

상전환법에 의한 다양한 기공크기를 갖는 폴리비닐리덴플루오라이드 막의 제조와 수계 및 비수계 용액 내에서의 막 성능

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Formation of Poly(vinylidene difluoride) Membranes with Various Pore Sizes by a Phase Inversion Process and Membrane Performance of Aqueous and Non-aqueous Solution System

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요 약: 비대칭 폴리비닐리덴플루오라이드(PVDF) 막을 상전환법으로 제조하였다. 도포용액은 PVDF를 용매인 N-ethyl-2-pyrrolidone (NMP)와 비용매인 1,4-dioxane, diethyleneglycol dimethyl ether (DGDE), acetone, γ -butyrolactone (GBL)의 혼합용매에 녹여서 제조한다. 여러 첨가제가 도포용액 특성, 투과특성과 막 구조에 미치는 영향을 조사하였다. 용고제인 물과 1,4-dioxane, DGDE, acetone과의 상용성이 NMP보다 낮아서 기공크기가 작아진다. 첨가제의 양을 조절하여 기공크기를 변화시켰다. 혼합용매(수계 및 비수계)가 막의 투과성능에 미치는 영향을 살펴보았다. 용액점도뿐만 아니라 표면장력도 용매 투과특성에 영향을 끼침을 알 수 있었다.

Abstract: Asymmetric PVDF membranes were prepared by the phase inversion from casting solutions containing PVDF, NMP as solvent and 1,4-dioxane, DGDE, acetone, or GBL as additives by immersing them in water. The effects of various additives on the casting solution properties, permeation properties, and membrane structures were investigated. Low miscibility of 1,4-dioxane, DGDE and acetone with the coagulant (water) compared with NMP resulted in reducing the membrane pore size. When DGDE is used as an additive, the pore size was reduced because of its incipient sharp interface formation in the water. GBL increased membrane pore size because of its polarity compared to that of NMP. The PVDF membranes with various pore sizes could be obtained by controlling the amount of additive. The effect of mixed solvent (aqueous and non-aqueous solution) on permeation through membrane was investigated. Not only solution viscosity but surface tension affected solvent permeation.

Keywords: Poly(vinylidene difluoride), additive, miscibility, permeation property

1. Introduction

Hydrophobic porous membranes have been applied for oil/water separation[1-5], membrane absorption[6] and membrane distillation[7]. Hydrophobic porous membranes like polytetrafluoroethylene (PTFE) and poly-

propylene (PP) can be prepared by stretching and thermal method[8-10]. Despite of their excellent chemical stability and hydrophobicity, these membranes had a high membrane resistance due to their symmetric structure[8]. Moreover, it is not easy to fabricate PP and PTFE membranes with small pore sizes. Wang *et al.* showed that the mass transfer coefficient of porous asymmetric membranes is higher than that in the hy-

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drophobic PP hollow fiber membrane[8]. Among hydrophobic materials, poly(vinylidene difluoride) (PVDF) can be used to prepare asymmetric membranes using the Loeb-Sourirajan phase inversion method. A casting solution is precipitated in a coagulation bath. Among various methods to control the membrane pore size, the additive introduction in casting solution has been widely used. In order to prepare a membrane with better hydrophobicity, the membrane pore size should be decreased. According to the Laplace equation, the wetting pressure is inversely proportional to the membrane pore size.

The pore size and porosity of the membrane depend on the relative diffusion rate of solvent and nonsolvent. The diffusion rate can be controlled by changing the casting solution, casting conditions and coagulation bath compositions. The diffusion rate is defined as the ratio of non-solvent inflow to solvent outflow. If the solvent outflow velocity in the casting solution toward a coagulant is faster than the nonsolvent inflow velocity toward the casting solution, a membrane with smaller pore size and denser skin layer is formed[1,2,11-13]. We have reported on the effect of the additives like diethylene glycol dimethyl ether (DGDE), acetic acid and 1,4-dioxane on the asymmetric polyetherimide (PEI) membrane performance. According to these reports, those additives could decrease the PEI membrane pore size[14-16].

The relationship between membrane permeability and solvent properties (viscosity, surface tension and solubility parameter, etc) has been reported by some researchers[17-19]. However, there are fewer reports on the use of ultrafiltration (UF) membranes with non-aqueous organic solutions. Lenki and Williams[17] investigated relative resistance of UF membranes in terms of solubility parameter between membrane and solvents (aqueous solvent solution) of different molecular weight cut-off (MWCO). They reported that anisotropic membranes appear to be constricted by membrane swelling, leading to an increase in membrane resistance, but, isotropic membranes are expanded by solvents, decreasing membrane resistance. Shukla and Cheryan[18] studied several membranes (asymmetric and composite membranes) with ethanol-water mixtures.

The method of conditioning the membrane had a major effect on solvent flux, membrane integrity and their pressure ratings. Machado *et al.*[19] observed that surface tension and viscosity of the solvents mainly affected the flux of either pure or mixed solvents with silicone-based nanofiltration membranes.

In this study, asymmetric PVDF membranes with different MWCO were prepared by using additives such as 1,4-dioxane, DGDE, acetone, or GBL in the casting solution. The effect of additives on membrane performance was also investigated. The flux of solvent mixtures (aqueous and non-aqueous solvent mixtures) was observed.

2. Experimental

2.1. Materials

PVDF (Kynar grade 760, Elf Autochem) having an average molecular weight of 440,000 was used as a membrane material. NMP (Aldrich) was used as solvent. 1,4-dioxane, DGDE, acetone and GBL were kindly supplied from Aldrich and used as additives. Deionized (DI) water was used as a coagulation media. All the chemicals were used without further purification.

2.2. Membrane Preparation

15 wt% of PVDF was dissolved at 60°C with stirring in various solvent mixtures. The weight ratio of NMP and additive (NMP/additive) was changed to 85/0, 57/28, 50/35 and 42.5/42.5. The casting solution was kept at room temperature for at least 24 hr in order to remove air bubbles. The casting solution was cast on a polyester non-woven fabric with a doctor knife having 200 μm thickness. The nascent membrane was immersed in DI water without evaporation of solvents in the air. After the immersion, remained solvent mixtures were completely removed by keeping them in DI water for at least 24 hr.

2.3. Viscosity Measurements of Casting Solution and Feed Solution

Viscosity was measured by the Brookfield viscometer

Table 1. Compositions and Viscosities of the Different Polymer Solutions

Code	Composition (wt%) ^a	Viscosity (cP)	Code	Composition (wt%) ^a	Viscosity (cP)
	NMP/GBL			NMP/1,4-dioxane	
PVDF	85/0	1200			
	57/28	1320		57/28	1140
	42.5/42.5	1440		42.5/42.5	1120
	28/57	- ^b		28/57	1000
	NMP/DGDE			NMP/acetone	
	57/28	1000	PVDF-1	57/28	1270
	42.5/42.5	630	PVDF-2	42.5/42.5	1700
	28/57	- ^b		28/57	2120

^aPolymer concentration, 15 wt%; ^bAt this composition polymer solution could not be prepared.

(DV-II+, Brookfield, USA) at 30°C to investigate the state of each polymer solutions. 100 rpm speed of cone spindle was used. Viscosity of solvent mixtures was not found in literature except for aqueous ethanol solution. Therefore, viscosity of tested solvent mixtures were measured with a Ubbelohde viscometer at 30°C, calculated from:

$$\eta / \eta^* = t \cdot \rho / t^* \cdot \rho^*$$

Where η is the calculated viscosity (cP), η^* is the obtained viscosity of pure solvent from handbook (cP), t is the dropping time in the capillary of the viscometer, t^* is the dropping time of the pure solvent, ρ is the density of the solvent mixture and ρ^* is the density of the pure solvent.

2.4. Membrane Performance Measurement

The pure water flux and solvent fluxes were measured under pressure of 50 psi (3.5 kg/cm²), flow rate of 0.5 L/min and 25°C after compaction of membrane at 100 psi (7.0 kg/cm²) for 1hr using cross-flow system. The used solvents were methanol (MeOH), ethanol (EtOH), isopropanol (IPA), diethyl ether, methyl tertiary butyl ether (MTBE), ethyl acetate, acetonitrile and hexane. Solvents like MeOH, EtOH, IPA and acetonitrile were mixed with water. Solvents such as IPA, diethyl ether, MTBE and ethyl acetate were mixed with hexane. The relative flux is given by the ratio of the mixed solvent

flux to the water flux or hexane flux. The solute rejection rate was measured with poly(ethylene glycol) (PEG) 12000 and 35000, polyvinylpyrrolidone (PVP) 40000 and dextran 87000 at different pressure. The feed concentration was 1000 ppm in DI water. Permeate and feed concentrations were measured by HPLC (Waters Co.) equipped with a refractometer.

2.5. Morphology of Asymmetric Membranes

Membrane morphology (cross section and top layer) was observed with a scanning electron microscope (SEM, JSM 1025, JEOL). The membrane was cryogenically fractured in liquid nitrogen and then coated with gold.

3. Results and Discussion

3.1. Polymer Solution Properties

Table 1 shows the effect of various additives on the polymersolution viscosity using 1,4-dioxane, DGDE, acetone and GBL. The viscosity of the casting solution was found to be lower than that of the casting solution without additive if 1,4-dioxane and DGDE, which are cosolvents for the polymer, were used as additives. In contrast, in cases of GBL and acetone, which are swelling agents for the polymer, the viscosity of the casting solution was observed to be higher than that of the casting solution without additive. Generally, in concentrated polymer solutions, viscosity is lower in

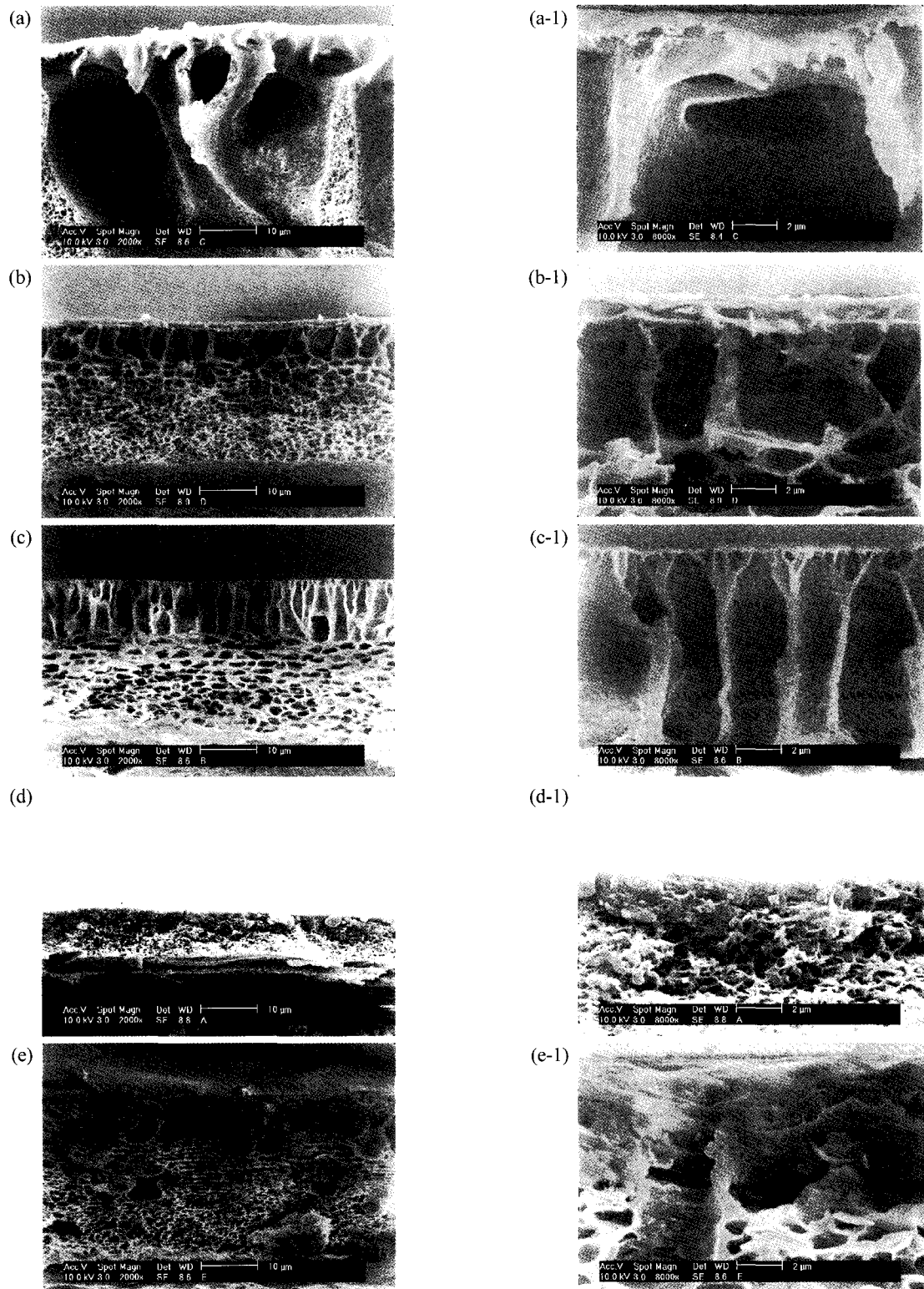


Fig. 1. SEM photographs of the cross-section of PVDF membranes (PVDF/NMP/additive (15/42.5/42.5 wt%): (a) without additive, overall; (a-1) without additive, upper part; (b) 1,4-dioxane, overall; (b-1) 1,4-dioxane, upper part; (c) DGDE, overall; (c-1) DGDE, upper part; (d) acetone, overall; (d-1) acetone, upper part; (e) GBL, overall; (e-1) GBL, upper part.

good solvents than in poor solvents, which means that the interaction between polymer and solvent becomes better than that between polymer molecules. In the polymer solution system including poor solvents, the polymers form a network structure. The network structure prevents the flow of the polymer molecule. In other words, polymer molecules disturb each other. However, in diluted polymer solution systems, the viscosity is higher in good solvents than in poor solvents. This is due to stretched linear shape formation of each polymer molecules. And polymer molecules are unperturbed each other.

The membrane morphology can be characterized from SEM photograph of Fig. 1. The SEM photographs can supply more detailed information on the structure of the membrane through the membrane cross-section and the magnified views of the upper parts. By using NMP as solvent, very large fingers (cavities) and a very thin top layer are seen toward the bottom of the membrane without a well-defined shape (Fig. 1 (a) and (a-1)). By adding various additives in the polymer solution, it is obvious that the membrane had smaller cavities than that of NMP. In the case of NMP/1,4-dioxane and NMP/DGDE solvent system (Fig. 1 (b), (b-1), (c) and (c-1)) the upper part layer of the cross-section exhibits a large number of short fingers, while the uniform and comparatively small globular cells separated by walls appear in the bottom layer. The magnified view gives an information that the more compact top layer is formed by adding 1,4-dioxane or DGDE in the polymer solution. In other words, both finger and sponge-like structure were formed. The length of the top layer of the two membranes is similar to that of NMP. The membranes prepared from 1,4-dioxane and DGDE additives are consisted of denser skin layers than that without additive. This result shows that by using cosolvent the membrane structure can be made more compressed. Oppositely, by using nonsolvent or swelling agents like GBL and acetone in the polymer solution, the membrane can be made more porous. In case of GBL, although fingers could not be seen in the cross-section of the membrane, the sponge structures

are looser than those by use of cosolvents. Moreover, the shape of the skin layer is not well defined. The membrane prepared from the polymer solution using GBL shows a mixed structure composed of small fingers and cells (Fig. 1 (e) and (e-1)). However, in case of acetone, although acetone is a swelling agent for PVDF, the size of the cross-section was largely compressed. Fig. 1 (d) and (d-1) are the SEM photographs of the membrane prepared from a polymer solution involved NMP/acetone as solvent system. The membrane exhibits a honeycomb-like structure without any fingers and cavities. The top layer shows the most compacted structure among other systems, and the skin layer was relatively dense. The size of the sponge was very small. This results from the volatility of acetone. Although the nascent membrane was immediately immersed in the coagulation bath, during casting and moving toward the coagulation bath, the acetone can be easily evaporated. By evaporation of acetone, the surface concentration of the polymer solution can be higher. The higher surface concentration of the nascent membrane can prevent the nonsolvent inflow into polymer solution. In other words, the exchange rate of polymer solution and coagulant can be lower. More important information from the photographs is that by using acetone, DGDE and 1,4-dioxane, a more certain separated top layer than NMP and GBL can be obtained. Once again, by introduction of the additives, the finger-like structure was changed to a sponge-like structure. However, the additives did not have the same appearance. In other words, although the cross-section is similar to sponge-like structure, the shape of top layer is very different.

3.2. Membrane Performance

Fig. 2 shows the rejection rate differences of various polymeric molecules at different operating pressure. Even though molecular weight of PVP is smaller than that of dextran, the rejection rate is much greater. This may be due to the differences in Stokes-Einstein radius of PVP 40000 and dextran 87000.

The average hydrodynamic radius R_h can be calculated

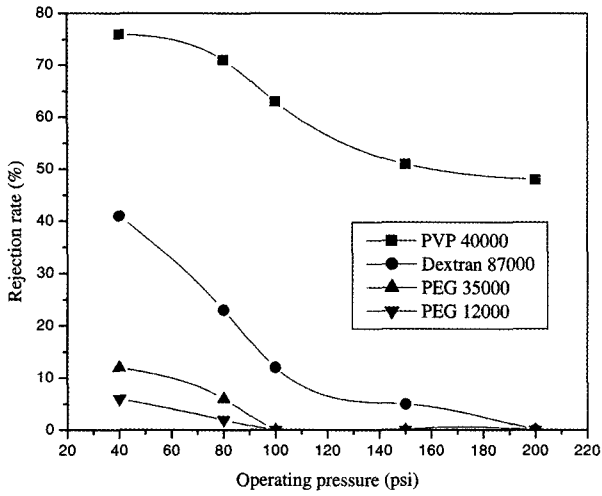


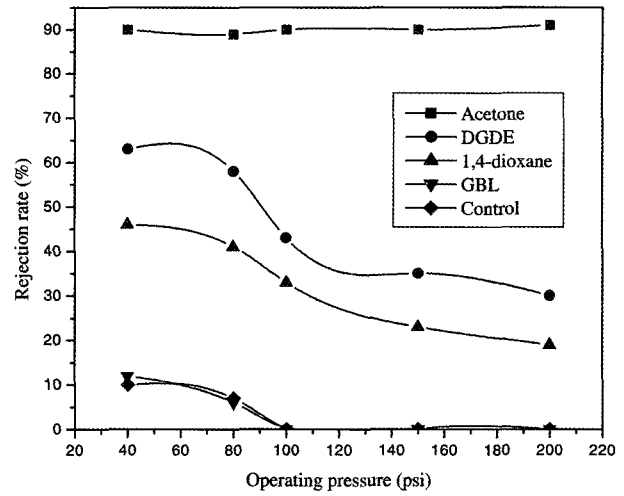
Fig. 2. Effect of various solutes on membrane performance. Membrane: PVDF/NMP (15/85).

by using the Stokes-Einstein relation, as follows:

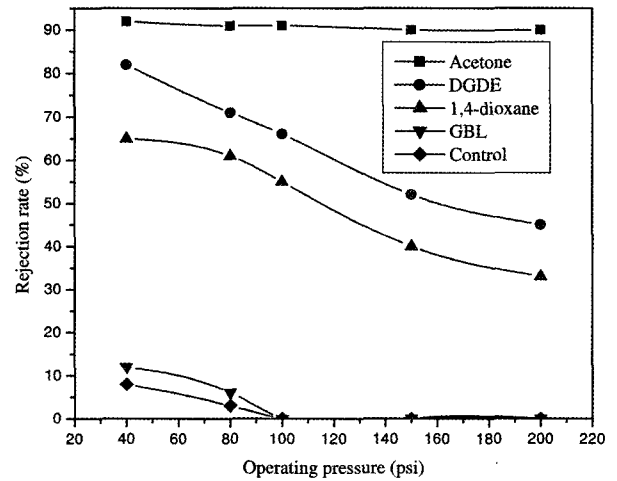
$$R_h = k_B T / 6 \pi \eta D$$

where k_B , T , η are the Boltzmann constant, the temperature in Kelvin, and the solvent viscosity in poise, respectively.

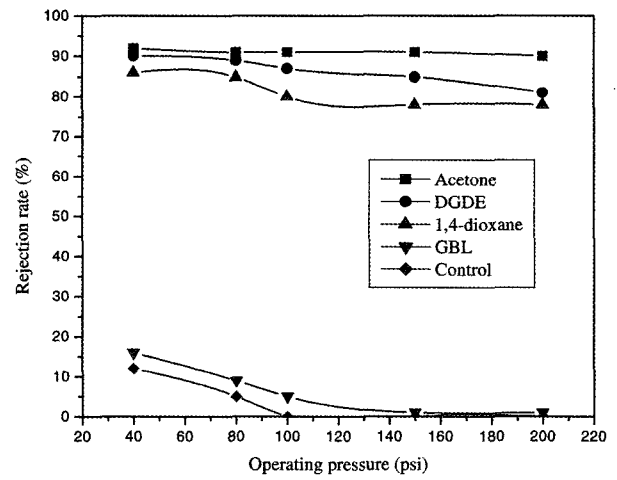
The drop in solute rejection rate at higher pressure is typical for porous membranes. This is due to the increase of solute concentration at the concentration polarization layer. The build-up of solute on the membrane surface results in faster solute transfer rate through the membrane at higher pressure compared to that of lower pressure. We chose PEG 35000 as a feed solute to investigate the pore size change with and without different additives and composition. Fig. 3 shows the rejection rate behavior with and without different additives and with the increase in the amount of additives in the casting solution. It can be observed that the rejection rate increases by using additives except GBL in the casting solution. In addition, the rejection rate of PVDF membranes increases with increasing the amounts of the additives (1,4-dioxane, DGDE and acetone) in the casting solution. Among several additives, acetone as an additive gave the PVDF membrane a much higher rejection rate. These results were consistent with observations of SEM,



(a)



(b)



(c)

Fig. 3. Effect of an amount of additives on membrane performance: (a) NMP/additive (57/28); (b) NMP/additive (50/35); (c) NMP/additive (42.5/42.5).

Table 2. Solubility Parameters of Various Compounds

Compound		Solubility parameter		
		δ_d (MPa ^{0.5})	δ_p (MPa ^{0.5})	δ_H (MPa ^{0.5})
Solvent	NMP	18	12.3	7.2
Coagulant	water	15.5	16	42.4
Additive	1,4-dioxane	19	1.8	7.4
	acetone	15.5	10.4	7
	GBL	19	16.6	7.4
	DGDE	15.8	6.1	9.2

suggesting that the 1,4-dioxane, DGDE, and acetone additives played a role of pore reducer in the skin layer to increase the rejection rate of PVDF membranes. In other words, among various additives, 1,4-dioxane, DGDE, and acetone can decrease the pore size. However, GBL cannot affect the pore size. This is due to the different miscibility of the additives. The miscibility of 1,4-dioxane and DGDE with water is poor compared to that of NMP as shown in Table 2. Table 2 shows the comparison of each solubility parameters (dispersion (d), polar (p) and hydrogen bond solubility parameter (H)). As can be shown, the dispersion solubility parameter is similar for each compound. And hydrogen bond solubility parameter of water is too large to compare with NMP and other various additives. Therefore, we compared the polar solubility parameter. If the polar solubility parameter of an additive is larger than that of NMP, the additive is more miscible with water than NMP. This means that an additive showing a smaller polar solubility parameter value as NMP can be slightly miscible with water compared to NMP. As can be seen in Table 2, the polar solubility parameter values of 1,4-dioxane, acetone and DGDE are smaller than that of NMP. This fact implies that when the casting solution containing 1,4-dioxane, acetone and DGDE is coagulated in water, the inflow rate of coagulant becomes slower compared to that of NMP alone. In view of the polar solubility parameter, the rejection rate of PVDF membrane prepared from 1,4-dioxane additive should be the highest. However, the membranes prepared from acetone

and DGDE additives have the smaller pore size. Therefore, other views should be investigated. In addition to this polar solubility parameter effect, DGDE can form a sharp interface with water. This is attributed to slower exchange rate of a polar solvent in the coagulation bath than inflow rate of water. This suggests that DGDE should inhibit water from entering into the polymer solution. In addition, even though the polar solubility parameter value of acetone is larger than that of 1,4-dioxane, the rejection rate is much greater. This is due to its relatively lower boiling point. This results in a rapid loss of acetone at the nascent membrane surface layer during the very short time interval prior to coagulation.

However, in case of GBL, the polar solubility parameter value is much larger than NMP. This implies that the entering rate of water in the casting solution is faster than NMP alone. Therefore, by using GBL as an additive, a more porous membrane could be formed. When 1,4-dioxane, DGDE and acetone were used as additives, the top layer showed very packed and dense shape due to their lower miscibility with water compared to NMP alone. Moreover, the sponge cells were closed. However, using GBL as an additive renders the top layer more porous. The size of the sponge became bigger and opened due to its higher miscibility with water compared to NMP alone.

3.3. Flux of Solvent Mixtures

Changes in viscosity, surface tension and density with aqueous EtOH concentration (wt%) are shown in

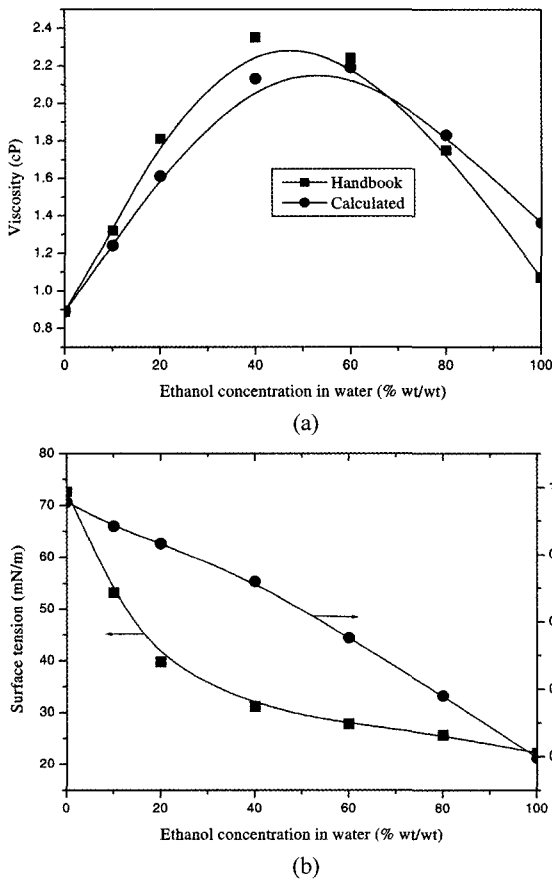


Fig. 4. Changes in physical properties of aqueous ethanol solution: (a) viscosity; (b) surface tension and density.

Fig. 4. The viscosity comparison of data from handbook and measurement shows that the viscosity gained from the measurement with the Ubbelohde viscometer is almost similar to the one from the handbook. From this method, the viscosity of solvents (not mixed solvents) was matched well with values of the handbook. The viscosity of the EtOH solution exhibits a maximum around 50 wt%. On the other hand, surface tension decreases exponentially with increasing EtOH concentration. The density of EtOH solution decreases linearly with EtOH concentration.

The effect of EtOH on the relative flux through PVDF membranes with different pore size is shown in Fig. 5. One can see that the relative flux is strongly affected by viscosity of EtOH solution. Lenki *et al.*[17] investigated the effect of EtOH on the flux through cellulose acetate (CA) and polysulfone (PSf) membranes.

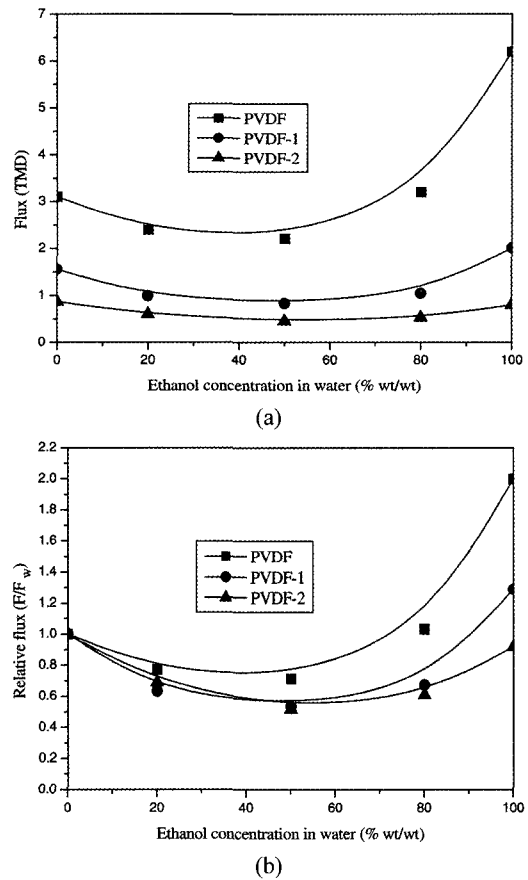
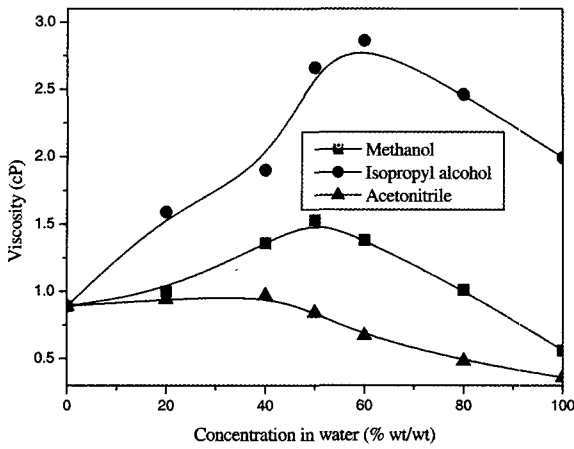


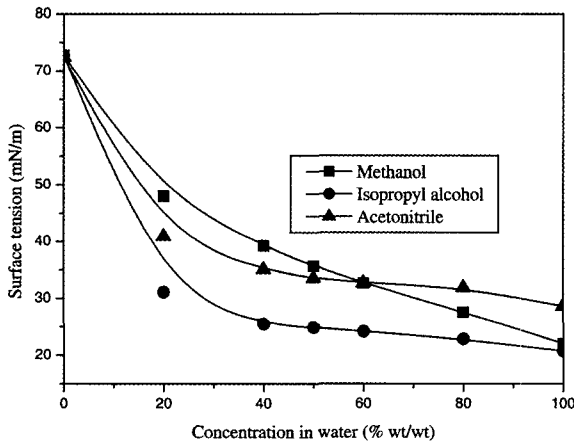
Fig. 5. Effect of aqueous ethanol solution on membrane performance: (a) flux; (b) relative flux.

They showed apparently different patterns because of the different surface property of membranes. As the pore size increases, the resistance to EtOH flow decreased. However, for PVDF membranes, the resistance to EtOH flow increased with increasing the pore size. This is due to the larger hydrophobicity of PVDF membrane than that of CA and PSf membrane.

Non-linear change of EtOH solution flux with EtOH concentration cannot be explained by the viscosity and surface tension variation. In other words, with viscosity and surface tension, the EtOH solution flux cannot be correlated. Moreover, with increasing the pore size, the variation of the relative flux was increased. This fact reveals that relations between pore size and solution properties are present. Because of the hydrophobicity of PVDF membranes, the wetting pressure of water increases with decreasing the pore size. The effect of a



(a)

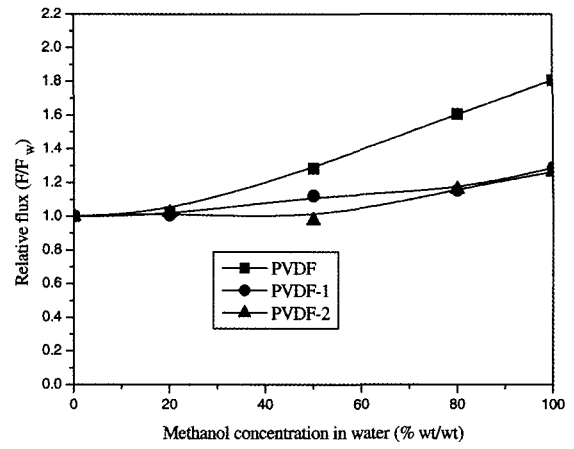


(b)

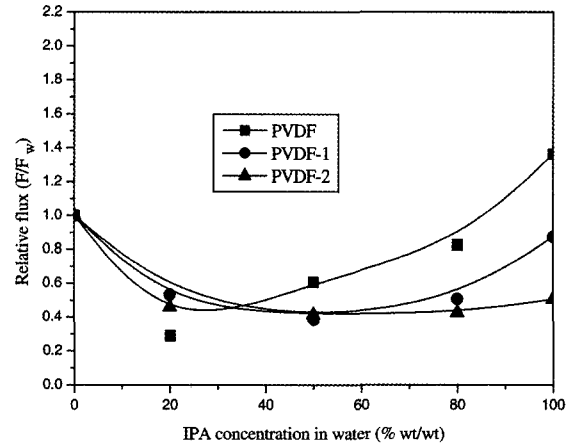
Fig. 6. Changes in physical properties of aqueous methanol, isopropyl alcohol, and acetonitrile solution: (a) viscosity; (b) surface tension.

membrane with larger pore size on solution properties (viscosity and surface tension) will be lower than that of one with a smaller pore size due to its larger permeation capability through pores. Compared to the PVDF membrane, CA and PSf membranes are less hydrophobic. In other words, the wetting pressure by water of CA and PSf membrane is lower than PVDF membrane.

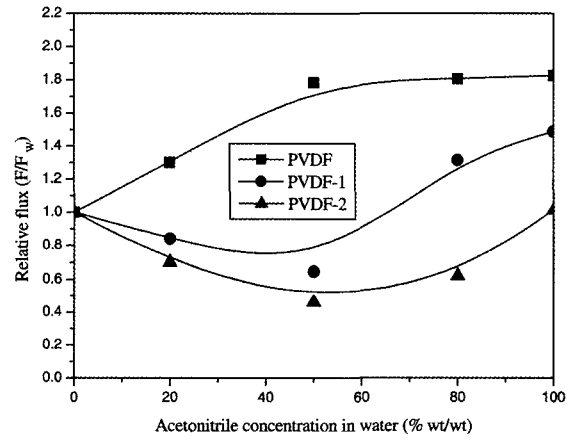
Other aqueous solvents of MeOH, IPA and acetonitrile were also investigated. The variation of viscosity is larger in the following order: IPA > EtOH > MeOH > acetonitrile (Fig. 6 (a)). The surface tension of alcohol series is decreasing with increasing the number of carbon atoms and decreasing the water content although three



(a)



(b)



(c)

Fig. 7. Effect of aqueous organic solution on relative flux: (a) methanol solution; (b) isopropyl alcohol solution; (c) acetonitrile solution.

pure alcohols showed similar values (Fig. 6 (b)). Fig. 7 shows the effect of aqueous solvent mixtures (MeOH,

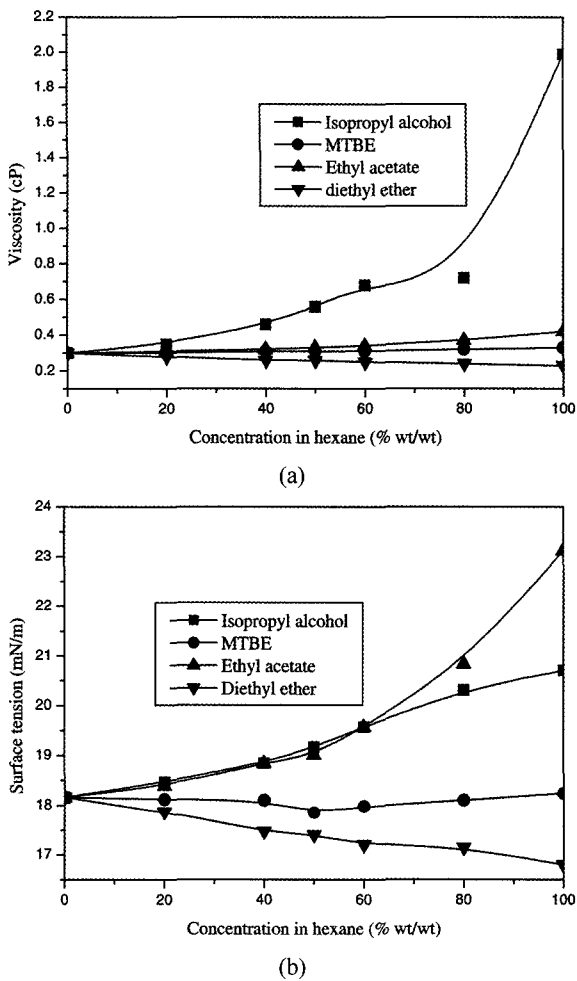


Fig. 8. Changes in physical properties of isopropyl alcohol, MTBE, ethyl acetate, and diethyl ether solution in hexane: (a) viscosity; (b) surface tension.

IPA and acetonitrile) on the relative flux through PVDF membranes with different pore size. The viscosity of alcohols peaked at approximately 50% alcohol, which means that the flux at this composition should be the lowest according to Darcy's law. However, although in case of EtOH solution, at the composition of around 50% EtOH, the flux was almost the lowest, for cases of MeOH and IPA different phenomena were discovered. In case of PVDF (the largest pore size), with increasing MeOH concentration of the solution the relative flux was almost linearly increased. However, the relative flux through membranes with smaller pore size (PVDF-1 and PVDF-2) was not changed. When aqueous IPA solution was

applied, with decreasing the pore size the minimum peak was moved towards pure IPA. The effect of acetonitrile on relative flux through PVDF membranes with different pore size apparently shows that surface tension can affect the flux. The viscosity was not changed until the acetonitrile concentration has reached 40%. However, exponential decrease of surface tension was observed. The relative flux through a PVDF membrane with the largest pore size was increased due to the decrease of surface tension. Moreover, with decreasing the pore size, a broad peak around 50% of acetonitrile concentration was observed.

In addition to aqueous solutions, the effect of non-aqueous binary mixtures based on hexane on the relative flux through PVDF membranes (flux of mixture (F)/flux of pure hexane (F_h)) was also investigated. Due to the largest hydrophobicity, low viscosity and surface tension of hexane, hexane flux was the highest. Changes in viscosity and surface tension with solvent concentration in hexane are shown in Fig. 8. The viscosity of binary mixtures (MTBE, diethyl ether and ethyl acetate in hexane) was almost unchanged. However, if adding IPA in hexane, the viscosity increased exponentially to a concentration of around 50%. The surface tension of MTBE and diethyl ether solution is decreasing with increasing solvent content in hexane. However, in cases of IPA and ethyl acetate, the surface tension is increasing. Fig. 9 shows the relative flux of IPA, MTBE, ethyl acetate and diethyl ether with increasing solvent concentration. In case of IPA, the relative flux is linearly decreasing although the increase of viscosity was exponential like (Fig. 8 (a)). However, surface tension is linearly increasing with concentration of IPA (Fig. 8 (b)). This fact reveals that surface tension is related to the flux through PVDF membranes. In almost all the cases, the relative flux through the membrane with larger pore was higher than that of membrane with smaller pore. In general, the resistance to solvent flow through a membrane with large pores is lower than that of membrane with small pores. Therefore, the relative flux will be higher. However, if interaction between membrane and solvent

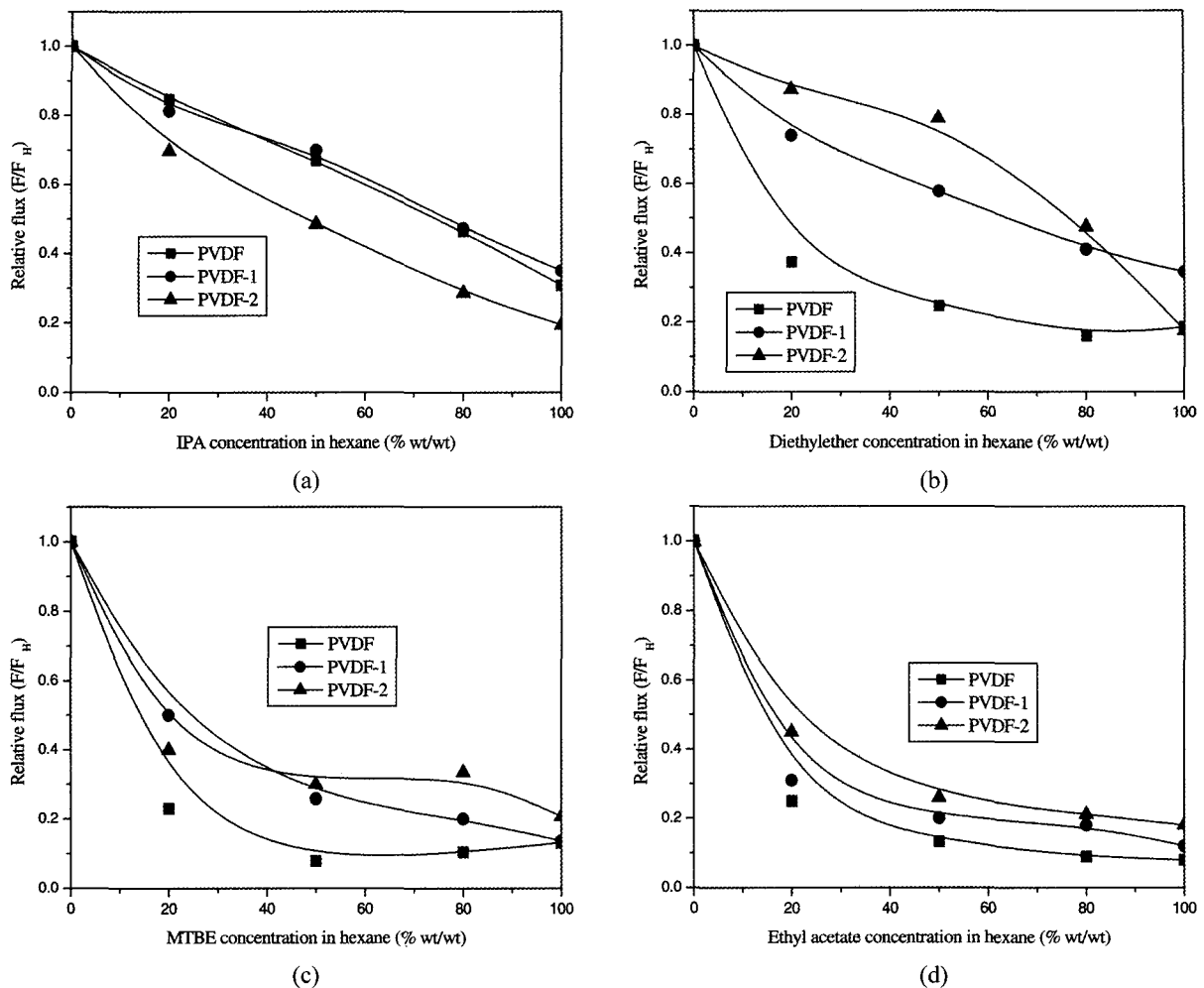


Fig. 9. Effect of isopropyl alcohol, MTBE, ethyl acetate, and diethyl ether solution in hexane on relative flux: (a) isopropyl alcohol solution; (b) diethyl ether solution; (c) MTBE solution; (d) ethyl acetate solution.

is present, the pore can be expanded or constricted by solvents. In cases of MTBE, ethyl acetate and diethyl ether, the relative flux through a membrane with larger pore was lower than that of membrane with smaller pore, which means that MTBE, ethyl acetate and diethyl ether can constrict the pore of PVDF membranes. Moreover, the membrane with smaller pore can resist being constricted. In other words, in case of the membrane with larger pore size (PVDF), solvents (MTBE, ethyl acetate and diethyl ether) can swell the matrix of the membrane (not the pore). In contrast, in case of the membrane with smaller pore size (PVDF-1 and PVDF-2), solvents can expand the pores of the membrane (not the matrix).

4. Conclusions

Asymmetric PVDF membranes could be prepared by the phase inversion method from casting solution containing PVDF, NMP and various additives (1,4-dioxane, DGDE, acetone and GBL). From viscosity measurement, it revealed that 1,4-dioxane and DGDE work as cosolvent for PVDF. And GBL and acetone work as swelling agents. A sponge structure of the membranes cross-sections is caused by additives. However, by using 1,4-dioxane, DGDE and acetone, the top layer showed a very packed and closed sponge structure in contrast to the porous and open sponge structure if using GBL. The pore size of the membrane

prepared from casting solution composed of 1,4-dioxane, DGDE and acetone was decreased. However, when using GBL, the pore size did not decrease. The relative flux was obtained with various aqueous and non-aqueous solvent mixtures. Both viscosity and surface tension can affect the solvent mixture flow. Especially, solvents like MTBE, ethyl acetate and diethyl ether can swell the matrix of a membrane with large pores and expand the pore of a membrane with small pores.

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