

Influence of Sodium Bromide Additive on Polyethersulfone Ultrafiltration Membranes

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ABSTRACT: The effect of sodium bromide (NaBr) on performance and characteristics of ultrafiltration (UF) membranes was studied. Asymmetric UF membranes were prepared by phase inversion technique from a multicomponent dope polymer solution consisting of the polymer; polyethersulfone (PES), solvent; *N, N*-dimethylformamide (DMF) and NaBr as micromolecular additive. The dissolution of PES-DMF-NaBr was carried out using microwave irradiation technique to induce rapid dissolution through minimal heating time. Various concentrations of NaBr were mixed with PES in the range of 1–5 wt % and its influence on membrane characteristics such as surface hydrophilicity was measured by contact angle and the performance in terms of water flux and rejection rates were evaluated using micromolecular test substances. The morphology and streaming potential of PES UF membranes were analyzed using scanning electron microscopy (SEM) and ζ -potential measurement, respectively. Overall, the results suggest that the membrane consisting of 1 wt % NaBr exhibits the best performance in terms of rejection and flux rates with molecular weight cutoff (MWCO) of 45 kDa and mean pore size of 6 nm. The membrane with the 1 wt % addition of NaBr demonstrates most negative charge which indicates less fouling characteristics and displays approximately three times higher permeation. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Membrane technology has now become an eminent separation tool over the years and has accomplished a significant place in process industries. It is used in an expansive range of applications for separation, concentration, and purification in chemical and pharmaceutical processing, water treatment and production, environmental control, as well as energy production. Ultrafiltration (UF) is typically applied in separation of macromolecular solutes and colloidal material ranging from the molar mass of 300–500,000 Da.¹ To achieve the desired enhanced membrane performance, characteristics of the membrane such as low fouling, high flux, and selectivity as well as possess performance stability during long-term operation² are identified as significant factors.

There are several steps involved in the production of polymeric membranes and these include the selection of membrane material, preparation of dope solution, fabrication of flat sheet, or hollow fiber membranes through phase inversion process and post-treatment of the membranes. The dissolution process of the main polymer, solvent, and additives is identified as the most time-consuming process as it may take more than two-thirds of the production time. The dissolution time is very much dependent on the type of polymers and additives used.³

Wang et al.⁴ reported that the complete dissolution of polymers in solvents for blend membranes production took approximately 2 h of heating. The most frequent dissolution time reported for dope solution preparation is in the range of 4–6 h.^{5–11} Ng et al.¹² produced dope solutions which required

8–10 h of dissolution for the formation of asymmetric polysulfone (PSf) flat sheet membrane for gas separation. Several researchers reported dissolution time of 12 h¹³ and 24 h of mixing and heating.^{14–18} In a particular case, a dissolution time of 48 h was reported in the preparation of PAN-based UF membrane.¹⁹

To ensure homogeneity and consistency, the polymeric solution need to be heated and stirred continuously throughout the process and this contributes to the high cost in production of membrane. To reduce the time and energy required for the dissolution process, the microwave irradiation was introduced.^{3,20} In general, the average microwave heating is known to save about two-thirds of the energy used by conventional heating^{21,22} and the cost of the microwave is not much more than that of conventional heaters. The microwave irradiation dissolution setup was introduced in membrane production and the results revealed that the resultant membrane produced via the microwave dissolution demonstrated better fluxes and performances compared to membranes produced via conventional heating technique.^{3,20,22} This technique reduced the overall dissolution time by nearly 95%.

Modification by the introduction of a third component also known as additives in the mixture was proven to influence the macro voids formation and consequently affects the performance and mechanical properties of the produced membranes.²³ Investigations on influence of various types of additives such as PEG^{8,9,15} and PVP^{24,25} on the microstructures and performance of membranes were widely reported. These additives influenced the pure water flux and solute rejection of the membranes. Several researchers^{15,26–32} reported that PEG and PVP influenced the structure as well as the thermodynamic and kinetic properties during phase inversion process.

Other researchers^{33–35} have reported on the effectiveness of introducing inorganic salts to casting solutions in the preparation of membranes with higher performance. The solvent properties and/or the interaction between the macromolecule chains are very much influenced by the presence of inorganic salt additives in casting solutions.³⁶ The inorganic salts especially lyotropic salts that give good membrane are those with lithium, zinc, calcium, and magnesium as cations and chloride, bromide, iodide, nitrate, thiocyanate, and perchlorate as anions.³⁶ These lyotropic salts are known to form complexes with the carbonyl group in polar aprotic solvents such as with acetone, dimethylacetamide, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and *N*-methylpyrrolidinone through ion–dipole interaction. Low-molecular-weight inorganic salts such as lithium chloride (LiCl),^{37–40} lithium fluoride (LiF),⁴⁰ lithium bromide (LiBr),^{3,40} zinc chloride (ZnCl₂),³³ magnesium chloride (MgCl₂), calcium chloride (CaCl₂), magnesium perchlorate (MgClCO₄), and calcium perchlorate (CaClCO₄)⁴¹ are some of the other less common additives used.

However, the use of halogenated-based additives in membrane production has not been widely explored and reported compared to additives such as PEG and PVP. Nevertheless, extensive studies on the effect of LiCl additive on the membrane were reported^{37–40} and the addition of LiCl as additive was found to

effectively enhance the vapor permeability of the membrane.³⁸ The rheological behavior of polyether sulfone polymer solution which consisted of LiBr additives,⁴⁰ as well as the performances of membranes containing various amounts of LiBr, LiCl, and LiF additives were systematically studied.⁴⁰ In our previous study,⁴⁰ the influence of LiCl on polyethersulfone (PES) membranes was studied and results revealed that concentration of LiCl was best kept at 3 wt % when dissolved in dual solvents DMF and acetone.

The results exhibited by the lithium halogenated-based additives seemed promising but to date no study has been reported on the influence of sodium bromide (NaBr) additives on membrane preparation. Previous studies^{2,20,22,38,40,42} emphasized on lithium halogenated-based additives and their effects on membrane properties and performance. However, these lithium halogenated-based salt additives are expensive and therefore are not practical from the economic perspective. Extensive efforts and studies are carried out in producing an economically high-performance membrane with improved properties. Moreover, NaBr is found to be a cheaper alternative compared to other halogenated salts. Thus, in this study, an attempt is made to investigate the influence of NaBr additive on the membrane performance and characteristics of asymmetric PES UF membranes. The polymeric dope solutions were prepared using the microwave irradiation technique. All the membranes are prepared by the dry/wet phase inversion method. The effect of NaBr concentration on solution viscosity and pure water permeation, solute separation, fluxes, morphology, hydrophilicity, and streaming potential of the membranes was investigated and discussed in detail.

EXPERIMENTAL

Materials

PES Ultrason® E 6020 P supplied by BASF (Ludwigshafen, Germany) was used as polymer in preparation of membrane casting solution. DMF purchased from Mallinckrodt Baker (Phillipsburg, NJ, USA) was used as the solvent. NaBr Reagent-Plus™ was provided by Sigma-Aldrich (St. Louis, MO, USA) and used as additive. Bovine serum albumin (BSA) with molecular weight of 67,000 Da was purchased from Sigma-Aldrich (USA) and PEG with molecular weights of 3000, 6000, 10,000, and 35,000 D supplied by Fluka (Sigma-Aldrich GmbH, Milwaukee, WI, USA) were used as solutes. All feed solutions were prepared using distilled water. For solute rejection test using BSA solution, Biuret Reagent was used to determine the concentration of BSA. Biuret Reagent consisted of potassium sodium tartrate (NaKC₄H₄O₆·4H₂O) was purchased from Fisher Scientific (HK) Ltd. (Hong Kong), copper (II) sulfate pentahydrate (CuSO₄·5H₂O) was obtained from QRec (Auckland, New Zealand)™, and sodium hydroxide (NaOH) was purchased from Merck (Darmstadt, Germany). The reagent was prepared using distilled water to characterize the separation performance of BSA. As for Dragendorff Reagent preparation for PEG separations, bismuth subnitrate (Bi₅O(OH)₉(NO₃)₄) was obtained from Mallinckrodt Baker (USA). Glacial acetic acid 100% anhydrous (HAc) was purchased from Merck (Germany) and potassium iodide was supplied by SureChem Products Ltd (Suffolk, UK).

Table I. PES UF Dope Formulations and their Viscosities

PES/UF membranes	Composition of casting solution (wt %)			Viscosity (cp)
	PES	DMF	NaBr	
N-0	20	80	0	276
N-1	20	79	1	361
N-2	20	78	2	371
N-3	20	77	3	444
N-4	20	76	4	453
N-5	20	75	5	724

Preparation of Dope Solution

Table I summarizes the dope solutions prepared from 20 wt % PES and various compositions of NaBr and DMF. The solutions were prepared using the MWA closed heating technique described explicitly in the previous studies.^{20,22} The domestic microwave oven (model NN-5626F, Panasonic, Singapore) used had an operation frequency of 2450 MHz with a rated power output of 900 W (240 V and 50 Hz). To ensure safety, the microwave oven was modified such that the wavelength was <5 cm and also to accommodate the two-necked vessel with fluid-sealed stirring device.

PES and NaBr were initially dried in the microwave oven for about 10 min at medium high pulse (450 W) to remove any moisture present. The solution was prepared by dissolving PES and NaBr additive in the DMF solvent placed in the glass vessel setup equipped with glass connectors attached to the reflux condenser, a thermocouple to control the temperature at 90°C (±5°C), and a fluid-sealed stirrer inside the vessel to ensure homogeneity. Heating time by microwave was 15 min (low to high pulses), whereas the dissolution time was kept maximum to 1 h with a stirrer speed of 700 rpm. The air bubbles in the resultant polymer solution were removed by ultrasonification process and the polymer solution was cooled to room temperature.

Viscosity Measurement

The effect of NaBr concentration on the solution viscosity was analyzed. The viscosities of the different dope solutions were measured using the Brookfield Digital Viscometer Model DV-III at 25°C equipped with a sample adapter (SC4-31). The viscosity is measured at room temperature (26 ± 0.5°C). To ensure reproducibility of the data, the experiments were performed at least three times.

Membrane Casting

The membrane was prepared by pouring the dope solution at room temperature into the gap of the casting knife which was placed on the clean rectangle glass plate. The casting knife with a thickness of 200 μm was slide across glass plate forming the thin film. The glass plate with the thin film was then immersed into a distilled water bath without any delay. Owing to the phase inversion process, a thin membrane film was produced and separated out from the glass plate. The membrane film was then washed with distilled water and transferred into a water bath. Membrane was visually inspected for any defects and ready for further membrane test and evaluation.

Post-Treatment of Membranes

To ensure that the additive was removed, the casted membranes were post-treated. The membranes were initially washed three times using distilled water and immersed in a beaker filled with 500 mL deionized water. The beaker was covered with aluminum foil and then placed in a microwave oven for 10 min at medium high pulse with the temperature controlled at 90 ± 5°C using a pico data logger. A standardized digital conductivity meter (Hanna Instruments model H18633, Selangor, Malaysia) was used to measure the conductance of the deionized water so as to ensure that the excess additive inside the membrane pores was totally removed. The treated membrane were then rinsed again in deionized water until the conductance readings reached values equivalent to those of pure deionized water.^{22,42} The membranes were then ready for testing.

UF Experiments

Membrane Compaction. The UF experiment was performed in a UF unstirred dead-end cell filtration system. The membrane was first compacted by performing the filtration of pure water at 450 kPa (which was higher than the operational pressure for the experiments) for 2 h (at least 1 h to achieve steady-state flux). Then, the compacted membrane was washed thoroughly and then tested for the pure water fluxes at operational pressure of 300 kPa and at room temperature. The membrane was placed in the dead-end UF cell in such a way that the active skin layer was facing the incoming feed.

Pure Water Permeation. The membrane performance was evaluated in terms of the permeation flux and rejection rates. The pure water (PWP) and solute permeation rates were calculated using the following equation:

$$\text{PWP} = \frac{Q}{\Delta t \times A} \quad (1)$$

where Q is volume of the permeate (l), A is the membrane surface area (m²), and t is permeation time (h).

Separation Experiments. Solute rejection of membrane was evaluated using PEG solutions of various molecular weights ranging from 3000 to 35,000 Da and BSA of 67,000 Da at 300 kPa. The concentration of PEG solution used was 1000 ppm. Each experiment was performed in triplicates so as to ensure reproducibility of data. The concentrations of the feed and permeate of PEG solution were determined by the method described by Jia and Tian.⁴³ Meanwhile, the BSA concentrations of feed and permeate were determined by Biuret Reagent. The concentration of PEG was determined based on absorbency on a UV-spectrophotometer at a wavelength of 510 nm. Meanwhile, the absorbance of BSA was measured at a wavelength of 550 nm against a reagent blank. The solute rejection of UF membrane was calculated using the following equation:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

where C_p and C_f are solute concentrations in permeate and feed streams, respectively.

Membrane Characterization by Solute Transport Data

Pore Size and Pore Size Distribution. The mean pore size and the standard deviation of the membranes were calculated using the solute separation data from UF experiments and equations derived by Singh et al.⁴⁴ According to Singh et al.,⁴⁴ the Stokes radius of PEG, a (cm) is determined as a function of molecular weight M as displayed in the following equation:

$$a = 16.73 \times 10^{-10} M^{0.557} \quad (4)$$

The solute diameter (d_s) is defined by

$$d_s = 2a \quad (5)$$

The percentage of solute separation as a function of solute diameter was plotted on the log normal graph. The mean pore size (μ_p) was determined from d_s corresponding to $R = 50\%$ on the linear regression line. Meanwhile, the standard deviations (σ_p) were determined from the ratio of d_s at $R = 84.13$ and at 50% . In addition, the MWCO was determined at $R = 90\%$.

Scanning Electron Microscopy

The cross-section of the membrane was observed using SEM. The membranes were snapped in liquid nitrogen so as to give a generally clean break. The sample was then placed on a sample stand and sputtered coated with gold before viewing under the SEM (Jeol USA JSM-6390 LV, Ibnu Sina Institute, UTM).

Contact Angle Measurements

The hydrophilicity of membrane surface was measured by performing CA measurement. Contact angle was measured using an optical CA measurement system CAM 101 (KSV Instruments). Five microliters of water was dropped on the membrane surface using a micro syringe at room temperature. At least, five measurements of drops at different locations were averaged to obtain CA for one membrane sample.

Zeta Potential

The zeta potential (ZP) measurement was performed in a polycarbonate UF module with an area of 10.4 cm^2 . Each set of experiment used a new piece of membrane. The streaming potential was measured with a pair of Ag/AgCl electrodes attached to both sides of the membrane. KCl solution with a concentration of $0.001M$ was used as the electrolyte solution and the measurement was carried out at different pressures between 0.1 and 2 bar. Throughout the experiment, the pH of the electrolyte solution was shifted up or down by adding small amounts of HCl or KOH. The filtration and measurement were carried out at a constant temperature of 25°C . The parameters (mass of permeate, temperature, streaming potential, pressure, and streaming potential) were collected by a computer and the interval time for data collection was 2 min. Streaming potential is an effective and best method to characterize the surface charge densities of membranes, thus the variability in charge density of the membrane surface can be successfully determined. The estimation of surface charge density of clean and fouled membranes in different directions can also be performed.⁴⁵

From streaming potential measurements, ZP can be calculated using the Helmholtz–Smoluchowski equation, giving

relative values for the ZPs, as shown in the following equation:

$$\zeta = \frac{\Delta E_s \kappa \mu}{\Delta p \varepsilon_0 \varepsilon_1} \quad (6)$$

where ζ is the ZP, ΔE_s is the induced streaming potential, Δp is the applied pressure, ε_0 is the permittivity in vacuum, ε_1 , κ , and μ are the dielectric constant, conductivity, and viscosity of the electrolyte solution, respectively.

RESULTS AND DISCUSSION

Polymer Solution Properties

Table I lists the formulations and casting solution viscosities of PES/DMF UF flat sheet membranes with different concentrations of NaBr additives. It was observed that NaBr additive significantly influenced the viscosity of the casting solutions. PES/DMF UF membrane in the absence of NaBr additive was used as control to evaluate and compare the effect of additive on the separation performance of PES/DMF/NaBr membranes.

The viscosities of dope formulations with different concentrations of NaBr additive were observed to increase with the increase amount of additive used. Table I shows that the viscosity of dope solution without additive (N-0) is 276 cp which is very much lower than the other dope solutions incorporated with additive. The viscosity of the dope solution with the highest amount of additive is almost twice more that of the solution without additive. In general, increase in the concentration of NaBr additive will subsequently increase the polymer solution viscosity. Low concentration of NaBr (1–2 wt %) increases the dope viscosity slightly by only 30% probably owing to NaBr low dielectric loss properties as explained by Ahmed et al.²² in his study when dealing with LiBr. At low NaBr concentrations, both the solvent and the additive interact efficiently with the PES because of their polar and ionic properties. Increasing concentration of NaBr beyond 2 and 3 wt % further increased the viscosity by 60% and almost double, respectively. The high viscosity at higher concentrations could be owing to the salt–solvent interactions and/or the association of Na^+ cations and the polymer network which consequently results in poor solvating power of DMF for NaBr.³⁰ Several researchers^{3,22} observed similar findings where higher viscosity polymer solution of PES was formed with DMF when LiBr was present compared to salt-free solution and this is not just solely owing to the salt–solvent interactions but also interactions between the Li^+ cations and the strong electron donating groups of polymeric material.

Flux Profile During Compaction

The effect of compaction time on PWP for all the membranes is shown in Figure 1. The PWP declines gradually owing to compaction with time and after about 2 h of compaction, it reaches a steady-state value. This is owing to the fact that the walls of the pores become closer, denser, and uniform, resulting in reduction in pore size as well as the flux during compaction.²⁰ As shown in Figure 1, membrane without additive, N-0 demonstrates steady-state PWP value of $6.32 \text{ L/m}^2 \text{ h}$. Meanwhile, N-1 membrane shows highest steady-state value of PWP which is $15.8 \text{ L/m}^2 \text{ h}$, much higher compared to N-0. Increasing

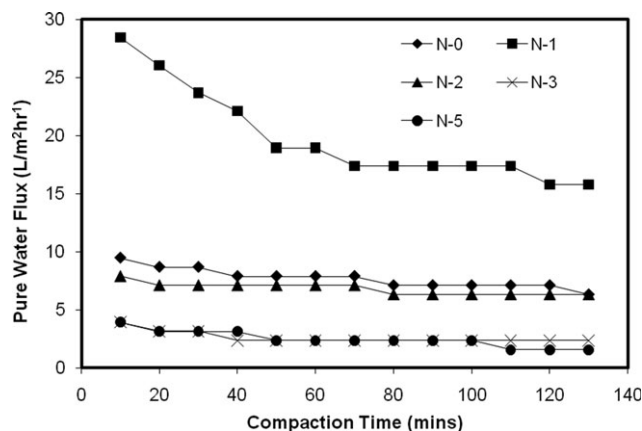


Figure 1. Flux profiles during compaction for PES/DMF/NaBr UF membranes.

NaBr concentration beyond 1% did not improve the PWP rates. In contrast, membrane with highest amount of additives, N-5 shows the lowest steady-state value of PWP, which is 1.58 L/m² h. The PWP test on each membrane is then performed after the membrane is compacted.

Pure Water Permeation

The PWP of the membranes produced from the different dope solutions containing different concentrations of NaBr additive are shown in Figure 2. This PWP test was carried out at a constant operational pressure of 350 kPa. It is observed that the membrane without NaBr, N – 0 exhibits PWP of 9.5 L/m² h. The findings revealed that PWP is very much influenced by the presence of NaBr into the dope formulation. Low concentration of NaBr (1 wt %) shows excellent PWP of 28.4 L/m² h as compared to N-0. However, further increase in the NaBr additive beyond 1 wt % does not improve the PWP. In general, the PWP for N-1 membrane is approximately three times higher than the N-0 membrane. The permeation rate of 28.4 L/m² h for N-1 is considered good and comparable to commercial spiral wound membranes (flat sheet is similar to spiral wound membrane). The permeation rates of commercially available spiral wound membranes can range from as low as 4.5L/m² h to as high as 53 L/m² h as listed in Table II. N-1 membrane also exhibited higher PWP compared to membrane with highest PWP in the dual solvent system as reported in our previous study, which used LiCl as salt additives.³⁸

Apparently, the concentration of additive is very crucial as it influences the hydrophilic property of the membrane. The differences in the permeability of membranes are probably related to the different salt–solvent interactions or solubility parameters as explained by previous researches.^{22,34} It is observed that at low NaBr concentration, the dissociation affinity for DMF is much higher and as such increases the permeate flux. Efficient polar interaction of NaBr, DMF, and PES under microwave irradiation condition enhances the hydrophilic properties of the membranes and thus improves the permeation rates. Similar reports^{46,47} revealed that the addition of inorganic salts has increased the permeability. However, when NaBr concentrations are increased further to 2 wt %, the permeation rates declined

probably owing to the complexes formed between NaBr and DMF which promotes the hydration effect and subsequently swell the polymer gel. The ZP and contact angle measurement will further support the hypothesis presented.

Molecular Weight Cutoff Profiles

The MWCO profiles for PES/DMF/NaBr membranes with different amounts of NaBr additive are shown in Figure 3. It is observed that the MWCO profile for the PES membrane containing 1% NaBr (N-1) is better than the PES membrane without NaBr (N-0). MWCO is defined as the molecular weight that is 90% rejected by the membrane.⁴⁸

Apparently, N-1 showed highest rejection rates compared to those without additive. N-1 and N-0 membranes approximately have MWCO of 45 and 53 kDa, respectively. However, membranes with NaBr additive amounting of 2 wt % (N-2), 3 wt % (N-3), and 5 wt % (N-5) have lower rejection rates with MWCO >45 kDa. Results show that the N-1 membrane exhibits both high flux and higher rejection rates compared to all other membranes, indicating the addition of 1 wt % NaBr has improved the hydrophilic property of the membrane, which improves not only the permeation rate but also the rejection rates. NaBr when added in small amount acts as a pore reducer as demonstrated by the reduction in the MWCO of the membranes that corresponded to their smaller pore sizes.

PES Membranes' Characterization Using Solute Transport Data

Figure 4 shows the log normal plots of solute separation versus solute diameter for the various UF membranes with different concentrations of additive. The solute diameter d_s was calculated using the Stokes–Einstein radius of PEG equation. Meanwhile, the value of mean pore size (μ_p), MWCO, and the standard deviation (σ_p) of these membranes were determined from solute separation curves. The results are summarized in Table III. In general, all the membranes pore sizes are in the UF range. Membrane without additive, N-0 displayed MWCO of 53 kDa with mean pore size of 6.5 nm. As for N-1 and N-0 UF membranes, results found that the mean pore sizes were 6.0 and 6.5 nm with MWCOs of 45 and 53 kDa, respectively.

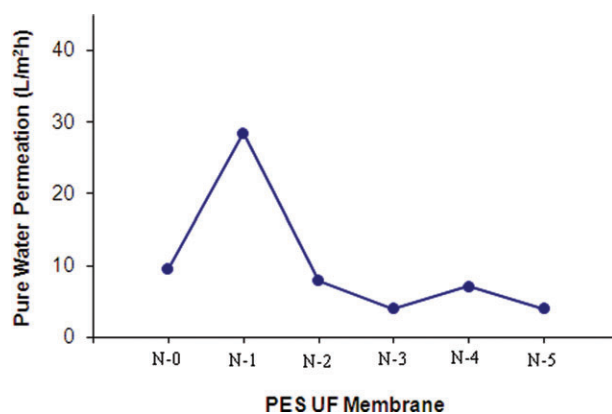


Figure 2. PWP for different PES/DMF/NaBr UF membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Spiral Wound PES Membranes

Manufacturer	Module	Material	MWCO (kDa)	Flux (L m ⁻² h ⁻¹)	Application
ami (USA) ²⁰	M-4040 PES (SW)	PES	10	4.54–18.16	Pharmaceutical and food industry
ami (USA) ²⁰	M-U2540PAN (SW)	Hydrophilic PAN	20	50	Waste water
KOCH USA ²⁰	HFK-131 (SW)	Semi-microporous PES	10	24–53	Waste water
KOCH ²⁰	HFK-328 (SW)	Semi-microporous PES	5	24–53	Waste water
PALL ⁵²	BTS tubular	Asymmetric pure PS	0.5–8	24–360	Pharmaceutical and food industry
Luxx Ultra-Tech USA ²⁰	L' Series Tubular	PVDF, PES, and PS	5	27–45	Waste water food industry
Millipore USA ⁵²	Ultracel; Biomax PB	PES	5	35–45	Protein Purification
Synder's CA ²⁰	PES100	PES (SW)	70	51	Gelatin concentration
TriSep CA ²⁰	UE10	PES (SW)	10	2.1	Dairy and food industry
TriSep CA ²⁰	UE50	PES (SW)	100	4.5	Dairy and food industry

Results show that the addition of 1 wt % NaBr additive does not seem to reduce the mean pore size of the membranes drastically; pore diameters reduce slightly from 6.5 to 6 nm. Meanwhile, the standard deviations decreased from 2.17 to 2.15. In addition, the N-2 and N-3 membranes showed slightly bigger pore sizes than the others, which were 11.25 and 13.33 nm and were in good agreement with their high MWCOs, which were 63 and 105 kDa, respectively. The analysis suggested that the addition of NaBr additive >1 wt % increases the mean pore size of the membranes as well as the MWCO. However, adding small amounts of 1 wt % of NaBr proved to be useful as higher rejection rates and fluxes were achieved despite the small reduction in mean pore size and MWCO.

Effect of Additive Concentration on Membrane Morphology

Figure 5 shows the SEM cross-sectional images of the flat sheet membranes. The addition of NaBr additive is observed to have an influence on the morphology of the membranes. Figure 5(a) shows the cross-sectional image of PES membrane without NaBr is very much thicker compared to the other membranes with different concentrations of NaBr additive although the casting knife was set constant at 200 μm thickness for every

casting process. In addition, the membrane without NaBr showed finger-like structure and obvious skin layer on the membrane surface.

Unlike cellulose acetate,⁴⁹ PES with DMF as its solvent undergoes slight shrinkage during phase inversion and the result is similar to the findings by other researchers.⁵⁰ The presence of NaBr induces further shrinkage to the membrane as shown in Figure 5(b–d). The thickness of the membrane with the 1 wt % NaBr is approximately 92 μm compared with the membrane without NaBr which is 162 μm . The presence of NaBr (1 wt %) has induced intermolecular association of PES chains, leading to a decrease in the power of the solvent and thus increased the viscosities (Table I). Consequently, the rate of precipitation is increased and a more dense structure with macro voids is favored. Such phenomena were also observed and reported by Strathmann⁵¹ in his early study. Such increase in precipitation rate also promotes the very thin skin structure, spongy-like membrane structure interrupted by macrovoids formation, enhances pore formation, and improves pore interconnectivity as shown in Figure 5(b). The very thin skin structure and pore

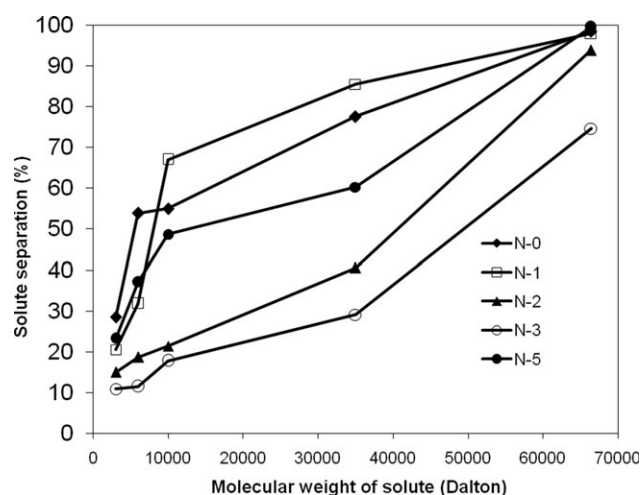


Figure 3. MWCO profiles of PES/DMF/NaBr UF membranes.

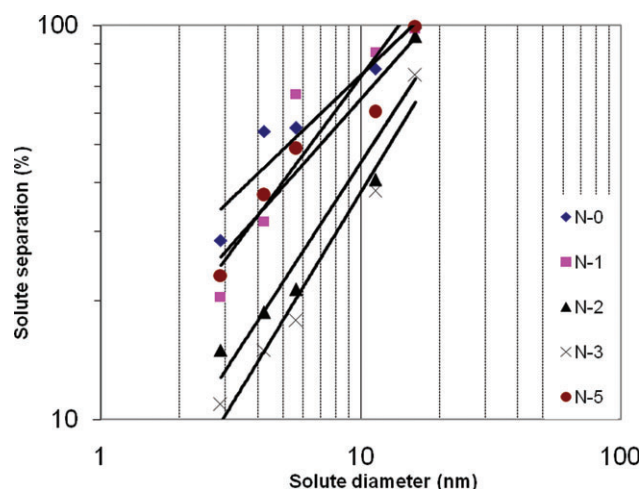


Figure 4. Solute separation curve for PES/DMF/NaBr UF membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Mean Pore Size, Standard Deviation, and Molecular Weight Cutoff of PES Membranes with and Without NaBr Calculated from the Solute Separation Curves

PES UF membranes	Molecular weight cutoff (kDa)	Mean pore size, μ_p (nm)	Standard deviation, σ_p
N-0	53	6.5	2.17
N-1	45	6.0	2.15
N-2	63	11.25	1.67
N-3	105	13.33	1.58
N-5	58	7.0	2.18

interconnectivity explains for the good rejection and flux rates achieved by the N-1 membrane.

Although further increase in concentration of NaBr beyond 1 wt % also induced intermolecular association of PES chains and consequently formed dense and homogeneous distribution of the associated polymer in solution; this only produces larger pores without any significant changes in porosity as shown in Figure 5(c–f). Such findings were also observed when salts such as LiCl, LiNO₃, and MgCl₂ were added to reverse osmosis carboxylated PSf membranes.⁴⁶ In another study, Kim et al.³³ found that 3 wt % ZnCl interacted with sulfone polymer chains and enhanced the membrane permeation properties.

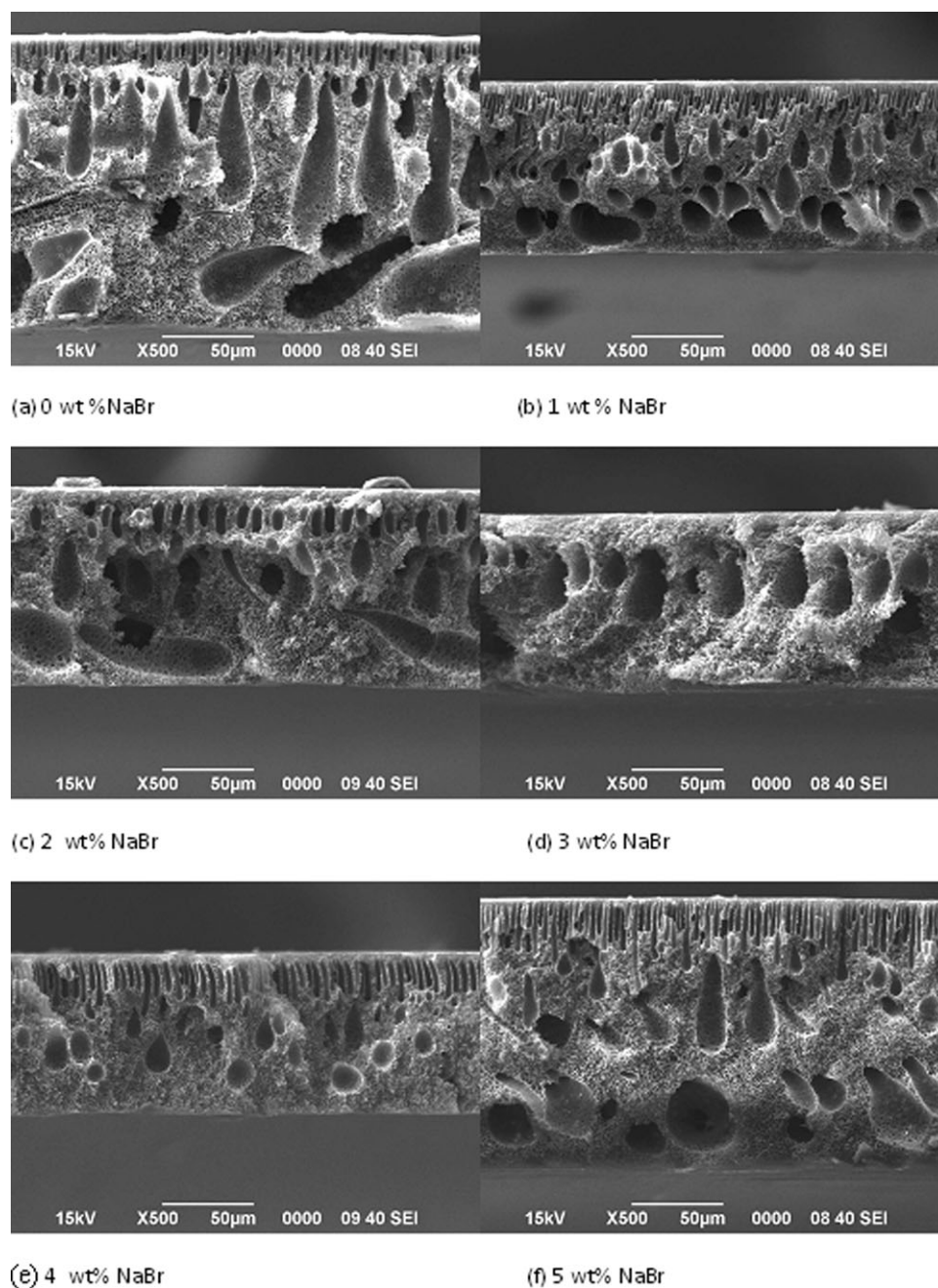


Figure 5. SEM images of the cross-section of PES/DMF membrane without and with NaBr additive.

Table IV. Mean Contact Angle Values of the Various PES Membranes

PES UF membranes	Mean contact angle (°)
N-0	67.4 ± 0.4
N-1	54.7 ± 1.5
N-2	68.9 ± 1.0
N-3	70.3 ± 1.3
N-4	69.2 ± 0.6
N-5	71.6 ± 0.1

In summary, the results show that the NaBr additive plays an important role by influencing the morphology and the overall structure of the UF membranes and the amount used is very critical and must be kept to 1 wt %.

Effect of Additive Concentration on Hydrophilicity

The hydrophilicity of membrane can be evaluated by contact angle measurement. The value of contact angle measurement for every membrane is different. As summarized in Table IV, membrane with 1 wt % NaBr, N-1 shows the lowest value of contact angle, as low as $54.7 \pm 1.5^\circ$, indicating that it is the most hydrophilic among all the membranes. Membrane without additive, N-0, shows a mean contact angle of $67.4 \pm 0.4^\circ$, indicating that it is less hydrophilic compared to N-0. The results explained for the lower PWP flux obtained in the previous section. Membrane with the highest amount of NaBr (N-5) shows highest value of contact angle, suggesting that it has the least hydrophilic and is in agreement with the water flux results. The analysis supports the suggestion that little presence of NaBr has improved the hydrophilic properties of the membranes, thus improving the flux rates by threefold. There is a possibility under microwave irradiation with small amount of NaBr (1 wt %) the halogen group introduced itself into the polymer chains and, because of continual radiation, surface modification might have occurred rapidly. The water flux results indicate that there is the possibility that Br ions were induced into PES ether group or sulfonyl group, and thus improved in the hydrophilic property.²⁰ However, higher amount of NaBr does not promote the hydrophilic properties as exhibited by its low flux rates

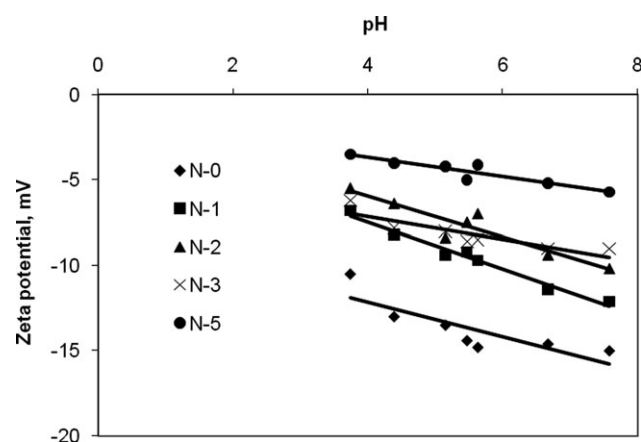


Figure 6. Apparent ZP versus pH for PES/DMF UF membranes with different concentrations of NaBr additive.

probably owing to the formation of salt–solvent complexes which diffused out during the phase inversion process. Similar findings³⁸ were also reported that LiCl and DMF formed salt–solvent complexes which resulted in hydration effect and caused swelling in the polymer gel.⁴¹

Effect of Additive Concentration on Streaming Potential

Streaming potential or commonly known as ZP is an important parameter used to determine whether a membrane is positively or negatively charged. The interaction between a charged membrane and a solution that contains charged solution is likely to cause aggregation of solutes into a larger unit, and thus lead to fouling phenomena. Figure 6 shows the plot of apparent ZP versus pH for the various UF membranes. In general, all the membranes are negatively charged. The negative charge decreases as the pH value increases. This showed that the membrane surface was more negatively charged at the higher pH.

As shown in Figure 6, the apparent ZP of all the membranes varies between -5 and -15 mV. The lowest ZP, which has the strongest negative charge, was obtained for N-0 membrane followed by N-1 membrane. In general, the addition of NaBr additive tends to produce membranes with less negative charge. Meanwhile, the permeabilities of the UF membranes with different concentrations of NaBr additive at different pHs are shown in Figure 7. The permeability is simultaneously measured with the surface charge of the membrane. In general, the permeability of these membranes at different pHs can be considered as stable owing to the little variation with pH changes. N-1 membrane displays the highest permeability at the various pHs, followed by N-0 membrane (Figure 7), and thus explains for the high PWP flux shown in the early part of this report. The analysis confirms the suggestion that a small amount of NaBr (1 wt %) is sufficient to improve the permeability properties and consequently exhibits higher flux. On the other hand, increasing concentration of NaBr (beyond 1 wt %) in the membrane formulation does not improve the performance of the membrane both in terms of rejection and in terms of permeability rates.

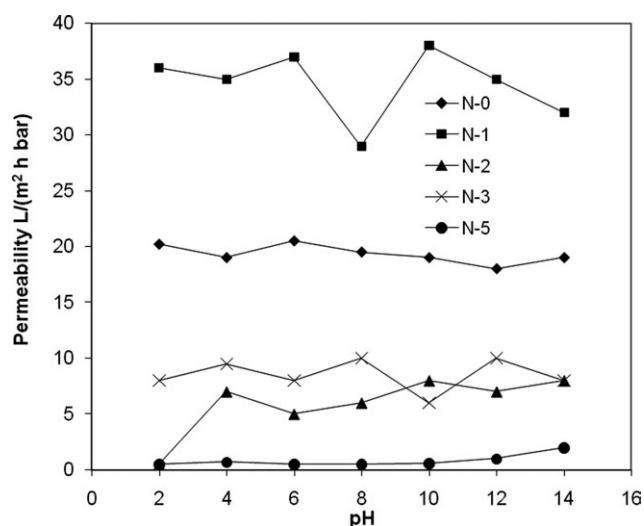


Figure 7. Permeability of PES/DMF/NaBr UF membranes at different pHs.

To summarize, flux is not only dependent on pore size of the membrane. There are several other factors that contribute to membrane flux, such as the surface charge, hydrophilicity, membrane properties, and also the structure of the membranes. Table III lists the pore sizes of N-2 and N-3 are bigger than N-1. However, the water flux of N-2 and N-3 membranes are lower than N-1. This can be explained by reference to Table IV, where contact angle values of N-2 and N-3 membranes are higher compared to N-1 membranes, indicating that they are more hydrophobic. This clarifies their low permeation rates as shown in Figure 2 although the pore sizes are big. These results are in good agreement with streaming potential findings (ZP data), which reveals both N-2 and N-3 are less negatively charge as compared to N-1.

CONCLUSIONS

In conclusion, the presence of NaBr as additive displayed a significant effect on the performance and characteristics of PES/DMF UF membranes. It was found that UF membrane with 1 wt % NaBr additive (N-1 membrane) exhibited the highest permeation rate of 28.4 L/m² h and highest rejection rate. The MWCO and mean pore size of N-1 is slightly smaller than the one without additive N-0, that is 6.0 nm compared to 6.5 nm. The 1 wt % NaBr is sufficient to induce interchain association in the polymer solution, leading to a decrease in the power of solvent and thus increases the viscosity. In addition, the rate of precipitation is increased and a more dense spongy structure interrupted by macrovoids is formed. Contact angle measurement revealed an improvement in the hydrophilic property of N-1 (54.7 ± 1.5°). Streaming potential measurement concluded that membranes with NaBr are all negatively charged with N-1 membrane, displaying the most negative charge compared to the other membranes. The negatively charged membranes help prevent aggregation of particles into larger flocs on the surface, and thus make the membrane is attractive owing to its low fouling characteristic. This was proven by the high rejection rates as well as high PWP showed by N-1 membrane. Consequently, the study suggested that low concentration of NaBr improved both permeability and rejection properties of PES/DMF UF membranes.

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