고분자 분리막에 관한 연구:
2. 사성분계로 제조된 셀룰로오스 아세테이트 막의 특성

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Studies on the Polymeric Membrane for Separation:
2. The Characteristics of Cellulose Acetate Membranes Prepared from Quarternary Casting System

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요 약 : CA-acetone-DMF-pore 형성제의 사성분계 제막용액으로 부터 평판형 막을 제조하였다. 막 제조과정에서 pore 형성제의 도입, acetone-DMF 용매계의 조성비 변화, 용매증발시간 등 몇가지 막제조변수들의 영향이 검토되었다. pore 형성제를 도입하여 제조된 막은 대체로 물질투과성능 (pure water flux)이 증진되었다. 용매계에서 acetone 함량은 막의 상부 표면층의 형성과 그에 따른 적정 성능을 갖는 막 제조 설계에 중요하게 작용하였다. 막의 구조는 용매계에서 acetone : DMF 조성비에 따라 크게 변하였다. 주어진 용매증발시간의 범위 내에서 pure water flux는 초기에는 감 소하다가 증발시간이 길어짐에 따라 증가한 반면, 용질배제성능은 이와 반대의 결과로 나타났다.

Abstract : Flat-sheet cellulose acetate(CA) membranes were prepared from CA-acetone-DMF-pore forming agents quarternary system by the combined evaporation-diffusion technique. Studies about the effects of the membrane preparation parameters such as the addition of pore forming agent(for-mamide or $LiNO_3$), the composition ratio of acetone-DMF solvent system, and the solvent evaporation period were carried out on the membrane performance and structure. A membrane prepared with a pore forming agent exhibited a higher pure water flux than that without it. Acetone content in sol-vent system affected significantly the top surface skin formation and subsequently the membrane establishment with optimum performance. Membrane structure appeared diversely depending on the acetone-DMF composition ratio. Over the range of solvent evaporation periods investigated, pure water flux was initially decreased and then increased afterwards with the increasing period. On the other hand, solute rejection results showed opposite trends.

INTRODUCTION

Since the discovery of cellulose acetate(CA) membranes having the high permselectivity by Breton and Reid,[1] the development of asymmetric porous membranes by Loeb and Sourirajan[2] was a significant step contributed to the enhancement of membrane performance. These asymmetric membranes consist of an extremely thin selective layer (0.1~0.5 μm) supported by a porous substructure (50~100 μm).[3]

The majority of the commercially available membranes are of this type of asymmetric skinned structure, and this structure can be easily obtained by the so-called phase inversion process, precisely by the combined evaporation-diffusion technique.[4] This process is by the following procedure : After casting or spinning a polymer solution, the resulting nascent film or fiber is allowed to contact air for a short time to partially evaporate the solvent followed by immersion in a coagulating agent.

Many investigations have been concentrated to elucidate the formation mechanism of the asymmetric structure of membrane prepared by this technique. As usual, the combined evaporation-diffusion technique makes use of liquid-liquid and/or solid-liquid phase separation and gelation phenomena, involving both thermodynamics and kinetics of demixing processes, and the exchange of solvent and nonsolvent during coagulation of the polymer.

Basically, in this process, a liquid homogeneous one phase polymer solution is transformed into a heterogeneous two phase system : a solidified polymer-rich and solvent-lean phase, which forms the membrane matrix, and a solvent-rich phase, which fills the pore volume.[5]

For the sake of the variety of membrane morphology, a few controllable process variables (preparation parameter) can be introduced. Frommer and Lancet[6] revealed the fact that for the same polymer different kinds of morphologies in the asymmetric membrane can be obtained by varying the membrane preparation condition including

process variables.

In the present paper, we will report on experiments done in our laboratory to obtain more information about the effects of various controllable process variables introduced during the preparation of CA membrane by the combined evaporation-diffusion process. Composition ratio of two-component solvent system and solvent evaporation period were introduced as the internal and external process variables, respectively. In our previous paper,[7] we reported the effects of process variables during the membrane preparation from cellulose acetate-cellulose nitrate blended polymer system and acetone-formic acid mixed solvent system.

Differently from the solvent system in the previous paper, especially in this study, acetone-N,N-dimethylformamide(DMF) mixed solvent system was used. Also, two types of aqueous pore forming agents were added in membrane solutions, respectively, and their effects on the membrane structure and performance were investigated ; the one was $LiNO_3$ as a salt-type pore forming agent, and the other was formamide as a solvent-type agent.

The object of this study, therefore, is to partially establish the fabrication guideline of CA membrane with optimum performance for ultra- or microfiltration application through the investigation of the effects of solution composition and solvent evaporation condition on membrane morphology and functional characteristics.

EXPERIMENTAL

Materials

Commercially available polymer, cellulose acetate (CA, DP180~185, acetyl content 38.9%, SKI) was purified by reprecipitation method and then used as a membrane material. Solvent system was of two components with consideration of their solvation behavior for CA and volatility difference ; acetone (bp 56.1℃, vaporizing pressure 400mmHg at 38.48℃) and N,N-dimethylformamide (DMF, bp 153℃, vaporizing pressure 3.7mmHg at 25℃). $LiNO_3$ and formamide were used as membrane

pore forming agents separately. These solvents and pore forming agents were of analytical grade.

Membrane Preparation

Membrane preparation conditions were similar to those of our previous report.[7] Flat-sheet membranes were made by machine-casting with a constant thickness of 250 µm. The temperature and relative humidity (RH) of the casting atmosphere were controlled at 30℃ and 65±5%, respectively. The cast films were exposed to air prior to immersion for various predetermined solvent evaporation periods, and then immersed into coagulating agent of distilled water kept at 4℃ for 2 hours. The film was subsequently stored in distilled water at room temperature for 24 hours.

Estimation of Membrane Performance

Estimation of membrane performance was done by the experiment in a stirred batch cell on pure water flux (membrane permeability) and solute rejection at an applied pressure of 3 atm. Testing materials for water flux and solute rejection were distilled pure water and 1000ppm aqueous solutions of various water soluble polymers, respectively. These aqueous solutions were of poly(ethylene glycol) (PEG $\overline{M}_w$ 20,000), or dextran ($\overline{M}_w$ 124,000), or poly(vinylpyrrolidone) (PVP $\overline{M}_w$ 360, 000). Pure water flux data were given in liter per square meter and hour. The solute rejection of membrane was expressed in per cent of the bulk solution concentration.

Scanning Electron Microscopy

The membrane structure was investigated by using AKASHI-DS-130 scanning electron microscope(SEM). The preparation method of SEM specimen was the same as that of our previous paper.[7]

RESULTS AND DISCUSSION

The Effects of Membrane Solution Composition

Quantitative results for cellulose acetate (CA) membranes prepared with $LiNO_3$ are listed in Table 1. Polymer concentration was adjusted to 12 wt% in all membrane solutions. 12 wt% was pro-

Table 1. The Effect of $LiNO_3$ as a Pore Forming Agent in Membrane Solution on CA Membrane Performance

Membrane Code	Polymer Concentration (wt%)	$LiNO_3$ Content (wt%/ CA wt)	Pure Water Flux (1/m² hr)
CA(0)-44,44-1	12	0	6.3
CA(10)-44,44-1	12	10	37.9
CA(25)-44,44-1	12	25	41.0

Code description : CA($LiNO_3$ content)-acetone : DMF vol. ratio-solvent evaporation period
total volume of solvent system : 88ml
acetone : DMF vol. ratio : 44 : 44 vol(ml)
$LiNO_3$ content : wt% against CA weight
solvent evaporation period : 1 min

ved to be suitable for flat-type CA membrane with ultrafiltration level from our previous report.[7] Pure water flux is larger in membrane prepared with $LiNO_3$ than in that without it.

$LiNO_3$ in membrane solution is believed to act as a swelling agent, and therefore to increase membrane porosity. During immersion in water, water molecules will aggregate about lithium ions. This complexing may weaken the coagulating power of water. That is, the role of water will be changed from that of a nonsolvent coagulating agent to that of a swelling agent. Thus, gelation of cast film will be retarded, and the porosity of final membrane will be increased. This opinion about salt effect in membrane solution has been sufficiently proved in many investigators.[8,9]

Formamide, solvent-type pore forming agent, was contributed to enhance the pure water flux (see Table 3). In general, the greater is the affinity among polymer, solvent, and coagulating agent, the more gradual will be 'sol 2-gel' phase transition step, proposed by Kesting,[10] in which final membrane structure is almost decided.

Thus, immediate dense aggregation of polymer molecules can be excluded. Therefore, the resulting membrane becomes more porous.

Formamide has excellent hydrogen bonding

capability with coagulating water and exhibits strong affinity for CA.[11] On immersion in water, the strong coagulating behavior of water will become meager and phase transition process will be retarded because of the existence of formamide in membrane solution. Consequently the porosity

and corresponding permeability of final membrane will be increased.

Table 2 and Table 3 show the effect of the composition of two-component mixed solvent system with consideration of their volatility difference on membrane performance. A higher DMF volume fraction produces a larger pure water flux. Especially, as listed in Table 3, CA membranes prepared with formamide have not only excellent water fluxes, but also noticeable solute rejections against poly(vinylpyrrolidone) (PVP) with molecular weight of 360,000. This high selectivity suggests the existence of a selective layer in membrane surface. More detailed observations on final membrane structure will be progressed in this paper with the analysis on the results in Table 2 and Table 3.

Fig. 1 and Fig. 2 list the scanning electron micrographs of CA membranes prepared with various compositions of acetone and DMF. Structural asymmetry is observed in all SEMs, consisting of a more or less dense top surface skin layer and porous substructure. From Table 2-Fig. 1 and Table 3-Fig. 2, it can be seen that a membrane prepared with a larger volume fraction of acetone produces a denser top surface skin layer and correspond-

Table 2. The Effect of Composition Ratio of Acetone : DMF Solvent System in Membrane Solution on CA Membrane Performance(pore forming agent : LiNO$_3$)

Membrane Code	LiNO$_3$ Content (wt% / CA wt)	Acetone : DMF Volume Ratio(ml)	Pure Water Flux (ℓ/m^2 hr)
CA(10)-44,44-1	10	44 : 44	37.9
CA(10)-33,55-1	10	33 : 55	40.3
CA(10)-22,66-1	10	22 : 66	95.1
CA(10)-11,77-1	10	11 : 77	125.5
CA(10)- 0,88-1	10	0 : 88	419.4

Code description : CA(LiNO$_3$ content)-acetone :
DMF vol. ratio-solvent evaporation period
polymer concentration : 12 wt%
LiNO$_3$ content : wt% against CA wt
total vol. of solvent system : 88ml
solvent evaporation period : 1min.

Table 3. The Effect of Composition Ratio of Acetone : DMF Solvent System in Membrane Solution on CA Membrane Performance (pore forming agent : formamide)

Membrane Code	Formamide Content(ml)	Acetone : DMF Volume Ratio(ml)	Pure Water Flux(1/m^{2}hr)	Solute Rejection		
				PEG 20,000	Dextran 124,000	PVP 360,000
CA(12)-88, 0-1	12	88 : 0	25	58	92	99
CA(12)-77,11-1	12	77 : 11	57	57	91	96
CA(12)-66,22-1	12	66 : 22	124	45	87	94
CA(12)-55,33-1	12	55 : 33	138	4	12	94
CA(12)-44,44-1	12	44 : 44	149	19	42	95
CA(12)-33,55-1	12	33 : 55	151	19	41	94
CA(12)-22,66-1	12	22 : 66	110	26	63	94
CA(12)-11,77-1	12	11 : 77	158	9	20	93
CA(12)- 0,88-1	12	0 : 88	195	4	13	94

Code description : CA(formamide content)-acetone : DMF vol. ratio-solvent evaporation period
polymer concentration : 12 wt%
total vol. of solvent system : 88 ml
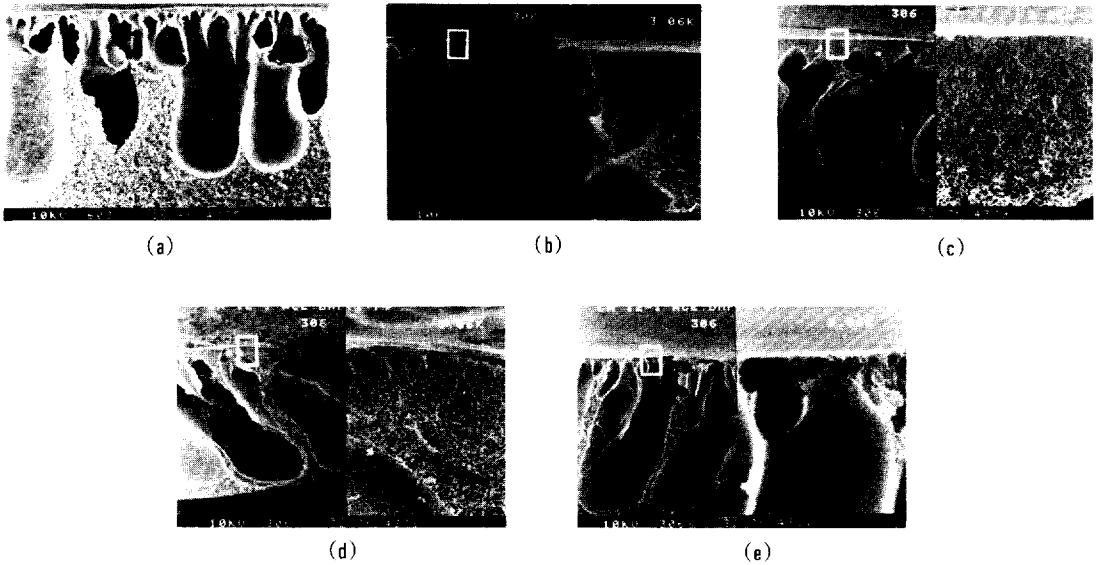solvent evaporation period : 1 min.

Fig. 1. Scanning electron micrographs of CA membranes prepared by various composition ratios of acetone-DMF mixed solvent system (pore forming agent : LiNO₃) composition ratios of acetone : DMF are ; (a) 44 : 44, (b) 33 : 55, (c) 22 : 66, (d) 11 : 77, (e) 0 : 88 vol. (ml).
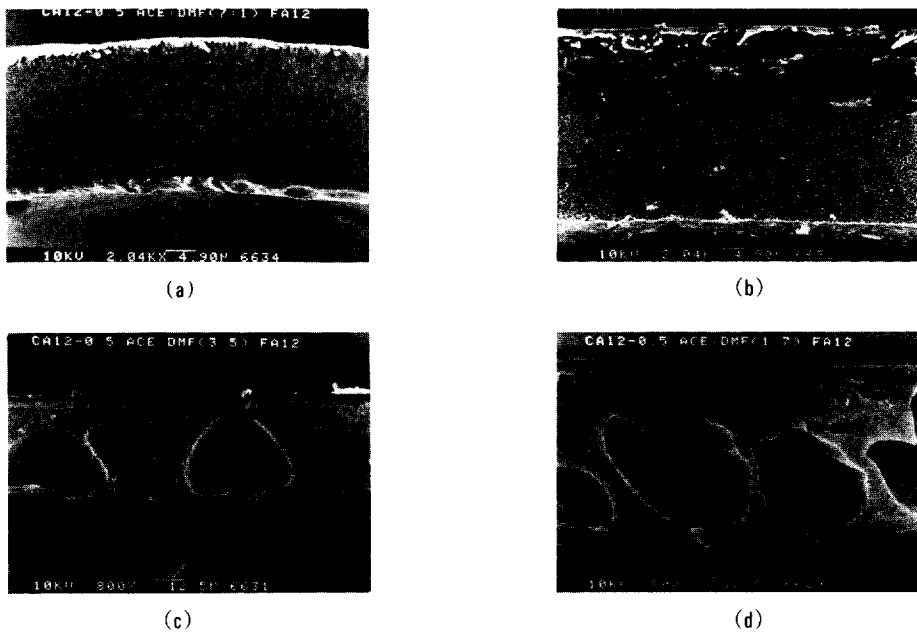

Fig. 2. Scanning electron micrographs of CA membranes prepared by various composition ratios of acetone-DMF mixed solvent system (pore forming agent : Formamide) composition ratios of Acetone : DMF are ; (a) 77 : 11, (b) 55 : 33, (c) 33 : 55, (d) 11 : 77, vol. (ml).

ingly exhibits a smaller pure water flux.

Acetone, in this study, is one of the representative volatile solvents, and is believed to enhance the supersaturation of CA molucules in the top layer of cast film through quantitative loss by its preferential evaporation. The critical nucleus size will be decreased as polymer supersaturation is progressed. A smaller nucleus size will produce a higher density of nuclei. Also, higher polymer supersaturation produces higher local polymer concentration in the top of cast film. At this time, the nuclei density becomes very high. This will result in a finely dispersed structure which makes the dense surface skin of resulting CA membrane as shown in Fig. 1(a)-(b) and Fig. 2(a)-(b).

On the other hand, large voids are observed in the membrane substructure in these figures. The formation of large void may result from the drastic inter-diffusion of DMF and coagulating water having their large chemical potential difference. By convective flowing,[12] void will grow faster than polymer coagulation front due to facillitated diffusion. And this phenomenon seems to be progressed in a case of a larger volume fraction of DMF. Also, membrane porosity seems to be increased in this case with increasing DMF volume fraction. This trend is well-explained in a series of SEMs in Fig. 2.

Fig. 2(a)-(b) shows the cross-sectional views of membrane prepared with smaller volume fractions of DMF. These membranes have sponge-like substructure without a void. In these membranes, skin surface will be formed densely due to the preferential evaporation of relatively larger portions of acetone. This denser surface skin can act as a mechanical barrier against drastic exchange of solvent and coagulating water. Instead of drastic void propagation, liquid-liquid phase separation will occur predominantly in the membrane substructure ; liquid droplets will form final pores, while concentrated CA polymer phases will form membranematrix through gelation.

Particularly, all voids observed in Fig. 1 and Fig. 2 have porous inner lining surfaces. Coagulating

water penetrating into the membrane is gradually diluted by mixing with solvent remaining in the membrane. Thus the coagulating behavior of water will become much meager at growing void interior. At the initial step of void formation, the boundary of void will be fluid state. Coalescence of small droplets from liquid-rich phase is possible. Therefore, many pores on the inner lining surface of void will be formed.

The Effect of Solvent Evaporation Period

Solvent evaporation period is important during membrane preparation in a view that this period can vary the concentration gradient from the top to the bottom across the entire membrane and subsequent structural asymmetry. It has been well-known that, in asymmetric cellulose acetate or polysulfone membranes, membrane permeability is gradually lowered, while solute rejection is enhanced with the increasing evaporation period.[13,14] In this research, however, the obtained results were only partially accorded with those of the previous reports.[13,14]

It can be seen from Table 4 and Table 5 that, in the course of the entire solvent evaporation period investigated, membrane performance are varied with a diverging point. Pure water flux was decreased initially and then increased afterwards with the increasing period. Solute rejection showed opposite result which was an initial increase followed by a decrease with the increasing period. These results are very noteworthy and will be discussed again through the structural interpretation in this paper.

A series of SEMs of cross-sectional views of membranes prepared with various solvent evaporation periods are listed in Fig. 3. Surface skin is more obvious in the membrane with evaporation period of 4 or 5 min, whose water flux showed minimum value as listed in Table 4, than any other skin in the membrane. On the other hand, the domain size of macrovoid is decreased till 4 min, and then turned to be increased.

Acetone seems to be evaporated very preferentially up to about 4 or 5 min, and contributed to

Table 4. Pure Water Fluxes and Solute Rejections of CA Membranes Prepared with Various Solvent Evaporation Periods (pore forming agent ; LiNO$_3$).

Membrane Code	Solvent Evaporation Period(min)	Pure Water Flux(1/m^{2}hr)	Solute Rejection	
			PEG 20,000	Dextran 124,000
CA(10)-44,44-0	0	88 : 5	61	92
CA(10)-44,44-0.5	0.5	80 : 3	60	92
CA(10)-44,44-1	1	37 : 9	71	93
CA(10)-44,44-2	2	30 : 3	66	92
CA(10)-44,44-3	3	27 : 6	67	92
CA(10)-44,44-4	4	23 : 3	84	92
CA(10)-44,44-5	5	17 : 6	85	94
CA(10)-44,44-7	7	20 : 5	76	93
CA(10)-44,44-9	9	29 : 8	71	93

Code description ; CA(LiNO$_3$ content)-acetone : DMF vol. ratio-solvent evaporation period

polymer concentration ; 12 wt%

LiNO$_3$ content ; 10 wt% against CA wt

total vol. of solvent system ; 88ml

acetone : DMF vol. ratio ; 44 : 44 vol. (ml).

Table 5. Pure Water Fluxes and Solute Rejections of CA Membranes Prepared with Various Solvent Evaporation Periods (pore forming agent ; formamide)

Membrane Code	Solvent Evaporation Period(min)	Pure Water Flux(1/m^{2}hr)	Solute Rejection		
			PEG 20,000	Dextran 124,000	PVP360,000
CA(12)-77,11-0	0	85	60	92	95
CA(12)-77,11-0.5	0.5	57	57	91	96
CA(12)-77,11-1	1	58	60	92	95
CA(12)-77,11-2	2	52	63	92	95
CA(12)-77,11-3	3	54	67	93	95
CA(12)-77,11-5	5	92	37	76	94
CA(12)-77,11-7	7	99	12	31	94
CA(12)-77,11-9	9	114	0	10	90

Code description ; CA(formamide content)-acetone : DMF vol. ratio-solvent evaporation period

polymer concentration ; 12 wt%

formamide content ; 12 ml

total vol. of solvent system ; 88 ml

acetone : DMF vol. ratio ; 77 : 11 vol.(ml).

form fine density of top surface skin. Diffusion of coagulating water into the membrane could be retarded due to the fine density of this skin. Therefore, liquid-liquid phase separation may be progressed in the membrane rather than direct gelation. As a result, sponge-type substructure occupies the major portion of membrane matrix in this period.

When the evaporation period is prolonged (Fig. 3-f) acetone in upper part of cast film will be almost evaporated, while DMF concentration will be increased in the film surface. Drastic inter-diffusion of coagulating water and DMF in film surface will be proceeded, and therefore, coarser surface skin will be obtained. This loosely arranged sur-
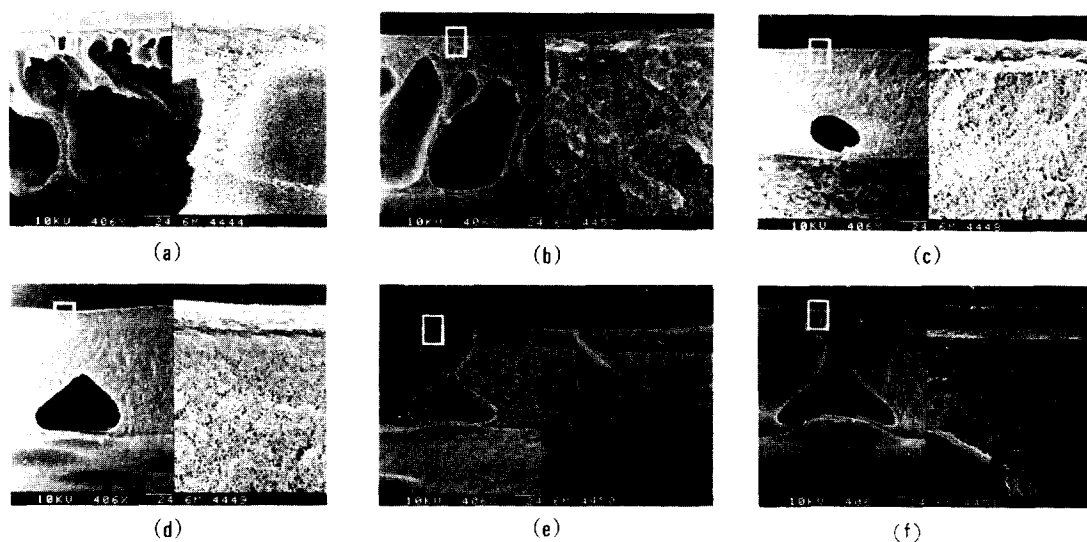
Fig. 3. Scanning electron micrographs of CA membranes prepared by various solvent evaporation periods (pore forming agent : $LiNO_3$) ; (a) 0.5 min, (b) 3 min, (c) 4 min, (d) 5 min, (e) 7 min, (f) 9 min.

face skin will make water flux increased and solute rejection decreased.

From these above results, it is suggested that membrane performance can be varied through the control of solvent evaporation period in the combined evaporation-diffusion process.

CONCLUSION

In the present paper flat-sheet cellulose acetate (CA) membranes applicable to ultra- or microfiltration were prepared by the combined evaporation-diffusion technique based on phase inversion process. Membranes were obtained from the two types of quarternary solutions containing pore forming agents : The one was CA-acetone-DMF-$LiNO_3$ system, and the other was CA-acetone-DMF-formamide system.

Pure water flux (membrane permeability) was enhanced with the addition of pore forming agents in membrane solution, but exhibited no linear relationship against their amount employed.

Pure water flux exhibited smaller value in a membrane prepared with a larger volume fraction of acetone in acetone-DMF mixed solvent system.

This lower flux may result from the increase of polymer density in top surface skin of membrane by the preferential evaporation of acetone and subsequently the enlargement of sponge-type membrane matrix.

Differently from the generally well-known facts, [13,14] within the predetermined solvent evaporation period, pure water flux of membrane was changed with an initial decrease followed by an increase afterwards with the increasing period. On the other hand, solute rejection appeared opposite to the water flux data. These phenomena are considered as a distinct feature exhibited in a series of membranes prepared from the solutions with two-component solvent system in which their volatilities are considerably different.

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