schematic of IP indicates that in the absence of an AA, diamine (e.g., MPDA) itself acts as an AA (tied up as the hydrochloride salts) due to its higher value of pK_a (5.11), which easily deprotonates hydrochloric acid (pKa -8) and facilitates the diamine dissociation. The dissociation of diamine controls the transfer rate of the reactant into the organic phase and becomes the rate-controlling step of the IP. An organic AA such as TEACSA salt, and inorganic AAs such as SH and TSP were added in aqueous phase due to its high solubility in water. While, an organic AA TPP was dissolved in hexane (organic phase) with TMC.

In TFC membranes formation, AA concentration needed was optimized by evaluating desalination performance of membrane. Figure 3 displays the effect of different AA concentrations on the water flux and the salt rejection of membranes. With increasing the concentration of AAs additive resulted in increase of water flux of the membranes. The salt rejection of membrane showed increasing trend to certain concentration of organic AA, further increase in concentration of AA produced membranes with less salt rejection ability. In case of inorganic AA inclusion, salt rejection slightly decreased. In all the cases the observed membranes flux was higher than the membrane prepared without AA. In case of inorganic AAs SH and TSP, the optimum concentration levels observed were 0.02 and 0.185 wt.% respectively and concentration greater than that resulted in membranes of less rejection (<96%). The percent enhancement in flux obtained was 30 and 13% at optimum concentration of SH and TSP respectively. Flux and rejection profile of membranes obtained using organic AAs TEACSA salt and TPP showed optimum concentration of 3.4 and 0.15 wt.% respectively. The concentration of TEACSA salt greater than 3.4 wt.% showed no increment in flux, and rejection value remained almost constant at 98.5%. While concentration of TPP >0.15 wt.% was resulted in higher flux membrane with less rejection.

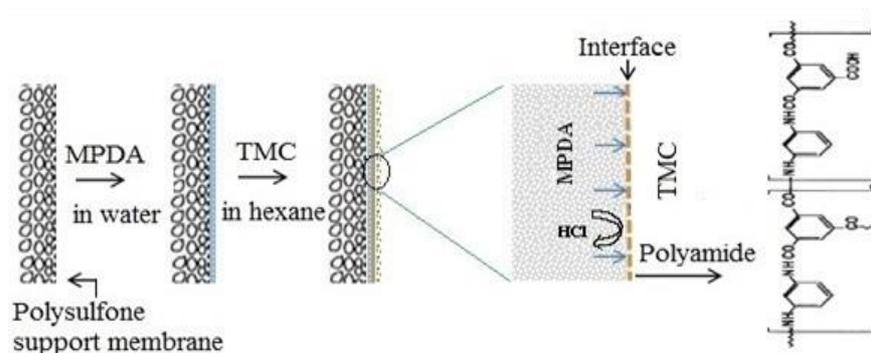


Fig. 1. Schematic of IP technique for TFC membrane preparation.

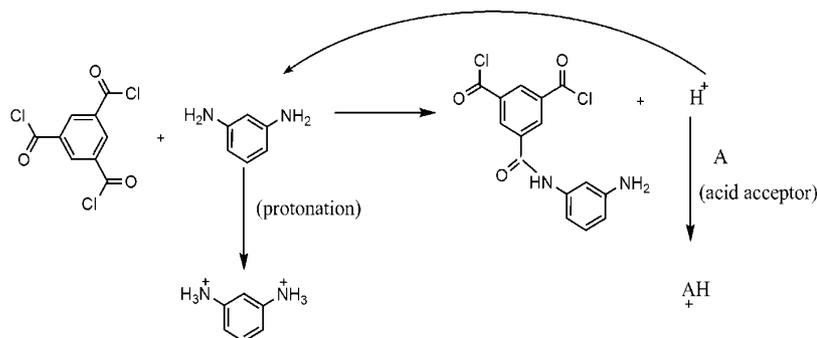


Fig. 2. Schematic of IP reaction mechanism in the presence of AA.

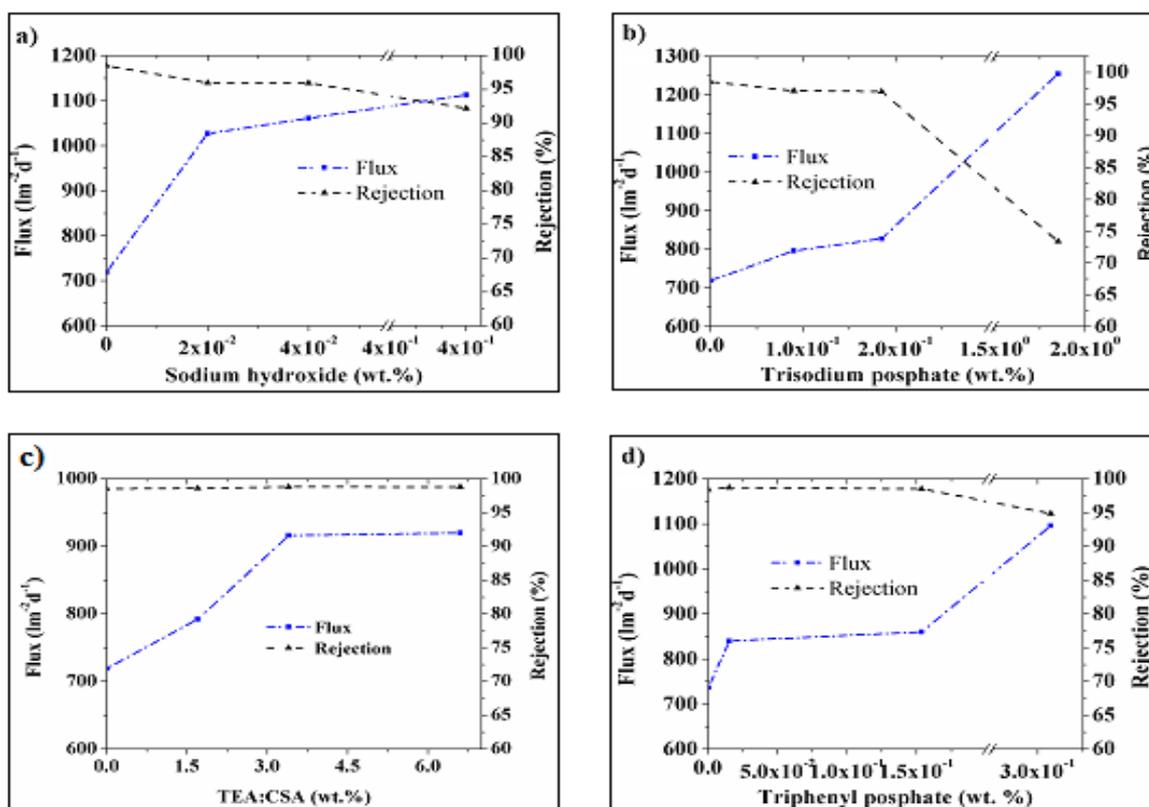


Fig. 3. Flux and rejection profile of TFC membranes made using different concentration of AAs (a) SH, (b) TSP, (c) TEACSA, and (d) TPP.

3.2. Physiochemical properties of membranes

Table 2 lists water flux, salt rejection, and physiognomies of composite membranes prepared at optimum concentration of AA. Composite membranes prepared in absence of AA and at optimum concentration of SH, TSP, TEACSA and TPP has designated as TFC0, TFCSH, TFCTSP, TFCTC and TFCTPP respectively. Membrane formed at optimum organic AA concentration showed significant improvement in the water flux without sacrifice of salt rejection. Additionally, membrane formed in presence of AA showed more consistency in water permeability and rejection that is revealed from their standard deviation data. These TFC membranes were suitable for use in RO applications.

Figure 4 demonstrates the typical distribution of height profile of the PA thin film isolated from TFC membranes. Measurement of small vertical features recorded in the form of height profiles as diamond stylus scanned across the specified length from glass surface to the PA surface. Membranes TFCTC and TFCTPP exhibited higher average PA thickness than TFCSH and TFCTSP. While, the TFC0 membrane had intermediate average PA thickness. Presence of organic AAs facilitated IP reaction and increased the diffusivity of aqueous monomer at interface that resulted in a thicker PA membrane.

Even having higher thickness of PA layer, the membranes produced with organic AAs gave high flux this is due to fact that the higher amount of amine dissolved in organic solvent (i.e. organic AAs) results in higher water flux [6]. Additionally, higher water flux of TFCTC membrane can be explained due to increase in number of network pores, in presence of organic additives like TEA [29]. Addition of an inorganic AA in aqueous phase directed two functions: (i) it acted as a catalyst and thereby increased reactivity of amine as the pH of aqueous phase was in the range of 10-11.5, which provided narrow reaction zone, (ii) complexation of inorganic AA with acid chloride groups of TMC ($pK_a = 3.11$) preferred to hydrolyze due to complete dissociation of strong base-sodium hydroxide, which could induce loose surface layer. Thinner, hydrophilic higher and flux membranes formed in presence of inorganic AA additive was mainly due to the competition of these two processes.

Figure 5 depicts SEM surface morphology of composite membranes. Nodular feature is clearly visible on membranes surface. In particular, TFCSH and TFCTSP have large closely spaced fold like protuberance. In case of TFCTC and TFCTPP have large asperities with spaced apart and TFC0 appeared combination of closely spaced large and small fold like protuberance and asperity.

Table 2
Properties of TFC membranes prepared at optimum concentration of AAs.

Membranes	Flux (lm^2d^{-1})	Rejection (%)	Properties			
			Thickness (nm)	rms, Roughness (nm)	SAD (%)	Contact angle ($^\circ$)
TFC-0	719 \pm 130	98.5 \pm 0.3	204	66.3	5.1	63.1
TFCSH	1061 \pm 25	95.8 \pm 0.4	116	79.8	8.4	61.3
TFCTSP	828 \pm 24	96.7 \pm 0.2	159	64.9	7.7	58.5
TFCTC	916 \pm 12	98.8 \pm 0.1	260	75.2	8.3	60.6
TFCTPP	860 \pm 23	98.5 \pm 0.2	178	69	7.9	60.8

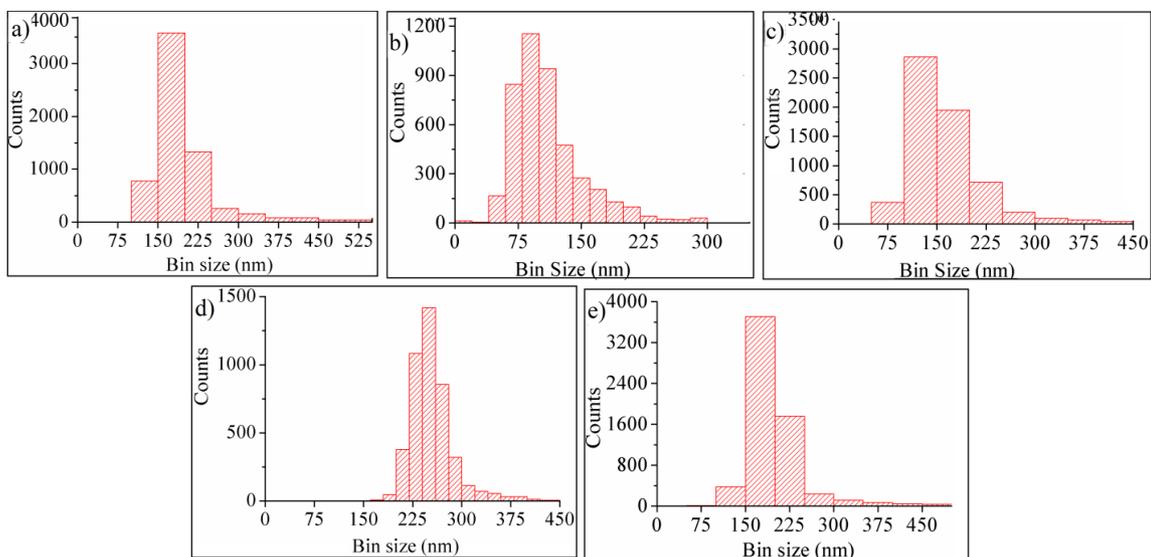


Fig. 4. Profilometry histograms showing thickness distribution of isolated PA film from (a) TFC0, (b) TFCSH, (c) TFCTSP, (d) TFCTC, and (e) TFCTPP membrane.

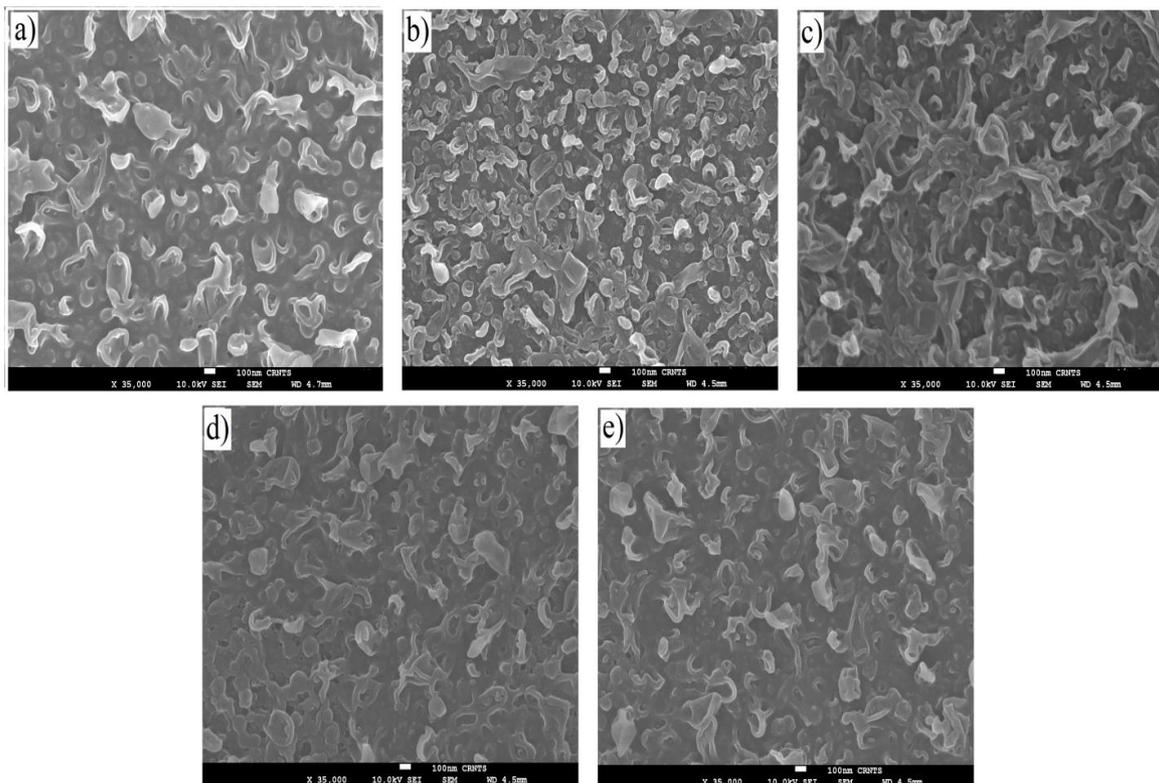


Fig. 5. FE-SEM topography of TFC membranes prepared (a) in absence of AA TFC0, and in presence of AA like (b) SH (0.02 wt.%), (c) TSP (0.19 wt.%), (d) TEACSA salts (3.4 wt.%) and (e) TPP (0.15 wt.%).

Figure 6 represents 2D and 3D surface topography images obtained from AFM with a projection area of $25 \mu\text{m} \times 25 \mu\text{m}$ for all composite PA membranes prepared at optimum concentration of AA. AFM provided the statistical quantification of physical properties such as surface roughness and SAD. It is clear from the topography images that the membranes produced in presence of AA gave more ridge-and-valley structure compare to bare TFC membrane. The bar at the right side of each image indicates the vertical deviation in the membrane surface; the lighter regions represent the peak, while darker regions represent valley or depression on the surface. Moreover, TFCSH, TFCTSP, TFCTC and TFCTPP appeared to have rougher surface than TFC0. The surface morphology of TFC membranes have been

successfully used to correlate the membrane flux and rejection characteristics [30]. It is seen from the Figures 5 and 6, in case of inorganic AA, the PA surface of TFC membranes appeared highly rough with large ridges of 300-500 nm size that may resulted in formation more aggregates pores, which eased water and salt transport through formation of nanopores and defect. In contrast, for the case of organic AA, the surface of PA TFC membranes apparently have more numbers of ridges with 100-300 nm size, which could enhanced formation of more network pores with less defect that ultimately improved water flux without loss of salt rejection.

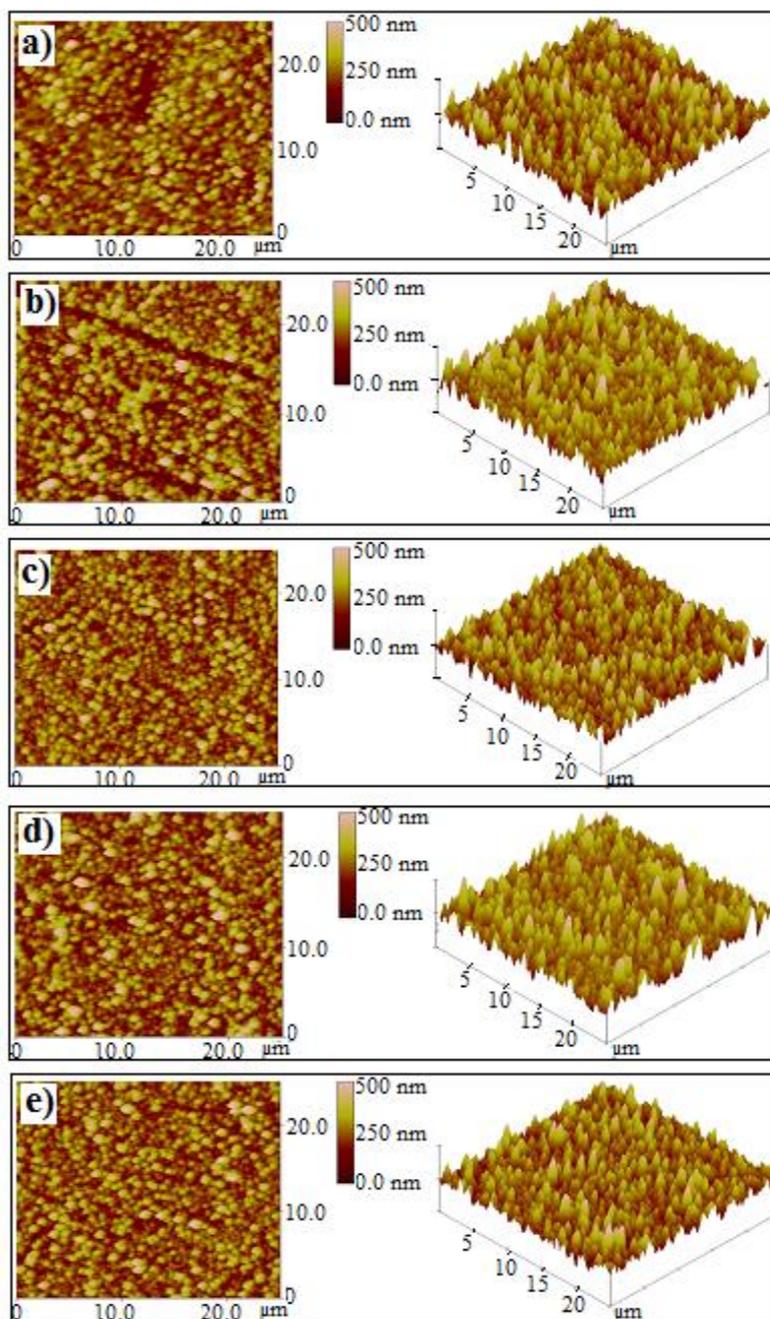


Fig. 6. 2D and 3D topography images obtained using AFM for TFC membranes prepared (a) in absence of AA, and in presence of AA like (b) SH (0.02 wt.%), (c) TSP (0.19 wt.%), (d) TEACSA salts (3.4 wt.%) and (e) TPP (0.15% wt.%).

Roughness properties of membranes prepared at optimum AA concentration represented in Table 2. TFC membranes produced using AAs had higher surface roughness and SAD than bare TFC membrane. The increased hydrophilicity, surface roughness and SAD of TFCSH, TFCTSP, TFCTC, and TFCTPP than TFC0 resulted in higher water flux rate than bare TFC membrane. In addition to the physiological features, to comprehend the effect of AA on the resultant PA membranes, the molecular structure revealed by chemical composition and cross-link density disclosed prominent effect on membranes performance. The EDAX probed on an isolated PA film to study the relative change in chemical composition especially with respect to amide linkages with respect to addition of AA. Table 3 lists the relative atomic concentration of carbon (C), nitrogen (N) and oxygen (O) studied by EDAX and calculated relative ratio of N/O, O/C, and N/C for the TFC membranes. To intimate the real chemical structure of PA barrier layer the cross-linked and linear fraction determined by considering a simple chemical formula of PA (Figure 7) suggested in [7]. In this formula, the cross-linked fraction retains one additional amide bond and linear portion has free pendant carboxylic groups. The chemical composition of cross-linked (x) and linear

fraction (y) of PA matrix calculated according to method described in [7], using the relative ratio of atomic concentration given in Table 3.

Computations of chemical formula of cross-linked portion ($C_{18}H_{12}N_3O_3$) and linear portion ($C_{15}H_{10}N_2O_4$) give $x+y=1$ and $N/O = (3x+2y)/(3x+4y)$. This estimation delivers the values of x and y as denoted in Table 4. The ratio of cross-linked fraction to linear fraction of polyamide for TFCTC (5.2) and TFCTPP (2.1) is higher compare to TFCSH (1.5) and TFCTSP (1.5), while TFC0 shows 1.8, which signifies that the content of cross-linked portion is reduced with respect to addition of inorganic AAs sodium hydroxide (TFCSH) and trisodium phosphate (TFCTSP).

The water permeation through RO membrane takes place by diffusion process, in which the water molecules first absorbs onto membrane surface and due to hydrogen bonding water molecules bind with PA layer and diffuses across the membrane, on the other side due to transmembrane pressure water molecules desorbs from the surface. Overall, for PA RO membrane the water permeation depends upon the thickness of the PA barrier and number of hydrogen bonding sites.

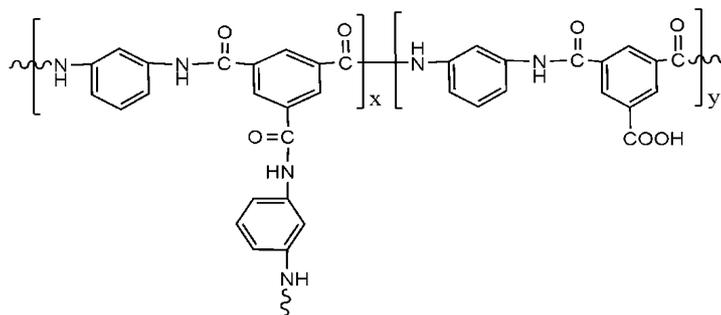


Fig. 7. Schematic of chemical formula of PA membrane showing cross-linked and linear repeating unit.

Table 3
Chemical composition of the TFC membranes.

Membranes	C atom %	N atom %	O atom %	N/O	O/C	N/C
TFC0	58.73	18.19	23.08	0.79	0.39	0.31
TFCSH	56.76	18.76	24.48	0.77	0.43	0.33
TFCTSP	55.82	19.14	25.04	0.76	0.45	0.34
TFCTC	54.19	21.72	24.09	0.9	0.44	0.40
TFCTPP	56.18	19.61	24.21	0.81	0.43	0.35

Due to hydrolysis of TMC in presence of strong acid acceptor catalysts SH and TSP membranes may have predominantly residual carboxylic acid group in PA that eventually offered a greater diffusion coefficient of water [31], and reduced mass transport resistance due to thinner PA barrier. On the other hand, TFCTC and TFCTPP membranes contained more number of amide bonds as revealed from higher crosslink portion, this is due to the fact that the organic AA reduces the solubility difference between two solution phases and enhances diffusion of diamine to the organic phase and thereby regulates the interfacial tension between two immiscible phases during IP. Thus, higher crosslink density of TFCTC and TFCTPP membranes aided in retaining rejection ability, while the more number of amide linkages and network pores [29] could increase the diffusional transport of water through network pores hydrogen bonding in spite of higher thickness.

Table 5 shows desalination performance of membranes produced using organic and inorganic additives along with TEACSA. As shown in Table 5 all the membranes produced using organic acid acceptor (TEACSA) gave higher water permeability than corresponding bare membranes. Further TFNCM produced using silica nanoparticles exhibited 2-3 fold higher water permeability than that produced without TEACSA (As seen from Figure 8). Thus, incorporation of acid acceptor catalyst during IP for TFC membrane preparation not only produced membrane with higher crosslink density but also enabled IP reaction and consistency in membrane formation that gave reproducibility of results in terms of water flux and salt rejection.

4. Conclusions

The objective of this study was to neutralize the hydrochloric acid produced during IP reaction using AA. The average water flux of membranes increased with addition AA during IP for all membranes. At optimum concentration of organic AA membrane maintained stable rejection, and for the case of inorganic acid acceptor the salt rejection slightly decreased although it was >96%. In particular organic AA, not only acted as AA but it also increased miscibility between aqueous and organic phase, which facilitated IP reaction by capturing byproduct hydrochloric acid. In presence of organic AA thicker membrane of higher SAD and hydrophilicity formed. The IP reaction in presence of inorganic AA produced thinner TFC membrane with lower cross-link density that allowed more water transport. Further, high performance best TFC RO membranes has produced by adding different organic (e.g. DMSO) and inorganic additives (e.g. nanoparticles) along with TEACSA acid acceptor.

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Table 4
Cross-linked and linear fraction of PA matrix.

Membrane	Cross-linked portion with amide linkage (%)	Linear portion with pedant COOH (%)
TFC-0	64	36
TFCSH	60	40
TFCTSP	60	40
TFCTC	84	16
TFCTPP	68	32

Table 5
Effect of TEACSA salt on membranes water permeability (P) and rejection (R).

Membranes	AA/additive (wt.%)	P (10^{12} m/Pa s)	R (%)	Ref.
TFC	-	5.3	98.5	This study
TFC-TEA	TEA-CSA (1.1)	6.8	98.2	This study
TFC-DMSO	DMSO (2)	7.8	97.1	[8]
TFC-DMSO	TEA-CSA/DMSO (1.1/2)	14	97.2	[8]
Silica-TFNCM	Silica nanoparticle (0.01)	2.7	93.6	[32]
Silica-TFNCM	Silica nanoparticle (0.01)	6.5	95.9	This study
Silica-TFNCM	TEA-CSA/Silica nanoparticle (0.01/1.1)	8.3	96	This study

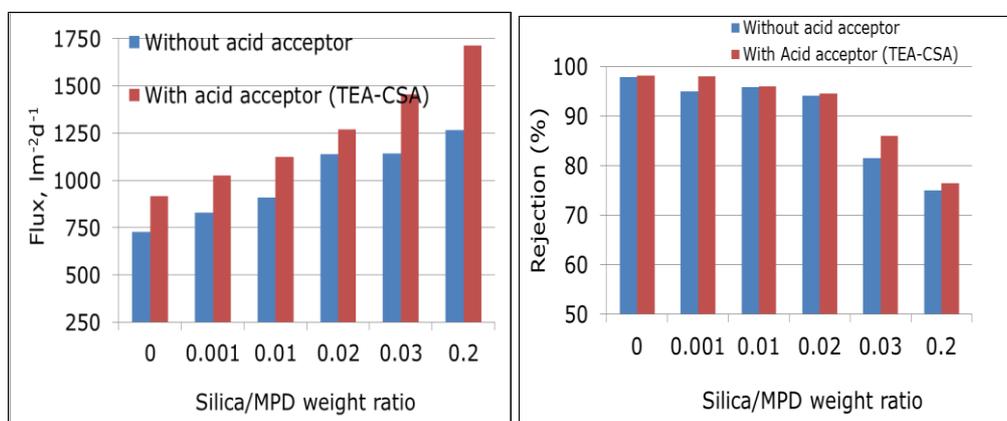


Fig. 8. Effect of TEACSA on the performance (flux and salt rejection) of thin film nanocomposite membranes prepared in presence of different content of silica nanoparticles.

Nomenclatures

AA	Acid acceptor
AFM	Atomic force microscopy
CSA	D(+)-10-camphorsulfonic acid
DMSO	Dimethyl sulfoxide
EDAX	Energy-dispersive X-ray spectroscopy
FEG-SEM	Field emission gun-scanning electron microscopy
IP	Interfacial polymerization
MPDA	m-phenylenediamine
NF	Nanofiltration
PA	Polyamide;
PA-TFC	Polyamide-thin film composite
PSF	Polysulfone
RO	Reverse osmosis
SAD	Surface area difference
SH	Sodium hydroxide
TEA	Triethylamine
TEACSA	Triethylamine camphorsulfonic acid
TFC	Thin film composite
TMC	Trimesoyl chloride
TPP	Triphenyl phosphate
TSP	Trisodium phosphate

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