

Effects Of Solvent Types On Structure And Performance Of Polyethersulfone Nanofiltration Membrane In Monovalent And Divalent Ions Separation

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Abstract

This study investigates the influences of solvent on the structure and performances of a nanofiltration (NF) membrane in the separation of monovalent and divalent ions. The asymmetric nanofiltration membranes were prepared by phase inversion process consisting polyethersulfone (PES) as a polymer, distillate water as a nonsolvent, polyvinylpyrrolidone (PVP) as a nonsolvent additive and different solvent type was also added either dimethylformamide (DMF), dimethylacetamide (DMAc) or *n*-methylpyrrolidone (NMP). Through turbidity titration method, the dope formulated was 23% polymer, 69% solvent, 3% nonsolvent and 5% nonsolvent additive. The morphological structures of produced membranes were examined using Scanning Electron Microscope (SEM). The SEM images exhibited the best morphological structure was discovered from the membrane produced using NMP as the solvent followed by DMAc and lastly, DMF. This study indicated that solvent with higher boiling point (in this study, NMP has the highest boiling point) produced a desired NF membrane with more finger-like structure. The diameters of pores in skin layer were measured by Steric-Hindrance Pore (SHP) and Teorell-Meyer-Sievers (TMS) model. The mean pore size of each produced membrane was about 1.28 nm, 1.47 nm and 1.59 nm for NMP, DMAc and DMF, respectively. The performances of the PES nanofiltration membranes were examined based on rejection and flux. Generally, the rejections of mono and divalent anions were identified to be within 29%-38%, and 81%-91%, respectively. As predicted by the morphological structure, NMP solvent-membrane showed the best salt rejection for both monovalent and divalent ions as compared to DMAc and DMF. Hence, solvent was discovered to affect the morphological structure and consequently, improved the performance of the polyethersulfone nanofiltration membrane.

Keywords : Nanofiltration, Polyethersulfone (PES), Monovalent and Divalent ions, Membrane structure, Membrane performance

Introduction

Most of the polymeric membranes with asymmetric structures are prepared by immersion precipitation [1]. In

this process, an initially single-phase homogeneous polymer solution is cast onto a suitable substrate to form a thin film and is then immersed in a coagulation bath, which results in diffusive exchanges of solvent and nonsolvent and the solidification of the polymer. Thus, the morphology and transport properties of the membrane are strongly depending on both the thermodynamics and the kinetics of the phase separation process [2].

Macrovoids are quite often observed on the asymmetric membranes made by the phase inversion process. They can be favorable for nanofiltration membranes by giving generally higher flux. However, they must be avoided from high-pressure operations such as gas separation and reverse osmosis, because they can be the weak points that lead to membrane collapse. Therefore, there have been numerous studies conducted on the macrovoid formation mechanism as well as the methods to suppress macrovoids in order to overcome this problem [3].

One of the methods proposed is the addition of polymeric additive to the membrane casting solution. This method has indeed showed quite successful results in terms of reducing macrovoids [4]. A water soluble polymer such as polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) are among the frequently used in the study of polymer additive effect. Boom *et al.* reported that there is a morphological change in membranes by the addition of PVP in a PES solution. PVP could change the membrane structure because of its tendency to precipitate (delayed or instantaneous) upon the addition of PVP.

Several researchers have reported that the addition of a third component into the dope solution indeed can either induce or suppress macrovoid formation in asymmetric. However, they concluded that the effect of PVP addition to a polyether sulfone (PES) solution on macrovoid formation is highly depending on the type of solvent used for the membrane system [4, 5].

Hence, this study is conducted to investigate the influences of different solvent on the morphological structure and performances of a nanofiltration membrane in separation of monovalent and divalent ions.

Methodology

Materials

Dope used in this study consisted of polyethersulfone (PES) as polymer, *n*, *n*-dimethyl acetamide (DMAc), *n*-methyl-2-pyrrolidone (NMP) and *n*, *n*-dimethyl formamide (DMF) as solvent, distillate water, as nonsolvent and polyvinylpyrrolidone as additive. All standard chemical grade materials used were supplied by Amoco Chemicals.

Preparation of membranes

The cloud point can determine the equilibrium thermodynamic data of a ternary system (polymer/solvent/nonsolvent/additive). The titration equipment and procedure as proposed by Van't Hof had been employed for this study to measure the cloud point of the system [6]. The turbidity titration process had resulted in a dope formulation of 23% polymer, 69% solvent, 3% nonsolvent and 5% additive.

The membrane solution consisted of PES as a polymer, different type of a solvent, distillate water as a nonsolvent and polyvinylpyrrolidone as an additive was prepared. It was stirred at a temperature of 50–60 °C for 4 to 6 hours to ensure that the solution was completely homogenous. Then, the solution was stored in a vacuum bottle and followed by subjecting it to an ultrasonic bath to remove any bubble that might be existed.

Asymmetric PES membranes were fabricated by a dry/wet phase inversion process using a pneumatically-controlled casting machine. The casting process was done at ambient temperature (30 °C). A small amount of casting solution was poured onto a glass plate with a casting knife gap setting at 200 µm. Then, force convective evaporation step was conducted on the cast membranes before immersing them into a coagulation medium [7]. After a complete coagulation, the membranes were transferred into a water bath for a day. Finally, the membranes were immersed in methanol for 2 days and later, dried at room temperature to remove any residual organic compounds.

Permeation tests

NaCl, MgSO₄, MgCl₂ and Na₂SO₄ solutions with concentration of 1000 mg/L each had been prepared as the test solutions. Then, their conductivities were recorded using conductivity meter.

The membrane permeation tests were performed using a permeation cell with an effective permeation area of 0.00132 m² at an operating pressure of 3.5 bars as the permeation side was opened to the atmosphere, and at ambient temperature. Prior to testing, the pure water flux was measured to ensure that the membranes used were stable. The permeation rate and conductivity of each solution were determined [8]. The flux rate, *J* and salt rejection, *R* (%) can be defined in equation (1) and (3), respectively,

$$\text{Flux, } J = \frac{\text{Volumetric permeation rate}}{\text{rate}} \quad (1)$$

$$\text{Volumetric permeation rate} = \frac{V}{t} \quad (\text{m}^3/\text{s}) \quad (2)$$

$$R (\%) = \left[1 - \frac{C_p}{C_f} \right] \times 100\% \quad (3)$$

where *C_f* and *C_p* are the salt concentration in the feed and in the permeate that were determined by the conductivity measurement.

Characterization of membranes

Scanning electron microscopy (SEM) was used to examine the cross-sectional morphology of membranes. Firstly, the membranes were fractured cryogenically in liquid nitrogen. Then, the samples were sputtered with a thin gold layer. Prior to that, they were dried under vacuum at 30 °C overnight and then attached to an aluminium specimen stab. After 120 minutes of coating, the samples were scanned with Philips XL series 40 Scanning Electron Microscopy.

Determination of membrane pore size

The method of determining the membrane skin pore size as proposed by Ismail and Hassan was employed for this study [10]. NaCl-H₂O solution was fed to the system for this purpose. NaCl radius was 1.523 10⁻¹⁰ m. Considering the steric-hindrance effects, the ion-permeation flux inside the membrane can be expressed by the modified Nernst-Planck equation as in (4) [10, 12],

$$J_i = v_i k_i \left[H_{F,i} u_i c - H_{D,i} D_i \left(\frac{dc}{dx} + c \frac{z_i F d\phi}{RT dx} \right) \right] \quad (4)$$

i = 1, 2

H_{D,i} and *H_{F,i}* are the steric-hindrance parameters related to the wall correction factors of ion *i* under diffusion and convection conditions, respectively and expressed by the SHP model. In this model:

$$\sigma = 1 - H_F S_F \quad (5)$$

$$P_s = H_D S_D D_s \left(\frac{A_k}{\Delta y} \right) \quad (6)$$

where *D_s* is a solute diffusivity and the *A_k* is a membrane porosity. *H_F* and *H_D*, are the wall correction factors of the solute, while *S_F* and *S_D* are the convection and diffusion averaged distribution coefficients for steric effects only. These steric parameters can be further explained by the following equation,

$$H_F = 1 + \frac{16}{9} \lambda^2 \quad (7)$$

$$H_D = 1 \quad (8)$$

$$S_F = (1 - \lambda)^2 [2 - 1(1 - \lambda)^2] \quad (9)$$

$$S_D = (1 - \lambda)^2 \quad (10)$$

where $\lambda = r_s / r_p$, with r_s is the solute radius and r_p is the membrane pore radius.

Results and discussions

Effect of solvents on the structure of membrane

Generally, the higher the melting and boiling point of any material implies that the higher the viscosity will be. Based on Chemical Safety Data Sheet (MSDS), the boiling point of NMP is greater than DMAc and DMF. Thus, the viscosity of the dope solution produced with NMP solvent is higher. The solvent physical properties are tabulated in Table 1. The viscosity and boiling point of the solvent will determine the interaction between solvent and the nonsolvent of the system.

If this interaction is good enough, an adequate performance and homogeneous membrane can be produced. Thus, the homogeneous straight finger-like structure membrane that is favourable, is possible to be produced.

Table 1: Tabulated data physical properties for various solvent

Physical Properties	DMF	DMAc	NMP
Boiling Point (°C)	153	166	202
Melting Point (°C)	-61	-20	-24.4
Specified Gravity	0.950	0.937	1.027

Figure 1 to 3 show the SEM images of the nanofiltration membranes produced with different type of solvents.

NMP in Figure 1 displays the best structure as compared to DMAc and DMF in Figure 2 and 3, respectively. The finger-like structure with straight pore length is the most important criteria for causing a good separation. This structure allows solutes to easily diffuse from top to bottom layer of the membrane cause its performance to better than the spongy structure [9]. From observation, the membrane structure of NMP based membrane fulfills the requirements to be a high performance nanofiltration membrane. It has all the specifications such as apparent skin layer and a more open structure beneath the skin with asymmetric region. The porosity and thickness of the top layer, porosity of the sub layer and presence of finger like can be determined too.

The spongy structure at the top layer provided a good permeability and function as a support to the skin layer of the NMP membrane. The finger-like layer provided enough resistance to support the membrane upon any applied pressure [9]. The thickness of spongy top layer

and finger-like structure determined were 5 μm and 80 μm , respectively.

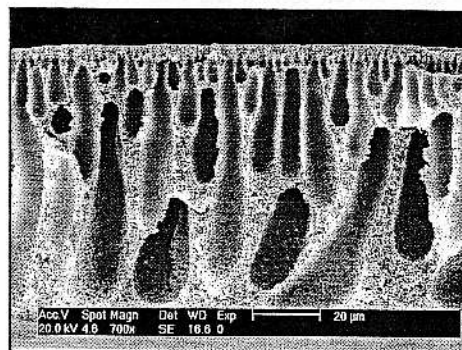


Figure 1: Structure of Nanofiltration Membrane using NMP as Solvent

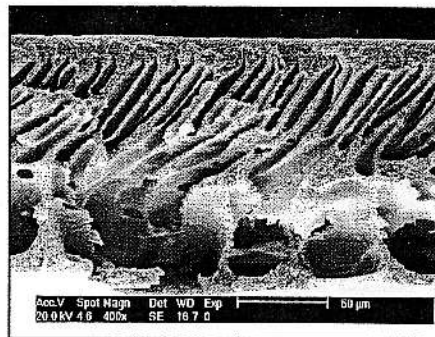


Figure 2: Structure of Nanofiltration Membrane using DMAc as Solvent.

Besides that, an asymmetric structure from top to bottom layer with homogeneous region can be clearly seen. This condition occurred due to the influence of the prepared dope viscosity. Since NMP dope had higher viscosity than the others, straight pore from top to bottom layer was formed. Viscosity of dope can also affect the size of pores at skin layer. This NMP dope produced membrane with small pores.

Figure 2 displays the morphological structure of DMAc membrane. It has a skin layer that determined the separation selectivity, spongy structure at top layer for diffusion, slanting finger-like structure and macrovoids at the bottom.

This membrane might perform well based on the existence of the finger-like structure but it was good not enough to be a high performance membrane. This is because it possessed good separation ability but did not have good pressure resistance. The macrovoids could cause the membrane to rupture or leaking if high pressure is applied in the separation process. Yang *et al.* had also made an effort in their study to eliminate as much voids as possible [14].

The slanting finger-like structure is produced due to the interaction between solvent and nonsolvent of the prepared dope. The more slanting type structure formed means the lower the interaction between solvent and nonsolvent of the membrane system before immersion in coagulant bath. This is because the evaporation rate of the solvent is higher than the permeation rate of nonsolvent into the membrane.

The skin and spongy structure at the top layer were formed because of the dry inversion process. The faster solvent evaporated, the denser the top layer of the membrane. This DMAc membrane sponge layer thickness was 25 μm , the finger-like layer thickness was 50 μm and the macrovoid layer took the thickness of 50 μm .

Thus, DMAC turned up to be quite an unsuitable solvent for the preparation of high performance asymmetric PES nanofiltration membrane.

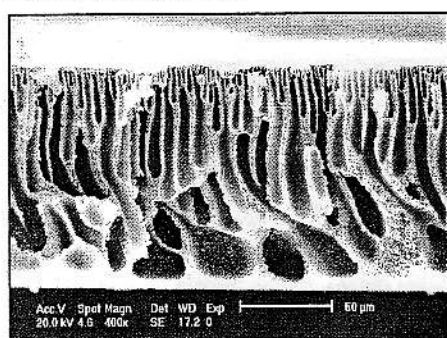


Figure 3: Structure of Nanofiltration Membrane using DMF as Solvent.

Figure 3 shows the cross sectional area of membrane using DMF. Like DMAc, this membrane might still perform well since it was only influenced by the selectivity of skin layer. On the other hand, the top layer structure was not as good as DMAc membrane.

From observation, the membrane structure consists of skin layer that determined separation selectivity, finger-like structure with slight slanting and no spongy structure at the top layer. As compared to DMAc and NMP, DMF has the lowest boiling point. So, the boiling point did influence the interaction between solvent and nonsolvent in the membrane system and hence the structure of the membrane.

A membrane with no sponge type structure has a very low-pressure resistance. Since the skin layer of this DMF membrane is thin with a thickness of approximately 1 μm , the spongy structure should exist to be a support to the skin layer. The selectivity of solute will not be affected unless the skin layer bleeds. This DMF membrane thickness was measured to be 50 μm for the finger-like layer and 50 μm for the macrovoid layer.

The membrane morphologies produced by those three different solvents proved that the interaction between solvent and nonsolvent is the major factor that influences the structure of the produced membrane.

Rejection and flux are two interrelated properties. If rejection increases, flux will decrease. The performance of each nanofiltration membrane was measured by testing it with various salts. From permeate concentration and time of permeation, the performance of rejection and flux can be calculated as in equation (1) and (3).

Effect of Solvent on the Performance of Membrane

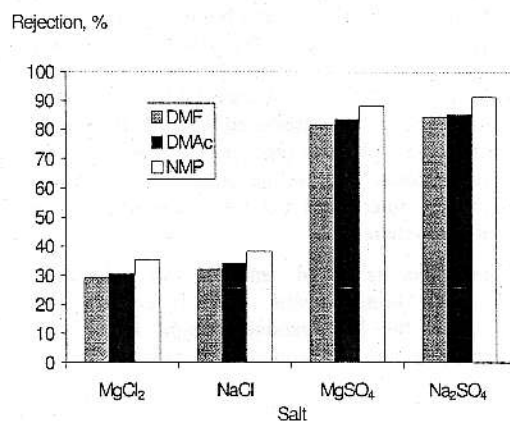


Figure 4: Effects of Different Type of Solvent Membrane on Salt Rejection

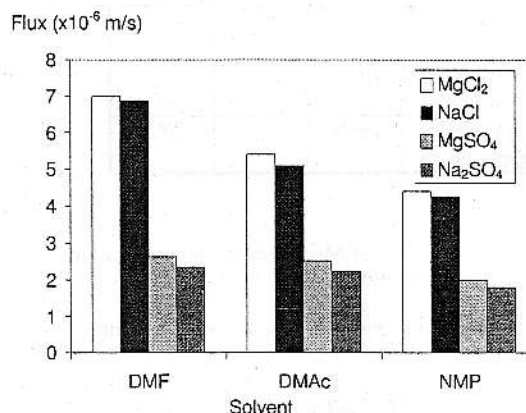


Figure 5: Effects of Different Type of Solvent Membrane on Flux

The separation performance of the three different NF membrane samples of NMP, DMAc and DMF were determined by type of salt solutions namely, MgCl₂, NaCl, MgSO₄ and Na₂SO₄. The results are given in Figure 4 and 5. From the graphs, the divalent (cation) salt MgCl₂ has lower rejection but higher flux as compared to NaCl, which is the monovalent (cation) salt. The same pattern was identified when the MgSO₄ and Na₂SO₄ were compared. These findings were almost identical as the results of the study conducted by Teixeira *et al.* [11].

On the other hand, in term of anion, the rejection of divalent anion containing SO_4^{2-} was higher while the flux was lower than the monovalent anion Cl^- . The rejections of the monovalent and divalent anions were identified to be within 29-38% and 81-91%, respectively. This behavior could be caused by several mechanisms such as the membrane pore size, electroviscous effect and the osmotic pressure gradient [11]. A detailed study on these mechanisms could explain the behavior of nanofiltration membrane better in the future.

As expected and discussed previously, NMP membrane shows the best salt rejection for all mono and divalent anion/cation compared to DMAc and DMF. As the rejection was high, the flux of NMP membrane shows the opposite. Although DMF membrane shows the highest flux values in Figure 5, the existence of macrovoid layer caused the membrane unable to resist any high pressure separation process.

Thus, NMP is still considered the best solvent for PES nanofiltration membrane because of it possessed high rejection, moderate flux and a favourable morphology that was able to resist any high pressure process.

Effect of Pore Size on the Performance of Membrane

Table 4: Data Of Rejection Flux And Pore Diameter For All Membranes Using NaCl As Solute.

Membrane	Rejection %	Flux(10^{-6}m/s)	dp(nm)
DMF	32.02	6.87	1.595
DMAc	34.21	5.09	1.473
NMP	38.27	4.26	1.285

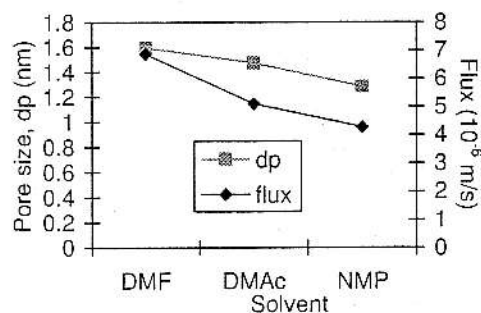


Figure 6: Relation Between d_p and Flux For Various Membranes (NaCl as Solute)

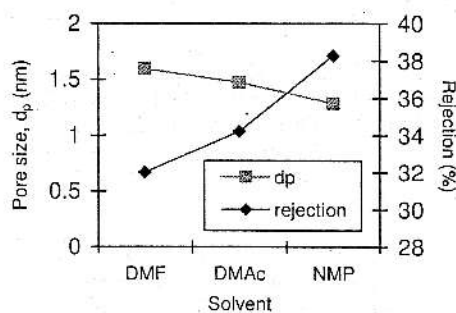


Figure 7: Relation Between d_p and Rejection For Various Membranes (NaCl as Solute)

As per discussed, the higher the viscosity of the dope, the smaller the pore size will be. This can be clearly seen in Figure 6 and 7 that shows the pore size of membrane is in turn of NMP possessed the smallest, followed by DMAc and DMF had the biggest pore size. We can also clearly see that as the pore size decreases the flux increases while the rejection increases. According to Wang and Chung the smaller the pore size, the higher selectivity can be achieved [13].

Conclusion

Interaction between solvent and nonsolvent was discovered to be the main parameter to determine the best membrane structure and thus, membrane performance. Good interaction between these two materials can provide the best rate of evaporation of solvent and equal to the best rate of permeation of nonsolvent [10]. The viscosity of dope influences the resulting pore size besides the concentration of additive polymer. The higher the viscosity of the dope and concentration of additive, the smaller pore size will be.

The membrane using NMP as solvent gave the best morphology compared to other membrane. The best structure with selective skin, sponge type at top layer, finger-like structure with asymmetric region provides good selectivity and membrane resistance [10]. DMAc and DMF had less favourable structure due to their physical properties.

Thus, when tested with monovalent and divalent salts, the NMP membrane with the smallest pore size was found to be the best solvent having the highest rejection and moderate flux followed by DMAc and DMF since boiling point took the major influence in shaping the membrane structure.

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