

The Effect of Low Molecular Weight Additives on the Properties of Aromatic Polyamide Membranes

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Synopsis

Salts contained in aromatic polyamide solutions were found to have a considerable effect on the performance and structure of reverse osmosis membranes cast from these solutions. As in cellulose acetate membranes, certain salts greatly increase membrane fluxes without a detrimental effect on rejection. Highly dissociated salts such as LiClO_4 or $\text{Mg}(\text{ClO}_4)_2$ exert a stronger influence than the commonly used LiCl . With mixtures of different salts, stronger effects may be obtained than with a single additive. Many experimental facts indicate that the "salt effect" in aromatic polyamide membranes is due to a general effect on solvent activity and thus on the kinetics and equilibria associated with evaporation and coagulation processes.

INTRODUCTION

We wish to report on the effect of low molecular weight additives, added to membrane casting solutions, on the properties and structure of aromatic polyamide reverse osmosis membranes.

It is a common practice to add salts (most often LiCl or CaCl_2) to aromatic polyamides in order to facilitate dissolution of the polymer in polar aprotic solvents such as dimethylacetamide, dimethyl sulfoxide, etc.¹ Some of these polymers are completely insoluble in these solvents unless salt is added to the mixture.² Recently, highly salt-rejecting membranes have been prepared from such polymers.^{3,4} Similar membranes are of interest in processes in which the retention of urea and other low molecular weight organic compounds is desired.⁵ To our knowledge, no detailed report has yet appeared on the effect of salts contained in solutions of aromatic polyamides on the properties of membranes cast from these solutions, though mention has been made of this effect in the patent literature.³

The effect of certain inorganic salts added to the casting solution on the properties of cellulose acetate (CA) membranes has been known for a relatively long time and is well documented.⁶ These salts were found to be effective in increasing water permeation rates of CA membranes without a detrimental effect on salt rejection.

During a study on highly urea-rejecting membranes,⁵ it was found that the performance of aromatic polyamide membranes is very strongly affected by the presence of various low molecular weight additives in the polymer solution. Membranes cast from solutions containing such additives exhibit considerably higher fluxes than membranes prepared without additive. Typically, an aromatic polyamide membrane cast under certain conditions from a binary solution, containing only polymer and solvent, exhibited a water flux of $0.85 \text{ l./m}^2\text{-day}$ at 50 atm. Membranes prepared under the same conditions from the same polymer but with an appropriate additive may exhibit fluxes as high as $250\text{--}600 \text{ l./m}^2\text{-day}$

and good rejections of salt and urea. Generally the effect increases with increasing additive concentration up to a certain limiting value. Different additives exert this influence to different degrees, depending on their chemical nature.

EXPERIMENTAL

Polymers were prepared by low-temperature solution polycondensation.³⁻⁵ The main polymer used in the present study was obtained from a 1:1 mixture of *m*- and *p*-phenylenediamine and isophthaloyl chloride.⁵ The polymerization was carried out in *N,N*-dimethylacetamide. The additive was added either to the polymerization mixture, after completion of the polymerization, or to the precipitated and redissolved polymer. The mixture was stirred under anhydrous conditions until completely clear. Membranes were prepared by a casting-leaching process as described previously.⁵

The membranes were tested in thin-channel flow-through high-pressure cells. The testing pressure employed was 50 atm, and the test solution consisted of 0.1% (w/v) NaCl and/or 0.1% (w/v) urea. Salt rejection was determined by conductivity measurements. Urea was determined spectrophotometrically.⁵

The "precipitation point" of the polymer solutions was determined by slow addition of water to the solution until a perceptible precipitate that did not redissolve during 12 hr was formed.

RESULTS

The effect of the concentration of salt additive in the casting solution on the flux of the resulting membranes could clearly be observed with a series of poly(*m*-*p*-phenyleneisophthalamide) membranes⁵ prepared from solutions containing different concentrations of pyridine hydrochloride (this salt is present in the polymerization mixtures when pyridine is used for neutralization of the acid liberated during polymerization). In order to determine the effect of this salt on membrane performance, measured amounts of pyridine hydrochloride were added to previously precipitated and redissolved polymer. Some typical results are summarized in Table I.

It is clear from the data shown in Table I that an increase in the concentration of pyridine hydrochloride in the casting solution leads to an increase in membrane

TABLE I
Dependence of the Reverse Osmosis Properties of Aromatic Polyamide Membranes on the Concentration of Pyridine Hydrochloride in the Casting Solution^a

Salt	Salt concentration		Urea rejection, %	Membrane flux, l./m ² -day
	% (w/v)	Molarity		
None	—	—	80	0.84
Pyridine hydrochloride	5	0.43	80	6.3
Pyridine hydrochloride	10	0.86	80	12.6
Pyridine hydrochloride	20	1.72	85	59.0

^a All membranes were prepared under identical conditions, consisting of heating the cast solution in an oven at atmospheric pressure followed by coagulation in water. The casting solution consisted of 16% (w/v) polymer in dimethylacetamide containing the specified amounts of additive.

flux and has no detrimental effect on rejection. The same effect could be observed with other salts also, as shown in Table II.

It is usually impossible to increase the concentration of a salt in the polymer solution beyond a certain value because of solubility limitations. The overall salt concentration may, however, be increased further by adding a different salt, preferably one having no common ion with the first salt. This combination of two salts in the same solution brings about a further increase in membrane fluxes, as shown in Table III.

Still higher membranes fluxes may be reached by employing a vacuum evaporation step. In this case also, membranes prepared from salt-containing solutions exhibit significantly increased fluxes relative to membranes cast from solutions devoid of additive.

The change in membrane performance due to low molecular weight additives is accompanied by morphological changes, as shown by scanning electron microscopy (Figs. 1–4). Membranes prepared with no additive have a quite uniform cross section (Fig. 1). High-flux membranes, such as those prepared in the presence of pyridine hydrochloride, $Mg(ClO_4)_2$, or $Al(NO_3)_3$, contain a thin, dense layer on top of a highly porous substructure (Figs. 2–4). However, from literature data⁴ on similar membranes, it seems that the selective “skin” constitutes only a small part of the dense layer observed in the micrograph.

TABLE II
Effect of Various Salts Contained in the Casting Solution on the Performance of Aromatic Polyamide Membranes^a

Salt	Salt concentration		Rejection, %		Membrane flux, l./m ² -day
	% (w/v)	Molarity	Urea	NaCl	
LiCl	5	1.2	77	—	34
LiClO ₄	5	0.47	85	—	42
LiClO ₄	10	0.94	78	—	51
ZnCl ₂	5	0.36	72	93	19
ZnCl ₂	10	0.73	83	99	46
Mg(ClO ₄) ₂	5	0.22	80	96	38
Mg(ClO ₄) ₂	10	0.45	72	96	63

^a For casting solution composition see note, Table I. These data indicate that the commonly used lithium chloride exerts a smaller influence than many other salts when used at the same percent concentration. Thus, lithium perchlorate added to the casting solution to a concentration of 0.47M yielded membranes possessing a flux of 42 l./m²-day, while with LiCl even at 1.2M, membranes were obtained, under otherwise identical conditions, with fluxes of only 34 l./m²-day.

TABLE III
Reverse Osmosis Properties of Membranes Prepared in the Presence of More than One Salt^a

Salt	Concentration		Rejection, %		Membrane flux, l./m ² -day
	% (w/v)	Molarity	Urea	NaCl	
ZnCl ₂	10	0.73	83	99.0	46.2
{ ZnCl ₂ + Pyridine } Hydrochloride	10	0.73	88	99.0	92.4
	20	1.73			
Mg(ClO ₄) ₂	10	0.45	72	96.0	63.0
{ Mg(ClO ₄) ₂ + Pyridine } Hydrochloride	10	0.45	80	99.9	189.0
	20	1.73			

^a For casting solution composition see note, Table I.

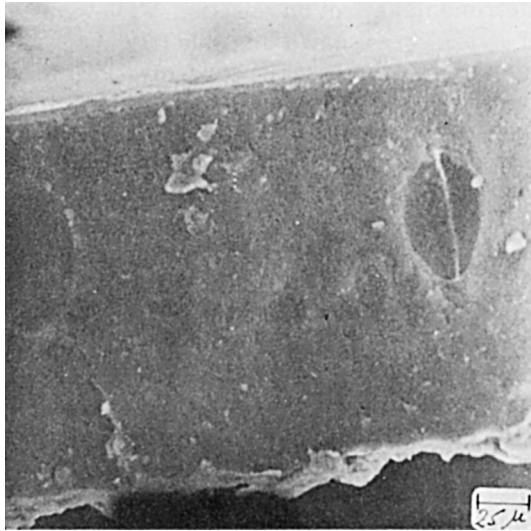


Fig. 1. Scanning electron micrograph (SEM) of an aromatic polyamide membrane prepared from a saltless solution.

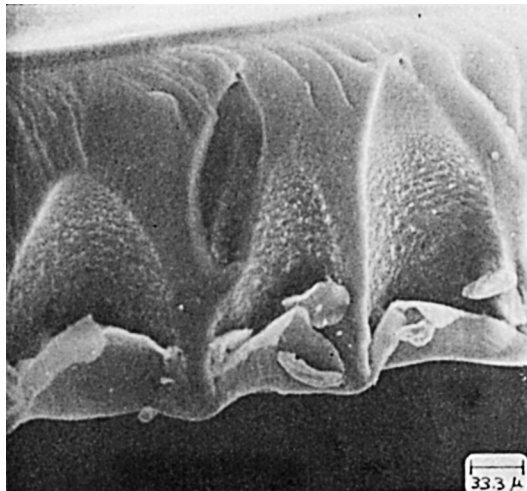


Fig. 2. SEM of an aromatic polyamide membrane from a solution containing 10% (w/v) $\text{Al}(\text{NO}_3)_3$.

In order to further clarify the “salt effect” in aromatic polyamide membranes, overall membrane thickness was measured as function of evaporation time with saltless and salt-containing casting dopes. It was found that with both kinds of dope membrane thickness is determined mainly during the first minutes of evaporation (Fig. 5). For example, in a certain set of experiments, membrane thickness changed by more than a factor of 2 during the first 10 min of evaporation but only by 50% during the following 50 min. However, membranes from saltless solutions are always considerably thinner than membranes from salt solutions when exposed to the same evaporation period. It was also observed that membrane thickness strongly depends on salt concentration in the casting

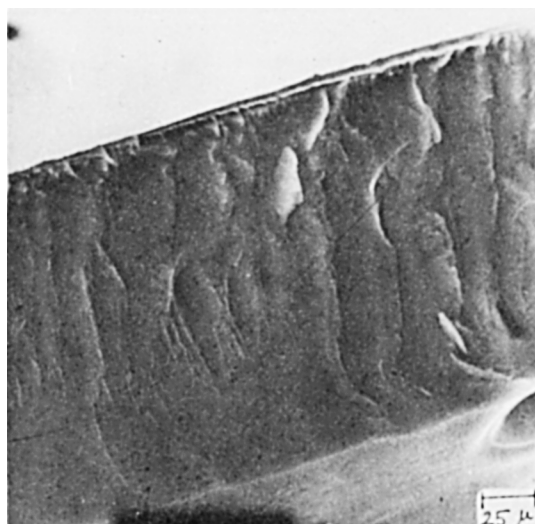


Fig. 3. SEM of an aromatic polyamide membrane from a solution containing 5% (w/v) $\text{Mg}(\text{ClO}_4)_2$.



Fig. 4. Detail of Figure 3.

solution. Thus, a membrane prepared under certain evaporation conditions from a dope containing no additive was 0.05 mm thick. A membrane prepared under identical conditions from a dope containing the same concentration of polymer and 20% (w/v) pyridine hydrochloride was 0.12 mm thick, while a membrane prepared from a solution containing both 20% pyridine hydrochloride and 10% $\text{Mg}(\text{ClO}_4)_2$ was 0.20 mm thick.

The precipitation point (see experimental section) was found to depend on the type of salt contained in the solution. With certain salts (e.g., $\text{Mg}(\text{ClO}_4)_2$, LiClO_4 , $\text{La}(\text{NO}_3)_3$) precipitation required less water (e.g., 10.7% water for 10% LiClO_4 in a 10% polymer solution) than a saltless solution (17.7% water for a 10% polymer solution). With others (e.g., LiCl , CaCl_2 , $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$) more water was

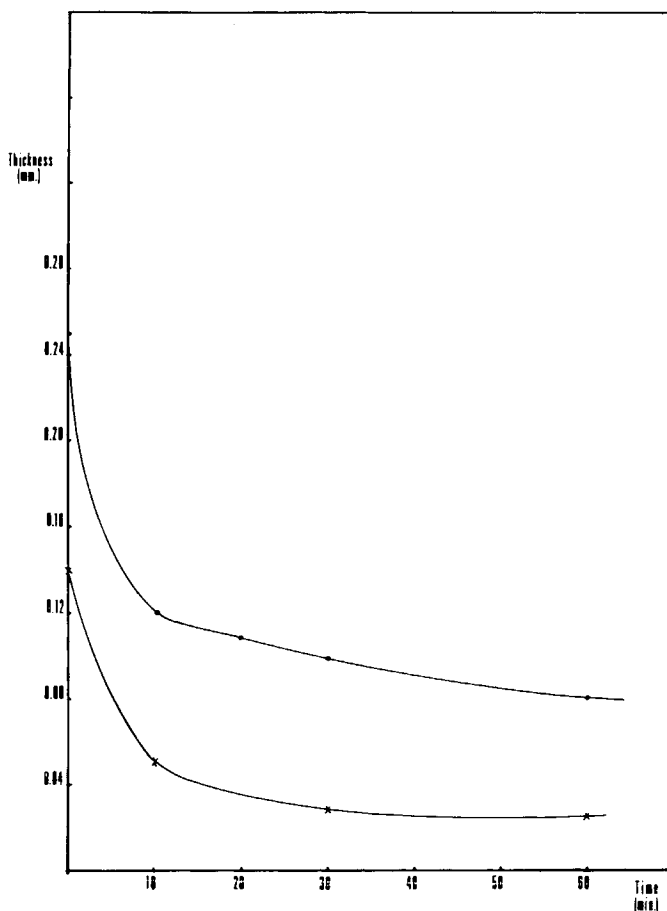


Fig. 5. Dependence of membrane thickness on evaporation time: (●) salt-containing solution; (x) saltless solution.

needed (e.g., 21.2% water for 10% LiCl in a 10% polymer solution). A third class of salts (e.g., KCNS) had no effect on the precipitation point.

It should be pointed out, however, that all three types of salts brought about an increase in membrane fluxes. The implications of the above findings on the mechanism by which salts affect membrane structure are discussed below.

DISCUSSION

A number of experimental facts imply that the "salt effect" described above is due primarily to changes in solvent activity. The fact that a large number of additives bring about an increase in membrane fluxes suggests that the effect is of a general nature. The finding that a mixture of two different additives is more effective than each one of them alone indicates that the important factor is not the nature of the species dissolved but rather the number of particles in solution. Also, when comparing salts having a common cation and different anions on an equal molar basis, it is found that salts with a greater dissociation tendency are more effective in increasing membrane flux (e.g., LiClO_4 vs. LiCl). Evidence along similar lines is obtained from NMR spectra of polymer solutions.

It was observed recently that the interaction between LiCl and aromatic polyamides is accompanied by a downfield shift of the NMR signal of the amide protons of the polymer.⁷ In our hands this phenomenon was verified (a 0.56 ppm shift at 90 MHz in a 1% (w/v) solution of polymer in dimethylacetamide containing 1% (w/v) LiCl). However, no shift could be detected with LiNO₃, which exhibited an effect on membrane flux similar to that of LiCl.

Therefore, it seems that the "salt effect" in aromatic polyamide membranes is best explained by solvent transport phenomena during evaporation and coagulation, as previously proposed by Banks et al.,⁸ Strathmann et al.,⁹ and Frommer et al.¹⁰ for cellulose acetate membranes (*vide infra*).

At given evaporation conditions (temperature, pressure, time), the amount of solvent lost from a "protomembrane" (cast membrane before coagulation) will decrease with increasing additive concentration. This is due, obviously, to a decrease in the solvent's vapor pressure. Therefore, by increasing the additive concentration, the protomembrane will contain a higher solvent-to-polymer ratio at the instant of coagulation, and a more open structure will result. Moreover, solvent evaporation will lead to an asymmetrical structure already in the protomembrane (as was shown recently by scanning electron microscopy),¹¹ and asymmetry should be more pronounced the higher the additive concentration. As solvent evaporates, salt and polymer concentrations near the solution-air interface increase, and this impedes further evaporation of the solvent (diffusion is slow in the highly viscous solution, and thus salt and polymer concentration equalization is slow relative to evaporation rate). Thus, upon coagulation polymer concentration is higher at the upper surface and lower inside the protomembrane, and an asymmetrical structure results.

Indeed, as was shown above, overall membrane (and presumably protomembrane) thickness changes mainly during the first minutes of evaporation and only very slowly afterward. It was also demonstrated that a higher salt concentration in the dope leads to membranes of greater overall thickness.

An alternative or complementary explanation, similar to that proposed by Strathmann et al.⁹ and Frommer et al.^{10,12} for CA membranes, evokes solvent transport phenomena during coagulation of the protomembrane. It has been proposed¹⁰ that:

A. The density of each layer of the final membrane is dependent on the density of the corresponding layer of the cast polymer solution at the precipitation point.

B. The volume concentration of the polymer in the solution at the precipitation point is determined by (1) the rate of flow of solvent out of the cast polymer solution, (2) the rate of flow of nonsolvent (coagulant) into that solution, (3) the concentration of nonsolvent (coagulant) required for precipitating the polymer from the solution.

Regarding the salt effect in cellulose acetate membranes, it has been shown by Frommer¹² and Strathmann⁹ that the presence of salt in one of the two phases comprising a coagulation system (polymer solution and coagulant) will decrease the rate of diffusion of liquid from this phase (the salt-containing phase) into the other phase, due to a decrease in its chemical potential. The diffusion rate of solvent from a saltless polymer solution was found by Frommer et al.¹² to be essentially unaffected by the presence of salt in the coagulation bath.

The precipitation equilibrium (the concentration of coagulant necessary for

initiating precipitation in the casting solution) was found, in most cases studied, to be little affected by the presence of salt either in the casting solution⁹ or in the coagulation bath.¹² However, in both of these cases salts had a very pronounced effect on the porosity of the membranes obtained.

Based on these experimental observations and on the above general assumptions, the rationale for the formation of more porous CA membranes from salt-containing dopes would then be as follows: Precipitation equilibrium and rate of coagulant flow into the polymer solution do not change appreciably due to the presence of salt in the casting dope. However, salt contained in the polymer solution does affect the rate of solvent outflow; the amount of solvent escaping from the polymer dope before the instant of coagulation will be *smaller* in salt-containing dopes than in saltless solutions. The net result will therefore be precipitation of a more dilute solution, namely, a thicker and more porous membrane.

In the present study it was found that the precipitation equilibrium *does* change considerably in the presence of salt additives in the polymer dope (vide supra). Therefore, an explanation such as the above would be applicable only to those salts which either do not affect the precipitation point or exhibit a salting-out effect (less water needed for precipitation than in the absence of salt). With salts exhibiting a salting-in effect, the equilibrium and kinetic effects operate in *opposite* directions, and no general conclusion concerning the effect of coagulation on structure may be drawn in these cases.

Undoubtedly, both evaporation and coagulation phenomena are important in determining the final structure of aromatic polyamide membranes. However, since highly rejecting membranes are obtained only following an evaporation process, coagulation phenomena alone are not sufficient to fully explain the mechanism of formation of these membranes.

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