

Transport Properties and Morphology of Aromatic Polyamide Membranes

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(Received October 8, 1984 : Accepted October 31, 1984)

Abstract : As a membrane material, poly(m-phenylene isophthalamide) was prepared by low-temperature solution polycondensation. The ultrafiltration measurement and dialysis test were performed to study the transport properties of the aromatic polyamide membranes. The effects of the drying temperature, addition of inorganic salts(LiCl, CaCl₂) and the precipitation medium on the membrane performance and morphology were also investigated. In ultrafiltration measurement, the water flux was determined with an Amicon Model 8050 Ultrafiltration cell. In dialysis test, the permeability coefficients of urea, ethylene glycol and polyethylene glycol through aromatic polyamide membranes and a commercial cuprophane membrane were determined using a continuous flow dialysis apparatus. The morphology of aromatic polyamide membranes was investigated with the aid of the scanning electron microscope(SEM).

1. INTRODUCTION

Membrane separation processes are playing an important role in applications such as water desalination, industrial and municipal waste treatment, gas separation and biomedical engineering. Membrane processes are attractive for several reasons comparing with other conventional separation techniques. They are:(a) The processes are inherently simple. (b) There is no phase change involved, which reduces energy requirement. (c) The operation is essentially at ambient temperature which is very important in certain applications where temperature-sensitive substances are involved. In 1959, Reid and Breton¹ discovered that cellulose acetate was an effective membrane material for reverse osmosis. Following this discovery, extensive

investigations have been initiated in search for superior membranes for reverse osmosis applications. In 1971, as a novel membrane system based on aromatic polyamide and poly amide hydrazide polymers, it was found that these membranes^{2,3} unlike cellulose acetate membranes, are not subject to hydrolysis and biological attack, and in comparing the range of pH they can operate, aromatic polyamide membranes can work in the pH range of 4-10 while for cellulose acetate membranes pH must remain in the range of 4-5. Furthermore, aromatic polyamide membranes have wider operating temperature range (up to 120°F) than cellulose acetate membranes(up to 94°F). Sourirajan et al.⁴ by using the liquid chromatographic technique, have proved that polyamide membranes show better performance in separating polar organic solutes. Dickson⁵ and

Matsuura et al.⁶ have successfully used aromatic polyamide membranes to separate organic materials such as alcohol, phenol, ester, ketone, aldehyde, etc. Chiang and Fang⁷ have shown that aromatic polyamide membranes are superior to cellulose acetate membranes in organic separations. The reason for this, according to the authors, is that aromatic polyamide membranes are much less polar than cellulose acetate. An improvement on the durability of membrane, expressed in terms of water flux change as a function of time, was reported by employing crosslinking based on ionic bonds⁸.

Although a number of types of natural and synthetic macromolecules have been studied as reverse osmosis membrane materials, two types of asymmetric reverse osmosis membranes, i.e., cellulose acetate and aromatic polyamide, are broadly received in industry. In this study, the permeability characteristics and morphology of aromatic polyamide membranes were investigated.

2. EXPERIMENTAL

2-1. Preparation of Poly (m-phenylene isophthalamide)

To a 4-neck 1000ml round flask, 0.12 moles of m-phenylene diamine (MPD) was charged with mixed solvents of 80ml hexamethyl phosphoramide (HMPA) and 160ml N-methyl pyrrolidone (NMP). The mixture was stirred for 15 min to dissolve MPD completely. Fine powders of 0.12 moles of isophthaloyl chloride (IPC) was charged with vigorous stirring under nitrogen flow. The reaction was continued for one hour and the temperature increase up to 50°C was noted during the reaction. The inherent viscosity in 96 wt% sulfuric acid was 0.8.

2-2. Membrane Preparation

Poly(m-phenylene isophthalamide) is soluble to many solvents. In this study, NMP was used as the solvent of the membrane casting solution. The conventional techniques for preparing membranes were applied: The polymer solution was cast onto a dry, clean, polished glass plate with thickness of 10mils by using a film applicator. Certain amount of the solvent was allowed to be evaporated from the surface of the solution for a controlled time interval by exposing the cast solution in a vacuum oven. The standard drying condition was set at 90°C for 15 minutes under 125mmHg vacuum. After air drying, the glass plate with the casting solution was dipped in water or some other gelating agent for the film coagulation.

In membrane preparation, the polymer concentration of the casting solution and the membrane thickness were fixed at 10wt.% and 10mils.

2-3. Ultrafiltration Test

In ultrafiltration test, an Amicon Corporation Model 8050 Ultrafiltration cell was used to determine the water flux. This cell has an effective membrane area of 13.4cm². In this test, the cell was operated at 0.4, 0.6, 0.8kg/cm² pressure at room temperature. Water flux was determined by collecting permeates for 5 min after a steady state flux was achieved.

2-4. Dialysis Test

Fig.1 shows a schematic diagram of the continuous flow, flat plate type dialysis system used in this experiment. The dialyzer consists of two acrylic compartments each of which contains a flow channel and baffles to obtain uniform flow pattern through the cell. One compartment of the cell is connected via a centrifugal pump and a rotameter to a small reservoir containing the solution to be dialy-

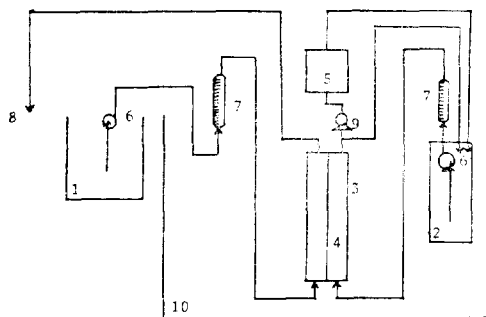


Fig. 1. Schematic diagram of the dialysis apparatus.

1. distilled water bath
2. dialyzing solution reservoir
3. dialysis cell
4. polymer membrane
5. differential refractometer
6. centrifugal pump
7. rotameter
8. drain
9. micro feeding pump
10. constant temperature bath

zed. The other compartment is connected to a larger reservoir containing distilled water. Both the dialysis cell and the small reservoir were immersed in a constant temperature bath. The solution to be dialyzed was continuously recycled through the rotameter past one side of the membrane and part of the recycle was passed through a continuous flow differential refractometer (Waters Associates R403) to measure the solid concentration. Distilled water was pumped past the other side of the membrane and allowed to go to the drain. Thus the largest possible solute concentration gradient is maintained across the membrane. The initial solute concentrations were 0.1wt% and at this concentration osmotic effect across the membrane was negligible. As the solution was dialyzed, the differential refractometer continuously monitored the change in refractive index of the solution. The reference cell of the differential refractometer was filled with distilled water and operated under static

conditions during the dialysis run.

The test conditions were as follows:

Test conditions:

- operating temperature; 37°C
- flow rate of dialyzing solution; 20ml/min
- flow rate of water; 200ml/min
- volume of dialyzing solution; 200ml
- effective membrane area of dialysis cell; 33.6cm²

2-5. Scanning Electron Microscope Study

The morphology of the membranes was investigated with the aid of the scanning electron microscope (ETEC SEM). Wet membrane samples were fractured in liquid nitrogen, coated with gold and examined with a ETEC SEM. The observation was done in magnifications from 500 to 15,000.

3. RESULTS AND DISCUSSION

3-1. Ultrafiltration Measurements

3-1-1. Effect of the temperature of the solvent evaporation

Solvent evaporation rate during the film formation refers to the rate of solvent removal from the surface which ultimately forms the dense microporous layer in the resulting asymmetric porous membrane. The evaporation rate is a function of temperature of the casting solution, temperature of solvent evaporation. The higher the temperature of the casting solution or the solvent evaporation temperature, the higher the solvent evaporation rate. Higher solvent evaporation rate and a longer evaporation time result denser structure of the membrane. Fig.2 shows the ultrafiltration data for water permeation through membranes prepared with solvent evaporation temp. of 85, 90, 95°C (evaporation time: 10 min).

3-1-2. Effect of low molecular weight additives

The effect of certain inorganic salts added

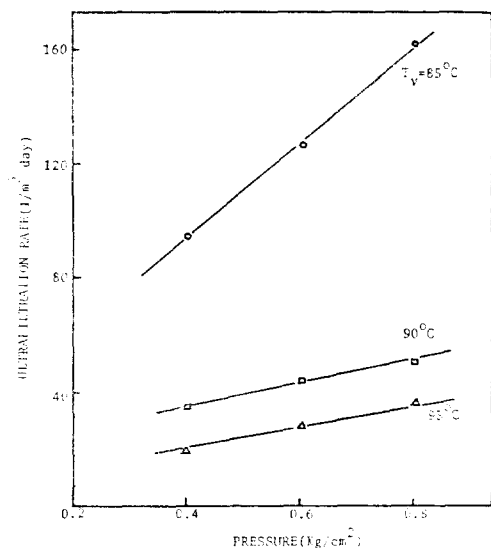


Fig. 2. Effect of evaporation temperature (T_v) on the ultrafiltration rate.

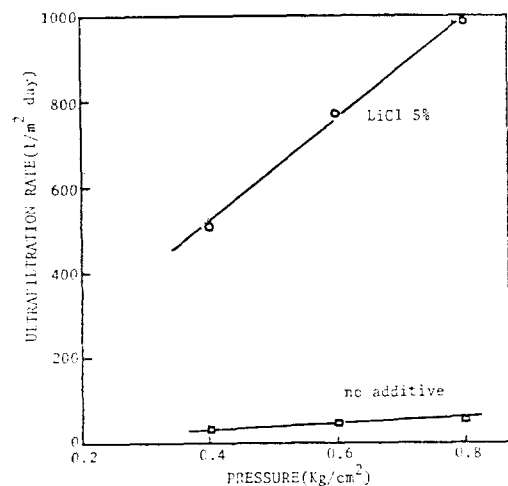


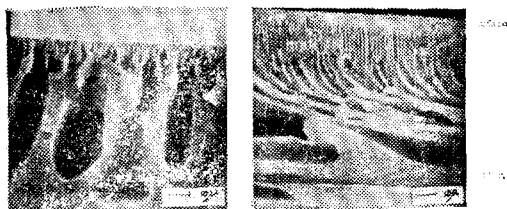
Fig. 3. Effect of low molecular weight additives on ultrafiltration rate.

to the casting solution on the properties of cellulose acetate membranes has been known⁹. For the aromatic polyamide membranes, it was known that the use of organic or inorganic low molecular weight additives (LiCl, CaCl_2 and pyridine hydrochloride) in the polymer solution^{10,11} could improve water flux.

Fig. 3 shows the effect of salt contained in the casting solution on ultrafiltration rate of aromatic polyamide membranes. The aromatic polyamide membrane cast without the additive exhibited a water flux of 30-50 l/m²day while membranes prepared under the same conditions with an appropriate additive exhibited a water flux as high as 1000 l/m²day. The change in membrane performance due to low molecular weight additives was accompanied by morphological changes. Fig. 4 shows the different structures of membranes which were prepared from salt-containing and saltless casting solution respectively. Comparing the structure of these two membranes, it was found that the existence of salt had a noticeable influence on the structure of the cross section of the membrane. At a given evaporation conditions, the amount of solvent lost from a "protomembrane" (cast membrane before coagulation) decreased with the addition of low molecular weight additives. This was due, obviously, to a decrease in the solvent vapor pressure. Therefore by the addition of the low molecular weight additives, the protomembrane contained a higher solvent-to-polymer ratio at the instant of coagulation, and a more open structure results.

3-1-3. Effect of coagulating agent

Strathmann et al.¹² made systematic SEM observations on aromatic polyamide Nomex RO membranes and concluded that there were two typical structures of finger-like and sponge-like pores depending on the rate of precipitation. As the result of the work on various asymmetric membranes prepared by air drying at a relatively high temperature from different types of aromatic polyamide materials and with different preparation conditions, Jiayan et al.¹³ found that besides finger-like and sponge-like structures, there could be other



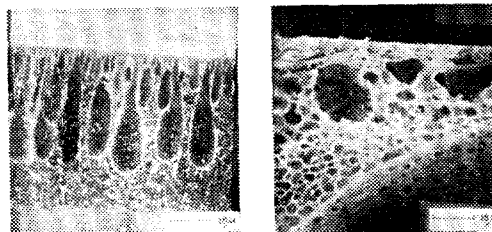
(a) (b)

Fig. 4. SEM photomicrographs of aromatic polyamide membranes cast from (a) a saltless solution (b) a solution containing 5 wt% LiCl (evaporation temp.: 90°C, evaporation period: 15min, coagulant: water)

structures of cross section, i.e., needle-like and pseudo-poreless structures. In order to investigate the effect of coagulating agent on membrane structure, four coagulating agents (water, CH_3OH , acetone and glycerine) were considered. Fig. 5 shows the influence of the four agents on the cross section structure of aromatic polyamide membranes. In Fig. 5 (a) and (b) finger-like structure appeared while (c) and (d) showed sponge-like structures. With the gelating agent such as water and CH_3OH , the rates of the exchange of the solvent and the gelating agent during precipitation of the polymer was higher than with acetone and glycerine. Fig. 6 shows the effect of the coagulating agent on the ultrafiltration rate of the aromatic polyamide membrane precipitated into water-glycerine mixture. As the precipitation rate decreased with increasing glycerine content, the cross-sectional structure became sponge-like and the ultrafiltration rate was also decreased.

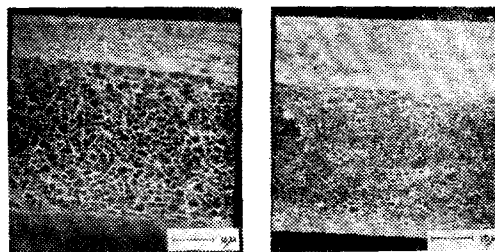
3-3. Dialysis properties

Dialysis runs were conducted on the poly(m-phenylene isophthalamide) membranes and for commercial cuprophane membranes using urea and ethylene glycol with different molecular weight. Typical dialysis data are plotted in the form of $\ln(\text{Co}/\text{Ct})$ changes with incre-



(a) (b)

Fig. 5. SEM photomicrographs showing finger structures precipitated in (a) water (b) CH_3OH (evaporation temp.: 90°C, evaporation period: 15min, casting solution: no additive)



(c) (d)

Fig. 5. SEM photomicrographs showing structures precipitated in (c) acetone (d) glycerine (evaporation temp.: 90°C, evaporation period: 15min, casting solution: no additive)

asing time of dialysis. Co is the initial concentration of solute, Ct is the concentration at time t . In dialysis runs, only membranes with significant water flux ($>30 \text{ l/m}^2 \text{ day}$) which corresponds to the value of a commercial membrane were taken into consideration. In spite of the high water flux, membranes precipitated in water showed very poor dialysis results even for urea. This indicates that the physical structure of the membrane is important for the transport of the molecule in dialysis. In this work, aromatic polyamide membranes prepared from 5 wt% of LiCl and CaCl_2 containing casting solution and precipitated in water-glycerine mixture were evaluated for the dialysis test. Fig. 7-9 show dialysis data of the ar-

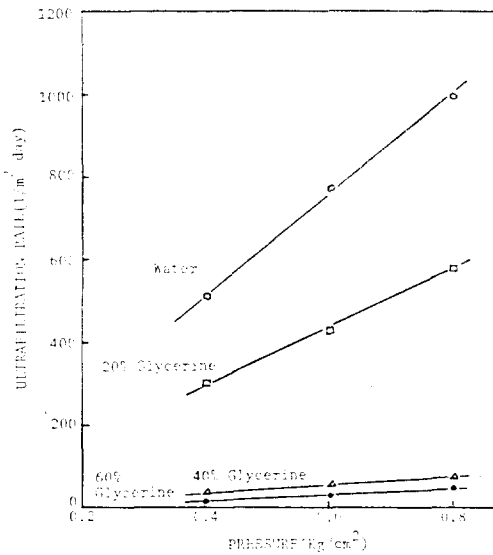


Fig. 6. Effect of coagulating agent (water-glycerine) on ultrafiltration rate.

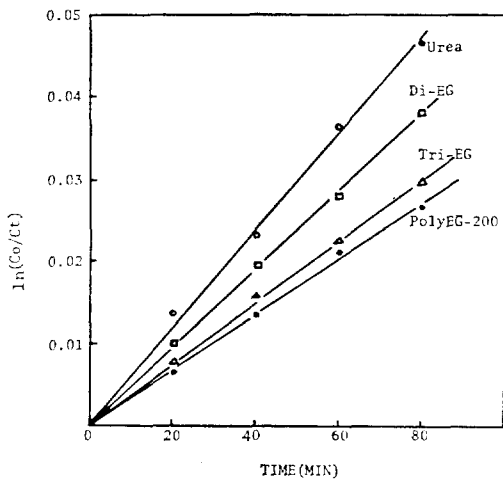


Fig. 7. Dialysis of urea and a series of ethylene glycols through MPD-I membrane precipitated in water-glycerine mixture (20wt. % glycerine).

matic polyamide membranes cast from 5wt% of LiCl containing polymer solution. As shown in these Figs. as the concentration of glycerine in coagulation mixture increases, the diffusion of the solute is lowered. Fig.10 shows

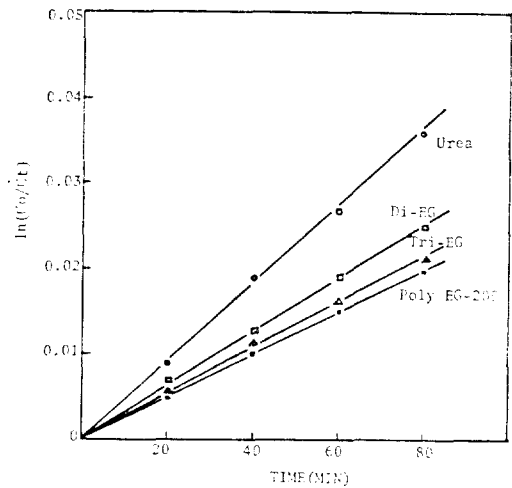


Fig. 8. Dialysis of urea and a series of ethylene glycols through MPD-I membrane precipitated in water-glycerine mixture (40wt. % glycerine).

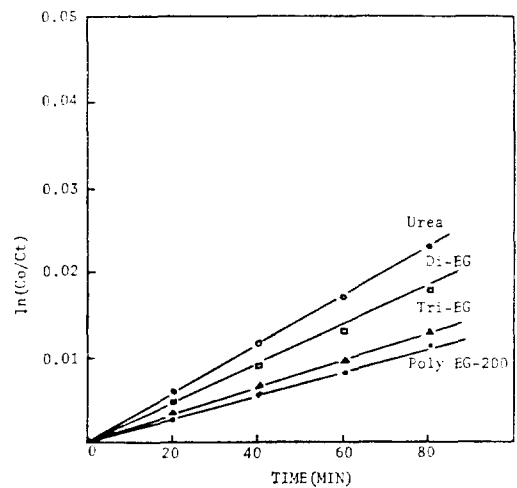
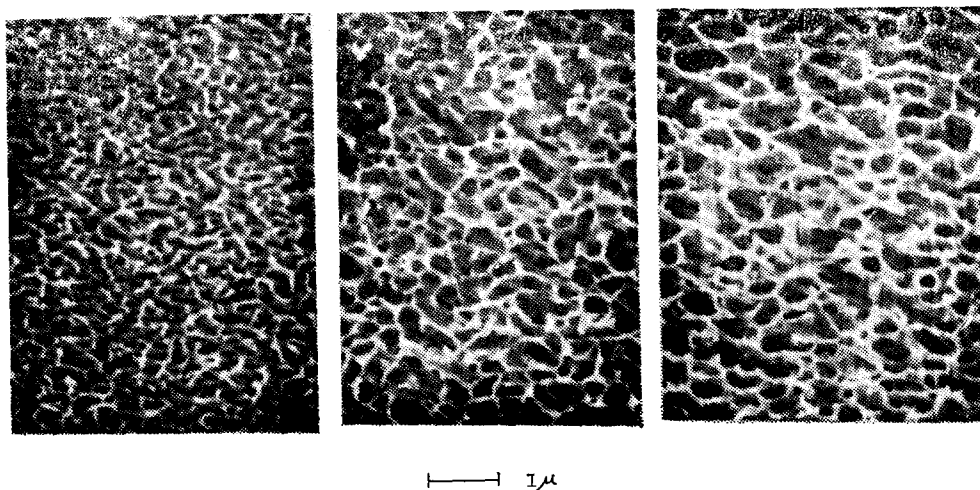


Fig. 9. Dialysis of urea and a series of ethylene glycols through MPD-I membrane precipitated in water-glycerine mixture (60wt. % glycerine).

SEM photographs of the cross sections of these membranes. As the glycerine concentration in the precipitation medium increased, a clear trend to a denser sponge-structure was observed because the precipitation rate was decre-



(a)

(b)

(c)

Fig. 10. Magnified figures of micropore structures in the previous (a)60% (b)40% (c)20% glycerine.

ased. These results of SEM observations are consistent with those of Strathmann's¹² who have observed that the cross section of Nomex membranes changes from finger to sponge structure by gradually replacing water, a good precipitant, with glycerine, a poor precipitant. The permeability coefficient is a function of the molecular size, and shape of the permeating species, the permeant-polymer interaction, the polymer morphology, the degree of cross-linking, and the degree of hydration of the membrane.

To find the relationship between the permeability coefficient and the permeant molecular weight, dialysis results for urea and ethylene glycol through the aromatic polyamide membranes were plotted in Fig.11. From this figure, it can be seen that the permeability coefficients are inversely proportional to the square root of the permeant molecular weight. The same result is given in the literature, when the dialysis runs were conducted for a commercial cellophane membrane and Kim et al.¹⁴ carried out dialysis runs for carboxylic group containing hydrophilic polymer mem-

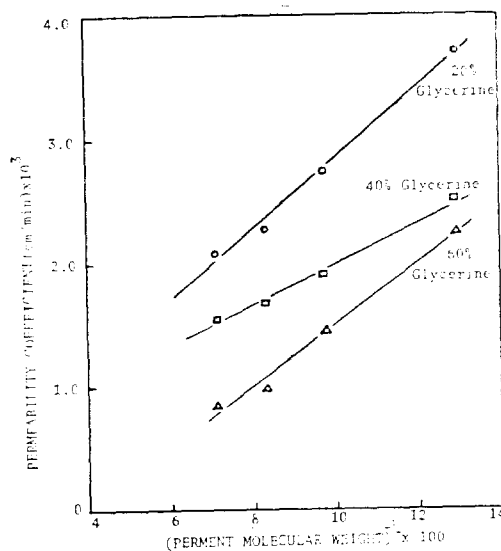


Fig. 11. Dependence of permeability coefficients of urea and ethylene glycol homolog on the permeant molecular weight.

anes. Aromatic polyamide membranes prepared from the casting solution containing CaCl_2 also gave higher water flux. The dialysis rates through aromatic polyamide membranes prepared with CaCl_2 as an inorganic salt were higher than those through the membranes

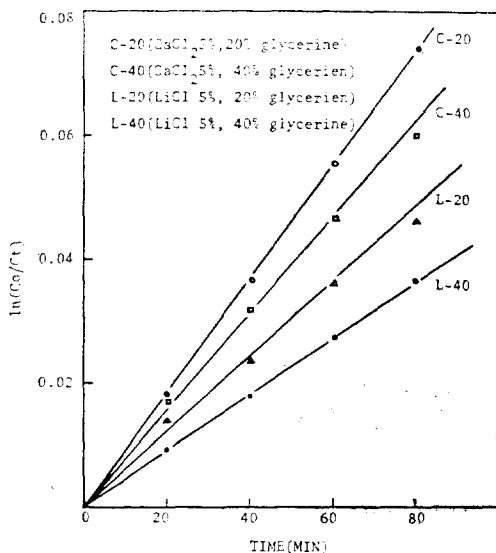


Fig. 12. Dialysis of urea through MPD-I membranes containing LiCl and CaCl₂ precipitated in water-glycerine mixture.

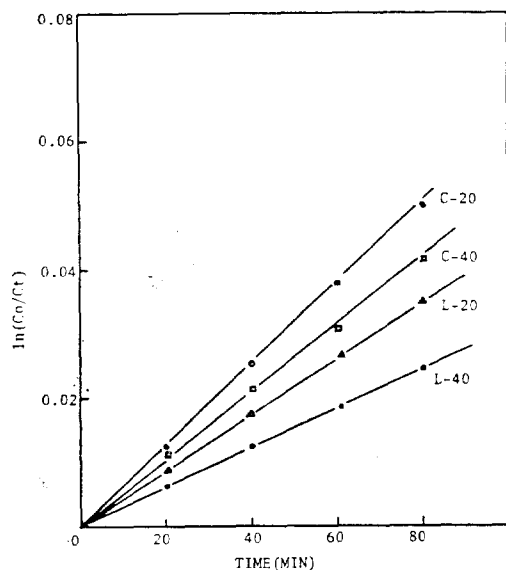


Fig. 13. Dialysis of Di-EG through MPD-I membranes containing LiCl and CaCl₂ precipitated in water-glycerine mixture.

prepared with LiCl. Fig 12-13 show these results. All the permeability coefficients through aromatic polyamide membranes are listed in

Table 1. Tabulated Results for the Permeability Coefficients of the Solutes through the Aromatic Polyamide Membranes*¹

Membranes	Permeability coefficients (cm/min)			
	Urea	Di-EG	Tri-EG	Poly EG-200
MPDI-L* ² -20* ³	0.0037	0.0027	0.0023	0.0021
MPDI-L-40	0.0027	0.0019	0.0017	0.0015
MPDI-L-60	0.0023	0.0014	0.0010	0.0008
MPDI-C* ² -20	0.0056	0.0038	0.0035	0.0027
MPDI-C-40	0.0048	0.0032	0.0023	0.0019

*¹ operating temperature and flow rate: 37°C and 200ml/min.

*² L denotes LiCl, C denotes CaCl₂ as the additive.

*³ number denotes % glycerine in the water-glycerine coagulating mixture.

Table 1.

The results obtained in this dialysis study indicate that an addition of inorganic salts into the casting solution and the choice of the proper gelating agent are important factors in determining the rate of transport of solutes through the aromatic polyamide membranes.

4. CONCLUSION

The ultrafiltration measurements and dialysis tests were performed to study the transport properties of the poly(m-phenylene isophthalamide) membranes. The morphology of the aromatic polyamide membranes were also investigated with the aid of the scanning electron microscopes(SEM).

It has been observed from this study:

(1) As the temperature of solvent evaporation increased, the water flux of the membrane decreased due to higher solvent evaporation rate which ultimately resulted thick, dense skin layer in the asymmetric membrane.

(2) An aromatic polyamide membrane cast from a binary solution, containing only polymer and solvent, exhibited a water flux of 30-50 (l/m² day) while membranes prepared

under the same conditions with an appropriate additives (LiCl , CaCl_2) exhibited a water flux as high as 1000 ($\text{l/m}^2\text{day}$).

(3) As the glycerine concentration in water-glycerine precipitation medium increased, a denser sponge structure of the membrane and lower permeation rates were observed. From the dialysis results through aromatic polyamide membranes precipitated in water-glycerine mixture, the permeability coefficients were inversely proportional to the square root of the permeant molecular weight.

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