The Effects of Inorganic Additives Contained in Precipitant (Water) on Formation Mechanism of Asymmetric Polysulfone Membrane

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Abstract: The present study was undertaken to investigate the effects of low molecular weight inorganic additives(electrolytes) contained in precipitant on membrane performance. The system studied was polysulfone(13 wt %) / dimethylformamide / water(or water + additive) and additives employed were NaCl, NaOH, KCl, LiCl, CaCl₂ etc. Asymmetric ultrafiltration membranes were manufactured from the immersion precipitation method by varying types and amounts of additives and tests on the structures and performances of the resultant membranes were made by measuring water content, porosity, membrane thickness, pure water flux,
dextran rejection (available only for NaCl), and SEM photographs. In addition, experiments on solvent outflow time and cloud point (phase separation) were carried out for elucidation of membrane formation mechanism. For the effective discussion of the "additive" effect, we divided the additive concentration range into three regions (low concentration, \(0 < m < 0.7\); intermediate concentration, \(0.7 < m < 3\); high concentration region, \(m > 3\)) and analyzed the experimental data in each region by taking account of the specific nature (e.g., the "salting-out" effect) of salt, decrease in water activity, increase in density difference between cast solvent and precipitant, variation in viscosity and mutual miscibility of liquids, etc., resulting from the presence of additives, which affect equilibrium thermodynamics and kinetic aspect during membrane formation process.

**INTRODUCTION**

Several attempts have been made to improve the performance of asymmetric ultrafiltration (UF) or reverse osmosis (RO) by simply adding low molecular weight components in either casting solution\(^{-2}\) or precipitation bath.\(^{3,4}\) Particularly, Frommer et al.\(^{16}\) investigated the effect of salt contained in precipitant on membrane performance, according to which the "salt-gelled" membranes exhibited the lower pure water flux (PWF) and the increased salt rejection (R) compared to the salt-free case, attributable only to the effect of the decrease in water activity\((a_w)\) by the presence of salt. However, to our knowledge few papers have appeared so far on the comprehensive study of the effect of additive contained in precipitant on the formation mechanism and the properties of asymmetric UF membranes. Hence, in this paper the system of polysulfone (PSf) / dimethylformamide (DMF) / water or (water + additive) was selected to study the "additive" effect. Asymmetric polysulfone UF membranes have been prepared by precipitating in water or aqueous solution containing such inorganic additives (electrolytes) as NaCl, NaOH, LiCl, KCl, CaCl\(_2\), etc., using casting solution consisting of 13 wt % PSf in DMF at 20°C. The structural (or performance) differences among the membranes thus obtained were analyzed by measuring the solvent outflow time, the amount of nonsolvent required for precipitating the polymer from casting solution, water content, porosity and thickness of the resultant membrane, membrane performance (like PWF and dextran rejection) and morphology. In addition, qualitative explanation was given in terms of the specific salt effect (for instance, the salting-out), and changes in activity, density, viscosity, mutual miscibility, etc. of liquids attendant upon the addition of electrolytes, affecting the equilibrium phase separation (binodal) curve and precipitation path, (as represented by the nonsolvent-in to solvent-out volume flux ratio, \(J_1 / J_2\)).\(^{7-10}\)

**EXPERIMENTAL**

The polymer used as membrane material was polysulfone purchased from Union Carbide (P-1700: average M.W., 30,000; density, 1.24 g/cm\(^3\); and \(T_g\), 190°C). All of the reagents used were GR grade. The polysulfone membranes used in this work were prepared by casting the polymer solution of 13 wt % in DMF on a glass plate (cast film thickness of 300 \(\mu\)m) and immersing it almost immediately in precipitant (water or aqueous solution of inorganic additive) at room temperature. Experiments on performance (PWF and R) and structural characterization (water content, porosity, and thickness) of the resultant membrane were carried out as described previously.\(^{11,15}\) The procedure for determining the incipient cloud point needed to make the ternary phase diagram of polymer / solvent / (nonsolvent with additive) was also identical to that described previously.\(^{12}\) As an auxiliary tool for studying the effect of the additive on precipitation mechanism for membrane
formation, the observation on the upward "convective" flow of solvent through the cast layer (arising from the density difference (\(\Delta d_{\infty}\)) between nonsolvent(1) and solvent (2) upon immersion in precipitant bath) was made using a grass coagulation bath with black-ruled background according to Cabasso's procedure.\textsuperscript{13}

In particular for the NaOH additive case, phenolphthalein was added in the cast solution to aid in the visual observation, and we designated the time interval between immersion and appearance of Schlieren pattern (i.e., light attenuation pattern resulting from the refractive index gradient) as "the solvent outflow time". Finally, water activities in aqueous electrolyte solutions of concentration m (molality) were taken from the literature data\textsuperscript{14} if available; or otherwise, calculated by means of eq. (1) derived from the Gibbs-Duhem relation on chemical potentials of electrolyte solutions.

\[
\ln a_w(m) = \sum_{\nu} \left( \frac{X_s}{X_w} \right) \left[ \ln \left( \frac{\nu^{+} - (m_{+})^{+}}{\nu^{-} - (m_{-})^{-}} \right) \right]
\]

(1)

Where \(\nu\) denotes the total number of ions per molecular equal to the sum of \(\nu^+\) positive ions and \(\nu^-\) negative ions: \(\nu\), the mean activity coefficient of the ion and \(X_w\) and \(X_s\), mole fractions of water and salt, resp.

**RESULTS AND DISCUSSION**

Before analyzing experimental data obtained on PSf membranes prepared from the additive-containing precipitant, we will briefly discuss the influences of both the specific salt effect and changes in some properties of the membrane system caused by the presence of the additive upon both thermodynamic and kinetic aspects, affecting the membrane formation mechanism.

It is generally believed that the higher the precipitation power of the nonsolvent (i.e., binao curve shifted toward the polymer-solvent axis in the ternary phase diagram) and the larger the value of \(J_1 / J_0\) (corresponding to fast precipitation), the more porous ("finger-like") becomes the membrane structure. Among the previous works regarding the additive effect on the membrane performance, Frommer\textsuperscript{6} and Strathmann\textsuperscript{2} have reported that the presence of salt in one of the two phases (casting solution and precipitant) will decrease the rate of diffusion of the liquid from this phase into the other phase due to the decreased activity or chemical potential, hence affecting the precipitation path.

However, the diffusing-out rate of the liquid from a saltless phase and the precipitation equilibrium may be little affected by the presence of salt, Martz\textsuperscript{15} explained the structural change by the additive in terms of viscosity or surface tension changes. In addition, Cabasso\textsuperscript{13} asserted that the density difference between nonsolvent and solvent plays an important role in asymmetric membrane formation. Namely, the presence of additive controls the relative magnitude of the upward convective flow of solvent over the simple diffusive flow arising from the concentration gradient, thus affecting the membrane structure. On the other hand, Frommer and Lemoney et al.\textsuperscript{16} studied the "specific" salt effect (i.e., the difference in electrostatic interaction between salt and polymer due to the specific nature of salt), according to which there are two types of salts based on the effect on the precipitation power of nonsolvent toward polymer: one is the "swelling" (or "salting-in") agent, and the other is the "gelling"(or "salting-out") agent. Hence, in order to investigate the effects of the separate terms in our system, observations on the solvent outflow rate were first made following Cabasso's procedure. For all cases, the initial solvent outflow rate was found to be largely increased by the addition of electrolyte, attributable to the increased density difference (\(\Delta d_{\infty}\)). As shown in Fig.1, \(a_w\) (calculated by eq. (1)) decrease and \(\Delta d_{\infty}\) (cited from ref. (17)) increase with the additive concentration (m), though exhibiting some differences among the electrolytes.

In addition, the viscosity change (in terms of relative viscosity \(\eta / \eta_0\)), as taken from the litera-
ture, of the precipitant (water) upon addition of the electrolyte is plotted in Fig. 2 as a function of molality for several electrolytes. This figure exhibits that the nonsolvent viscosity significantly increased with m (ie., so-called "structure-making" effect), this being more pronounced in cases of CaCl$_2$ and NaOH.

![Graph](image1)

**Fig. 1.** Water activity ($a_w$) and density difference ($\Delta d_p$) between aqueous solution and solvent as function of concentration (in molality m) of electrolytes contained in water at 25°C and 20°C, respectively. Data for $\Delta d_p$ were taken from ref. 17 and $a_w$ was calculated by eq (1).

![Graph](image2)

**Fig. 2.** Dependence of relative viscosity ($\eta/\eta_0$) upon molality for several electrolytes contained in water. The $\eta_0$ and $\eta$ are viscosities of water and aqueous solution, respectively. Data for $\eta/\eta_0$ were taken from ref. 17.

Usually, the viscosity effect in the system containing the additive in the precipitant is meant not only the viscosity change of the precipitant by the additive but also that of the cast dope caused by solvent depletion due to the convective flow, which may affect the precipitation rate and path.

Next, in order to study the additive effect on the precipitation power of nonsolvent, precipitation experiments (measuring the amount of nonsolvent required for precipitation of polymer from casting solutions) were carried out on dilute PSf (0.25 g) / DMF (50ml) solution at 16°C (except for the KCl case where at 27°C), whose results are summarized in Table 1.

For clear understanding of this effect, relation-

<table>
<thead>
<tr>
<th>Molality in Precipitant</th>
<th>$a_w$</th>
<th>Weight Fraction of Precipitant at Cloud Point</th>
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<tr>
<td>Pure Water</td>
<td>1</td>
<td>0.0195</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>0.5</td>
<td>0.9755</td>
</tr>
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<td></td>
<td>1.0</td>
<td>0.945</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>3.0</td>
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</tr>
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<td></td>
<td>4.0</td>
<td>0.6239</td>
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<tr>
<td>LiCl</td>
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<td>0.9829</td>
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<tr>
<td></td>
<td>1.0</td>
<td>0.9641</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>0.9211</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>0.8703</td>
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<tr>
<td></td>
<td>4.0</td>
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<tr>
<td>NaCl</td>
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<tr>
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<td></td>
<td>3.0</td>
<td>0.893</td>
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<tr>
<td></td>
<td>4.0</td>
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<tr>
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<td>0.8932</td>
</tr>
</tbody>
</table>

* Precipitation experiments at 27°C.
ship between weight fraction of precipitant at the incipient cloud point and water activity in electrolyte solution was graphically illustrated in Fig. 3 by using the data given in Table 1.

From Fig. 3, we can realize that the higher the concentration of additive (or the lower the $a_w$), the higher the precipitation power of precipitant (or the lower the weight fraction of non solvent at the cloud point). In particular, the cases of NaOH, NaCl, and KCl exhibited the initial sharp changes followed by gradual changes with $m$ as compared to other systems. In addition, the precipitation power of non solvent was found to decrease with increasing temperature, as expected. As shown in Fig. 3, precipitation power of aqueous electrolyte solutions at a given $a_w$ value (e.g., $a_w=0.95$) increased in the order of HCl < CaCl₂ < LiCl < NaCl < NaOH < KCl, this order being in close agreement with the increasing order of ionization tendency or electropositivity of metal elements of these electrolytes. From two optical microscope photographs inserted in Fig. 3, showing the dispersed state of polymer (latex) particles after phase separation, we can notice that for pure water, coagulated latex particles are finely dispersed in water whereas for NaCl aqueous of $a_w=0.8515$, particles become coalesced as a result of the strong precipitation power of the precipitant (due to the salting-out effect). Based on above considerations, the following proposal will be made for qualitative explanation on the structural differences among the membranes prepared with different additives. In the analysis of the effect of additive on membrane performance, not any one or two factors but the combined effect of the factors stated above should be taken into account. Namely, such factors as the specific salt effect, $\Delta d_{in}$ and $n / n_0$ should be included in the expressions for exchange process between solvent and non solvent during the immersion process. For instant, Cohen, and later Wijmans proposed the following phenomenological relation for the description of $J_1 / J_2$ at different times (See Fig. 4) for the additive-free membrane system.

\[
J_1 = -\left[ \frac{D_i(\phi_0, \phi_i)}{RT} \right] \phi_i \left( \frac{pV_i}{RT} \right) \tag{2}
\]

where $\phi_i$ (i=1 for non solvent and i=2 for solvent) is the volume fraction of i component, $V_p$ is the volume of polymer per unit area of membrane between the interface and the point of observation, $D_i$ is the diffusion coefficient in the polymer-fixed reference frame, $J_1$ is the volume flux of i component with respect to the polymer.

**Fig. 3.** Schematic representation of precipitation power vs. water activity for the PSf(0.5 wt%) / DMF / aqueous electrolyte solution membrane system. Optical microscope photographs (×40(i)) of latex particles coagulated after phase separation are inserted within the figure.

**Fig. 4.** Schematic representation of the immersion process at two different times. $J_1$ and $J_2$ are the non-solvent and solvent volume flux, respectively. The coordinate $z$ is fixed: the coordinate $V_p$ is measured in terms of the polymer volume per unit observation. Cited from ref. 9.
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ie., through surfaces of fixed $v_i$, and $\partial \mu_i / \partial v_i$ is the chemical potential gradient of $i$ component (driving force for $J_i$). For the successful application to the additive-containing system, in our opinion, the eq. (2) needs to be modified so that the terms $D_i$ and $\mu_i$ may include some factors like the specific salt effect and changes in density, viscosity, and miscibility of the liquids caused by the presence of additive. With this speculative idea in mind, then, we will investigate effects of additive on

![Graphs showing solvent outflow time and properties of membranes](image)

**Fig. 5.** Plots of solvent outflow time and properties of membranes prepared from PSf/DMF (13 wt%) cast system precipitated in aqueous solutions vs. $a_w$ and $\Delta d_w$. 
membrane performance. Experimental data on structural characteristics and performance tests as well as solvent out flow time for PSf membranes prepared by varying the type and amount of additive are collectively plotted in Fig. 5 as functions of $a_w$(left) and $\Delta d_{2w}$(right), instead of m, to test Frommer's assertion that the membrane performance depends mainly on $a_w$ irrespective of the type of additive. The concentration range covered in our experiments, for each additive in water, was limited because of solubility problems.

First, by inspection of data on solvent out flow time given in Fig. 5, we can realize that the solvent outflow time (starting time) increases with increasing m (decreasing $a_w$ or increasing $\Delta d_{2w}$) for all cases with the tendency of the initial sharp changes followed by gradual changes with $a_w$, similarly to the case of precipitation experiments (Fig. 3).

The difference in solvent out flow time at a given $a_w$ (or $\Delta d_{2w}$), for the respective additives may imply the specific effect of electrolyte, deviating from Frommers results. In addition, the behavior of variation in solvent outflow time with $a_w$ did not greatly differ from that with $\Delta d_{2w}$ similarly to the cases of other data given in Fig. 5. However, it will be desirable to consider not only the type (ie., specific salt effect) and amount of the electrolyte but also the terms like $a_w$ and $\Delta d_{2w}$ in discussing the additive effect on membrane performance, as judged from the results summarized in Fig. 5. As shown in Fig. 5, however, the membrane structure (as represented by water content, porosity, and thickness data) or performance (like PWF) has complicated dependence on m (and hence $a_w$), but exhibited a certain degree of regular pattern for most electrolytes studied.

For the effective analysis of additive effect, the concentration ($a_w$) range of each electrolyte was divided into three regions based on PWF data, and discussed separately in each region according to our qualitative scheme. In the first low concentration region (ca. $0 < m < 0.7$) as characterized by significantly decreased PWF values compared to those for the pure water case, such physical properties as porosity and water content of PSf membranes were gradually decreased by the addition of electrolytes for most cases, as shown in Fig. 5. In this region, as stated previously, changes in $a_w$, $\Delta d_{2w}$ and $\eta/\eta_0$ due to the presence of additive were found to occur gradually with increasing m.

In addition, the fast solvent outflow is induced by an appreciable increase in precipitation power of the precipitant (thereby promoting separation of solvents from the polymer molecules) relative to the gradual decrease in $J_w$, thus leading to $J_i/J_w<1$. Hence, membrane with the thin, dense top skin layer and the still porous, finger-like substructure evidenced by SEM (Figs. 6 and 7), was formed, yielding decreased PWF and increased rejection as compared to the pure water case.

Membrane rejection experiments were carried out only for a NaCl additive system, whose results are displayed in Table 2, Fig. 8.

This improvement in rejection performance by the addition of only a small quantity of electrolyte (NaCl) may suggest the possibility of eliminating the need for the laborious "annealing" process. Next, the intermediate concentration region (ca. $0.7 < m < 3$) may correspond to that surrounding the abruptly increased (peak) PWF value, possessing high fluxes and poor rejection (as found for the NaCl aqueous system, Fig. 8) compared to the salt-free case.

The decrease in rejection might be qualitatively understood by considering the following facts. That is, the significant increase in solvent outflow rate caused by both the strong precipitation power of nonsolvent and the increased density difference, dominating over the effect of decrease in penetration rate of nonsolvent by the addition of salt, may bring about the abrupt shrinkage (partly resulting in "fracture") of the top layer (Fig. 7), thereby yielding the poor rejection (Fig. 8).

In addition, the reasoning for significantly increased fluxes would be that the fast solvent outflow will also bring about the formation of a number of shortened finger-like cavities with large diameter in the substructure (Fig. 6) and the increase
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Fig. 6. SEM photographs of cross-sections of PSf (13 wt %) / DMF membranes precipitated in water or (water additive). The specification of additive is marked under each photograph. All photo magnitudes are \( \times 500 \).
Fig. 7. SEM and optical microscope photographs of the top and the bottom skin of PSf (13 wt %) / DMf membranes precipitated in water or (water + additive). (a)-(j): top skin; (j)-(l): bottom skin. The specification of the additive and photo-magnitude are marked under each photograph.
pore size for the bottom skin layer (Fig. 7). Lastly, the high concentration region (ca. m > 3) may be characterized by negligible PWF values and increased rejection (as found for the 6.2 m NaCl aqueous system) compared to the pure water case. Similarly, this could be explained as follows. In this concentration region, significant changes in a_w, \( \Delta d_m \), \( \eta / \eta_m \), etc. are expected to occur, as shown above. Thus, the effects of the decrease in water activity and increase in nonsolvent viscosity will impede the inflow of nonsolvent into casting solution whereas the effects of the increase in density difference and the very strong precipitation power of nonsolvent in this region will promote the solvent outflow, yielding \( J_1 / J_g \). Consequently, the viscosity of the casting dope will increase, thereby withstanding the inflow of nonsolvent. The net result will be slow precipitation of a concentrated solution leading to the formation of a membrane with dense (sponge-like) structure (refer to Figs. 6).

On the contrary to the general case, the fact that in spite of the strong precipitation power of nonsolvent caused by the presence of additive in large quantities, a dense membrane was obtained may suggest that the kinetic effect rather than equilibrium thermodynamics will dominate precipitation (or solidification) process for membrane formation in the present system. Meanwhile, some noteworthy, peculiar systems associated with the behavior of the high concentration region will be briefly touched upon herinafter. First, as can be seen from the data given in Fig. 5, the structure of membrane prepared from the LiCl additive system has changed from finger-like to sponge-like, as evidenced by PWF data and SEM photographs, at the fairly high a_w value (a_w \( \approx 0.85 \)), though the precipitation power for this system is not so strong as other systems like NaCl and CaCl_2 at about the same a_w value, as shown in Table 1 and Fig. 3.

This could be somewhat understood by considering the following features: (1) The solubility of LiCl in DMF (solvent) is fairly good, thus favoring the miscibility between solvent and nonsolvent, and the contact between salt and polymer molecules. (2) The viscosity of aqueous LiCl solution is considerably low compared to those of other electrolyte (notably CaCl_2) solutions at about the same a_w value, thus changing the nonsolvent to solvent.
flux ratio, $J_1 / J_2$ in the direction toward the structure formation yielding the above results. Here, it is interesting to note that when plotted against $m$ instead of $a_w$ in Fig. 5, the $m$ value where little or no flux is observed (corresponding to sponge-like structure) did not change so greatly depending on the type of additive. Next, the PWF value for the NaOH additive system showed the increase all the way beyond the concentration corresponding to $a_w=0.87$ whereas other properties like water content, porosity, and thickness did not change greatly within the concentration range covered. This abnormal behavior could be interpreted as follows. As shown before, the aqueous NaOH system exhibited the strong precipitation power, very poor miscibility, significant changes in $a_w$ and $\Delta d_m$ and in particular, the remarkable increase in $\eta / \eta_0$ at relatively high additive concentrations. Accordingly, the penetration rate of nonsolvent into the cast layer was decreased, but the outflow rate of solvent was increased compared to the salt-free case in the first time (corresponding to the slow precipitation), as required by the formation of sponge-like structure. However, the solvent outflow rate became slowed down with time because of the great viscosity of NaOH aqueous solution and of a high immiscibility between solvent and nonsolvent (corresponding to precipitation of a cast solution), yielding the porous membrane with large finger-like cavities (Fig. 6(1)).

Lastly, the CaCl$_2$ additive system also exhibited the structural change from finger-like to sponge-like, in accordance with the general rule for this region, though this change occurring at the fairly low $a_w$ values ($c_{NaCl}a_w=6.2$) relative to other systems (Fig. 5). However, as revealed by SEM photographs on the top skin layer of membranes precipitated from concentrated CaCl$_2$ aqueous solutions (Fig. 7(h) and (i)), the presence of a number of small pores in the skin layer was found, which may suggest the poor rejection as compared to the 6.2 $m$ NaCl system. However, it should be pointed out that because data on rejection experiments are available only for the NaCl system, no general conclusion concerning the effect of additive on membrane rejection can be drawn from this study. On the other hand, to aid in the understanding of the explanation associated with the relative high concentration region, ternary phase diagram for the PSf (13 wt %) / DMF / water or (water + additive) system has been sketched in Fig. 9, showing the variation of both the binodal curve (equilibrium thermodynamics) and the precipitation path (kinetic aspect) due to the presence of additive in water.

The starting point (13 wt % of casting dope concentration) and the final point (as obtained by the water content measurement) for the membrane formation are marked on the polymer-solvent and polymer-nonsolvent axes, resp., for each additive. As seen from Fig. 9, the binodal curve for the additive-containing system was shifted toward the polymer-solvent axis by the presence of electrolyte in water (in quantities of $a_w=0.8$ for all additives), though the tendency changing more or less from one additive to another. Nevertheless, the membrane with more dense structure resulted, except for the NaOH system, as judged from the final point (relating to the precipitation bath) and confirmed by flux experiments and SEM.

![Fig. 9. Ternary phase diagram of the system PSf(13 wt %) / DMF / water or aqueous solution, showing variation of cloud point (or binodal) curve and precipitation path by the presence of additive. The additive conc. for all cases was adjusted so that $a_w=0.8$.](image-url)
observations. As discussed above, this could be explained in terms of the combination of several effects due to the presence of additive. From the above considerations, at any rate, it is obvious that the membrane structure, and hence properties and performance of the membrane are considerably affected by the type and amount of additive contained in the precipitant, irrespective of the adequacy of the explanation. Finally, in order to test the validity of our qualitative scheme proposed for the interpretation of the additive effect on membrane performance, studies on the systems like PSf(13 wt %)/DMAC/Water, PSf(13 wt %)/NMP/water, PVC(14.5 wt %)/DMF/water, and PAN(8 wt %)/DMF/water are in progress.

**CONCLUSIONS**

In view of what has been said so far, we may conclude as follows:

1. In manufacturing asymmetric UF membranes by immersion precipitation method from polysulfone (13 wt %)/DMF casting solution, the presence of inorganic additives (such electrolytes as NaCl, NaOH, LiCl, KCl, CaCl₂, etc.) in nonsolvent (water) has been found to affect considerably both the equilibrium thermodynamic and kinetic aspects upon the membrane formation.

2. From performance tests (rejection experiments made only for the NaCl system) made on membranes obtained by varying the type and amount of the additive, we have found that in the low concentration region, pure water flux (PWF) decreased and dextran rejection (R) increased with increasing molality (m); in the intermediate region, PWF largely increased and R decreased with m; and in the high concentration region, PWF considerably decreased and R increased with m.

3. These findings could be qualitatively accounted for by considering the specific salt effect (like salting-out) and changes in some properties of the system caused by the addition of electrolyte (such as the decrease in water activity, increase in density of the precipitant, variation in viscosity and mutual miscibility of the liquids, etc.)

**REFERENCES**