

Electrochemical and Electrokinetic Characterization of Cellulose Acetate Polymeric Membranes

K. C. THOMAS, V. RAMACHANDHRAN and B. M. MISRA,
*Desalination Division, Bhabha Atomic Research Centre,
Bombay—400 085, India*

Synopsis

The electrochemical and electrokinetic aspects of cellulose acetate membranes of varying pore structure and desalting abilities have been investigated. The electrochemical studies included measurement of conductance and membrane potential for various membrane electrolyte systems. The electrokinetic characterization was made from streaming potential measurements. The data obtained are explained in terms of interfacial double layer phenomena prevalent in porous permselective barrier systems. The average pore diameter evaluated independently is also presented and an attempt has been made to understand the solute-water transport in terms of weak ionic character of membrane surface.

INTRODUCTION

The desalting ability of cellulose acetate membranes has been extensively studied, and numerous attempts have been made to characterize them in terms of solution-diffusion, preferential sorption-capillary flow, and irreversible thermodynamic parameters involving solute-water-membrane interactions. The above mechanisms,¹⁻³ though they adequately predict the transport properties of these membranes, do not reflect on the physical characteristics of the membranes. A few other mechanisms explain the behavior of semipermeable membranes in terms of selectivity criteria based on thermodynamic consideration⁴ and state of water in the membrane pores.⁵ Recently weak ionogenic properties of cellulose acetate membranes in electrolyte solutions have been reported.⁶ Consequently, a few electrochemical⁷ and electrokinetic aspects⁸ of cellulose acetate membranes are also investigated. However, these are not extensively studied with respect to different membranes of widely varying desalting performance.

Electrochemical characterization dealing with ion permeation through weakly permselective porous membranes is usually made by measurable parameters such as conductance and membrane potential. On the other hand, electrokinetic effects arise due to interfacial phenomena occurring in the movement of solute or solvent across a porous membrane under an applied emf or generation of potential difference (streaming potential) when the solvent is forced to flow under pressure resulting in forcible separation of oppositely charged layers at the membrane solvent interface. The magnitude of electrochemical and electrokinetic parameters is invariably related to the pore structure of membranes which incidentally affect their desalting perfor-

mance. Hence, it has become possible to characterize the desalting membranes in terms of these phenomena, which are generally observable in porous permselective matrices. The pore size of the membranes is also estimated to study the domain of validity of interfacial phenomena for membranes of ranging porosities. Cellulose acetate membranes of varying porosities are synthesized in our laboratory to study the separation possibilities of a variety of systems, relevant to nuclear industry.⁹⁻¹³ This paper deals with our studies on electrochemical and electrokinetic characterization of cellulose acetate membranes of varying pore size and their correlation with the observed water and salt permeation data.

EXPERIMENTAL

Asymmetric cellulose acetate membranes of varying porosities have been prepared as per Loeb-Sourirajan technique¹⁴ and subsequently annealing them in water baths maintained at different temperatures. AR grade sodium chloride, potassium chloride, and magnesium chloride salt solutions of different concentrations were used for characterization studies.

Performance data of these membranes were evaluated in terms of water permeation rate and solute separation using RO test cell described elsewhere.¹⁵ Feed and permeate solutions were analyzed by conductance measurement.

Membrane conductance was measured after equilibrating the samples in respective salt solutions and using platinized platinum electrodes. Concentration potential and streaming potential measurements were made with the help of a suitably designed two-compartment cell and using freshly prepared silver/silver chloride electrodes. In streaming potential measurements, hydrostatic pressure gradients were maintained using a glass capillary mounted vertically in one of the half cells, and flow measurements were made with the help of another capillary on the other side of the cell.

Poiseuille's equation expressed in a suitable form was used to calculate the average pore radius from the data on water flow under applied hydrostatic pressure, the membrane thickness, and water content¹⁶ as follows:

$$J_v = \frac{n\pi r^4 \Delta P}{8\eta l} = \frac{\epsilon r^2 \Delta P}{8\eta l} \quad (1)$$

where r = the average pore radius, $\epsilon = n\pi r^2$ (the void content and approximated to water content of the membrane), ΔP = hydrostatic pressure difference on the two sides of the membranes, η = coefficient of viscosity of water in the membrane, and l = membrane thickness.

RESULTS AND DISCUSSION

Membrane Conductance

The membrane conductance data of cellulose acetate membranes annealed at different temperatures ranging from 70 to 100°C, equilibrated in sodium chloride solutions of concentrations from 0.001M to 0.1M are presented in

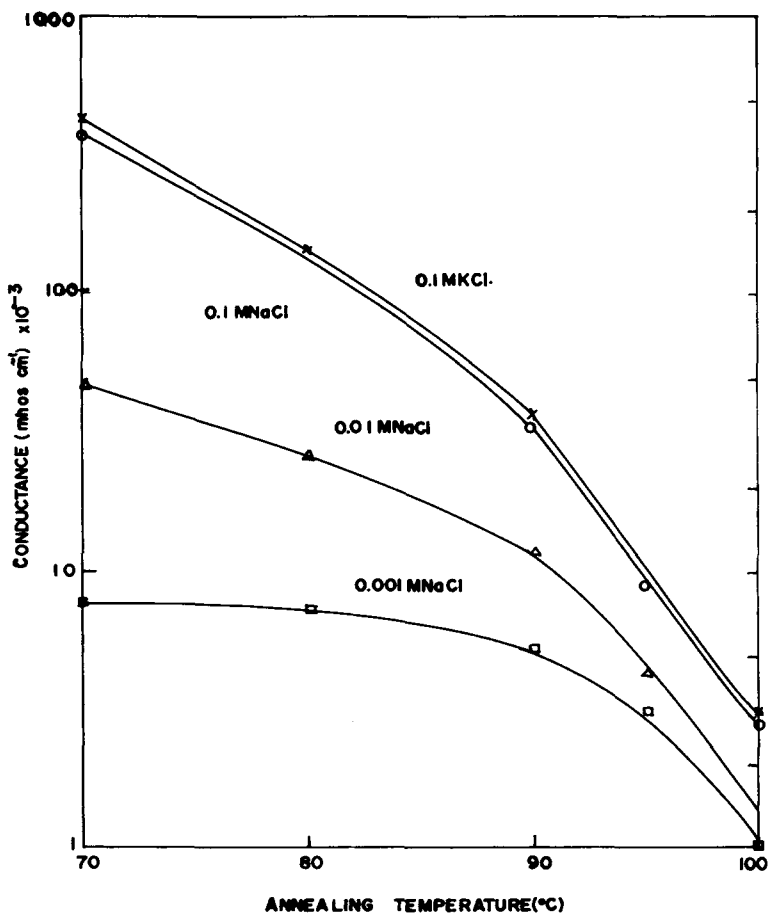


Fig. 1. Membrane conductance for different solute concentrations and annealing temperatures.

Figure 1. The results indicate that, as the annealing temperature increases, the membrane conductance decreases, more drastically for higher solute concentrations. Also, the ratio of the conductance values for different concentrations decreases with increase in annealing temperature. The decrease was observed to be gradual up to an annealing temperature of, say, 90°C, and thereafter drastic decline is noticed. This could be due to the reducing pore size of the membrane structure gradually up to 90°C and more drastically beyond. However, the membrane conductance data for unannealed membranes where more open channels exist do not indicate a simple linearity with different concentrations as observable in free solutions in the concentration range under study. This possibly indicates that solute entry into the membrane pore is somewhat restricted even in porous membranes and which could be perhaps explainable from the lower dissolving ability of bound water component of the pore water⁵ and also due to the Donnan exclusion because of the residual charge density of the membrane matrix. A charge density of 5×10^{-3} eq/L pore volume was reported for cellulose acetate membrane from simple analytical methods.⁶

TABLE I
Conductance Data for Cellulose Acetate Membranes in Various Electrolytes

Annealing temp (°C)	Membrane sp. conductance (mhos cm ⁻¹)							
	NaCl solution ($\times 10^{-3}$)		KCl solution ($\times 10^{-3}$)			MgCl ₂ solution ($\times 10^{-3}$)		
	0.001M	0.01M	0.1M	0.001M	0.01M	0.1M	0.001M	0.01M
Unannealed	10.17	50.6	411.0	12.6	52.1	454.0	10.14	—
70	7.54	47.5	364.0	9.5	52.1	425.0	8.64	45.4
80	7.3	26.4	136.4	3.63	25.1	140.4	7.82	18.9
90	5.1	11.6	33.5	5.67	12.5	37.7	5.0	8.2
95	3.11	4.18	8.63	3.31	3.2	9.68	3.14	3.38
100	0.94	1.31	2.88	1.01	1.12	3.06	0.95	1.03

The membrane conductance data for different electrolytes, namely, sodium chloride, potassium chloride, and magnesium chloride are presented in Table I.

It can be seen from Table I that the membrane conductance for potassium chloride is higher compared to sodium chloride, indicating the membrane preference for less hydrated potassium compared to sodium. This is in conformity with the increased separation noticeable in sodium chloride compared to potassium chloride. This order of selectivity appears to follow the hydrated ionic radii sequence. The various selectivity sequences are explained by attributing different attractive forces, mainly coulombic, exerted on different cations by water on the one hand and by membrane fixed charges on the other. A fixed charge of lower field strength is much less polarizable than water, and would yield the lyotropic sequence. The observed hydrated ionic radii sequence indicates the presence of weak sites of low field strength. It can be seen that the conductance for magnesium chloride was lower than that of sodium chloride equilibrated membranes, explaining better selectivity usually noticed in the case of bivalent ions.

Membrane Potential

The membrane potential data for cellulose acetate membranes annealed at different temperatures, determined by imposing a concentration difference of 0.001M/0.01M on either side of the membranes for various solute systems, are presented in Figure 2. The results indicate that the membrane potential values remain steady for membranes annealed up to 80°C, whereafter there is a drastic increase. The potential values increase more steeply for sodium chloride and potassium chloride solutes whereas, for magnesium chloride, the increase is relatively less. The potentials for all the membranes decrease in the following order, namely, K > Na > Mg. The potential values indicate that, beyond an annealing temperature of 80°C, the membranes become increasingly permselective with respect to univalent counterions. Although the concentration dependence of membrane potential and also of apparent transference number has not been determined in this paper, similar studies elsewhere have reported that this dependence is similar to what one would expect for cation exchange membranes of low ion exchange capacity.⁷

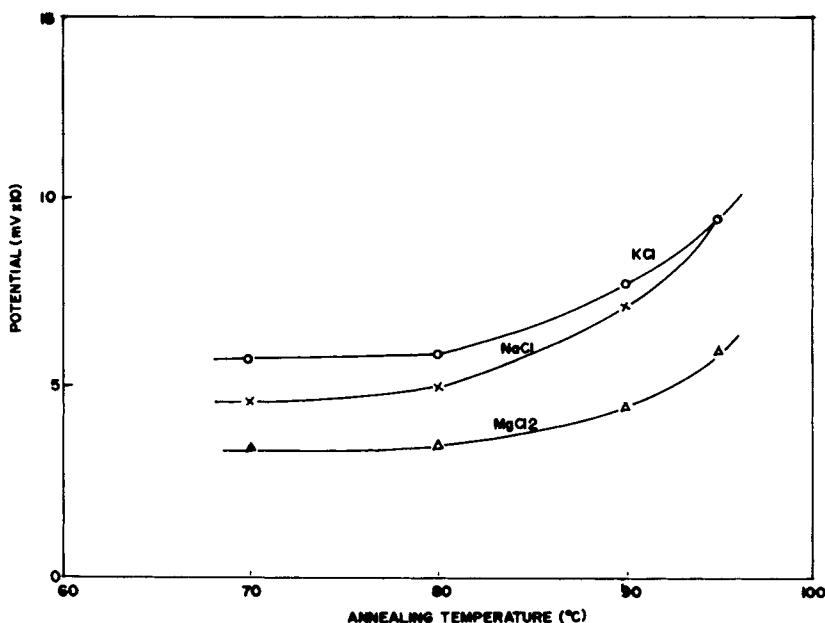


Fig. 2. Membrane potential for various solute systems.

It has been reported¹⁷ that the transport number of sodium in annealed cellulose acetate membranes varies from 0.85 to 0.03 at external concentrations of 0.0035–0.075*M*, respectively, which also indicate that annealed cellulose acetate membranes behave as low capacity ion exchange membranes. This low cation exchange capacity obviously cannot account for the high degree of desalination with feed concentrations as high as 0.5*M*. However, the salt concentration inside the membranes is very low, as indicated by our conductance data.

An increase in annealing temperature of cellulose acetate membranes leads to a decrease in volume flow and a corresponding increase in the permselectivity for solute. This can be seen from the RO performance data reported in Table II. This is consequent to the reduction of the pore size with annealing

TABLE II
RO Performance Data for Cellulose Acetate Membranes of Different Porosities^a

Annealing temp (°C)	Tubular membranes	
	Water flux (L m ⁻² d ⁻¹)	Solute separation (%)
70	4200	45.0
80	1800	78.0
85	1180	91.0
90	700	95.0
95	300	97.5

^a Feed 5000 ppm NaCl; evaporation time 40 s; Pressure 40 kg/cm².

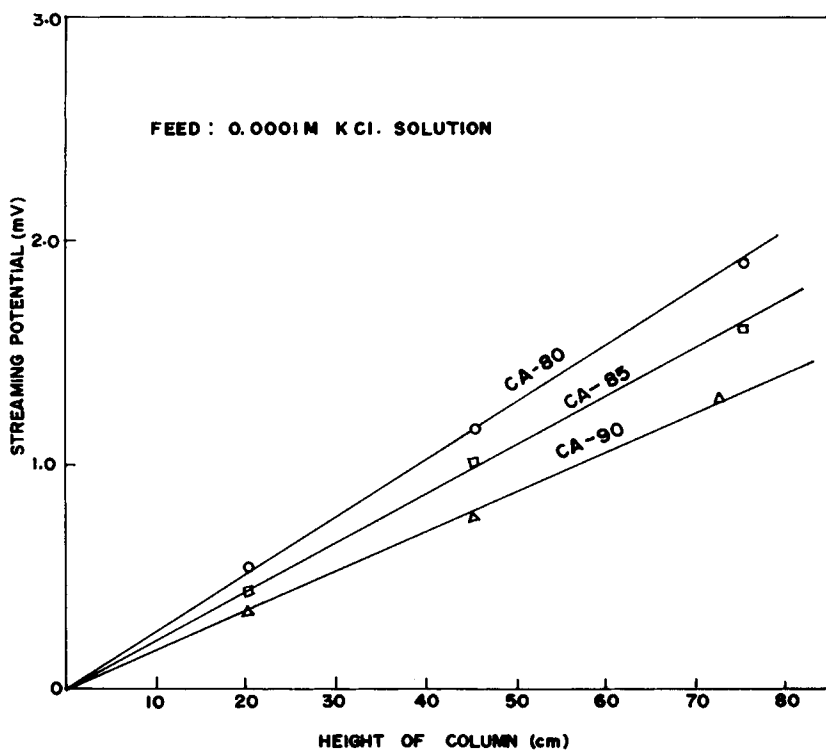


Fig. 3. Streaming potential values for cellulose acetate membrane.

as the pore walls are lined with negative charges⁶ (presumably carboxyl groups), which partially exclude coions from pores. This becomes more effective as the pore radius decreases.

Streaming Potential

The streaming potential values measured for cellulose acetate membranes annealed at 80, 85, and 90°C are reported as a function of applied hydrostatic pressure head in Figure 3. It can be seen from the figure that the streaming potentials were found to increase linearly with increasing hydrostatic pressure head for all the membrane samples. The streaming potentials were observed to be higher for 80°C annealed membranes than for 90°C annealed membranes.

The streaming potentials measured for millipore filter membrane (0.45 μm pore size) for different electrolytes are shown in Figure 4, as a function of hydrostatic pressure head. The potentials were found to be higher than that by cellulose acetate membrane systems. The decreasing potential values with decreasing pore size of membranes are clearly demonstrated in the two figures.

Also the streaming potential values decrease in the following order, namely, $\text{Na} > \text{K} > \text{Mg}$, which incidentally coincide with the order of solute transfer through the membranes.

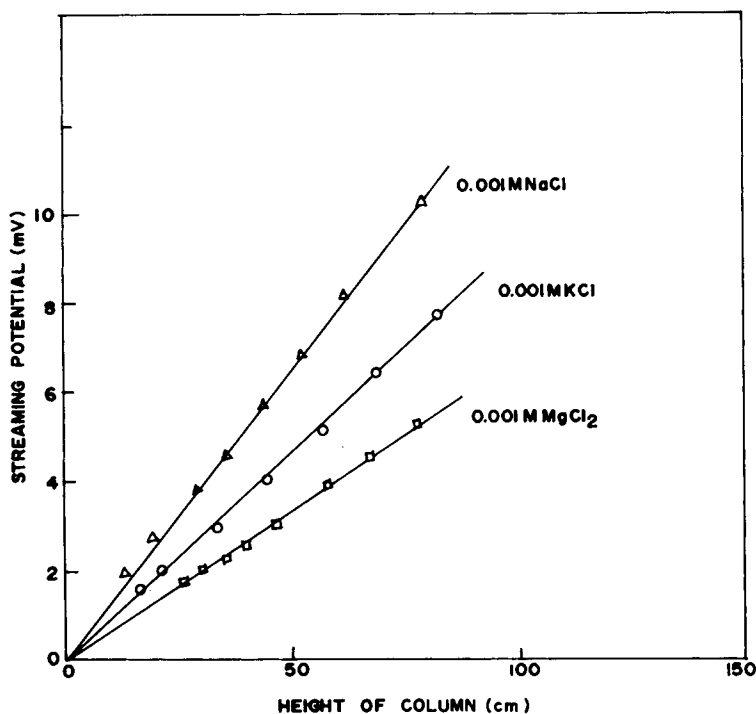


Fig. 4. Streaming potential values for millipore filter.

The decrease in streaming potential values with increasing annealing temperatures is clearly demonstrated in Figure 5. It can be seen that the streaming potential values decrease beyond 80°C annealing temperature, which also coincides with the sudden increase in membrane potential values and a corresponding decrease in conductance data noticed in Figures 2 and 1, respectively. The increase in streaming potential values for all the membranes with decrease in electrolyte concentrations is also expected from the classical electrokinetic phenomena noticeable in permselective porous membranes.

It is well known that there exists a double layer of electrical charges of opposite signs at the solid-liquid boundary, the thickness of which depends on the surface charge density, nature, and concentration of electrolyte and the diameter of the capillary. With decrease in membrane pore radius, the electrical double layers on the pore walls approach each other, and, as the pore size is comparable to the thickness of the double layers, the double layers collapse and get blurred. As the double layer thickness is of the order of a few molecular thickness only, in annealed cellulose acetate membranes where the average pore size is also of similar magnitude, the streaming potential values are lower in annealed cellulose acetate membrane systems.

It is also suggested^{6,18} by a few authors that, for weakly charged cellulose acetate membranes, there is a possibility of development of streaming potential with applied pressure because of the movement of water across the double layer formed at the membrane interface due to fixed charge density. The

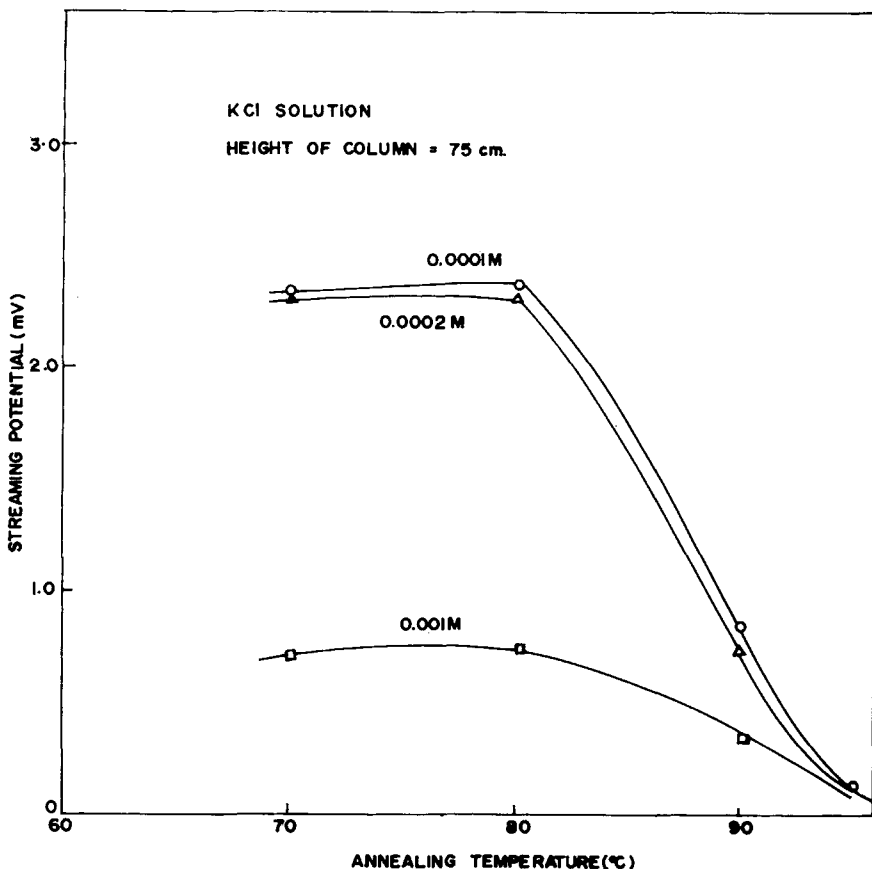


Fig. 5. Streaming potential data for different annealing temperatures for CA membranes.

magnitude and direction are likely to affect the solute and solvent permeation through the membranes.

Pore Size

The average pore radius determined using transformed Poiseuille's equation for cellulose acetate membranes annealed at 85, 90, and 95°C are presented in Table III. The results indicate that the average pore size vary between 4.6 and 1.7 Å. It can be seen from the performance data (Table II) that the transport properties are not fully explainable with pore size alone as it is seen that, although between 90 and 95°C annealing temperature, the pore diameter decreases only by 50%, whereas the % solute separation and permeate flux change sharply. The conductance, membrane potential, and streaming potential data also indicate a sharp change beyond 90°C annealed membranes where the average pore diameter is < 3 Å, indicating the significance of membrane surface charges in this domain. Below 85°C annealing temperatures where the average pore diameter is > 5 Å, these properties appear to assume lower significance, indicating the domination of solution properties. Apart from the modified Poiseuille's equation, other methods^{19,20} are also currently

TABLE III
Average Pore Diameter of Cellulose Acetate Membranes Annealed at Various Temperatures

Annealing temp (°C)	Water flux (mL/cm ² s)	Hydrostatic pressure (dyn/cm ²)	Average pore diameter (Å)
85	4.38×10^{-6}	6.77×10^4	4.58
90	2.39×10^{-6}	7.31×10^4	3.10
95	4.78×10^{-7}	4.61×10^4	1.68

being explored to check the average pore radius of the membranes. These studies will be separately communicated shortly.

It is also worthwhile to mention the state of water in the membrane pore, which is also reported⁵ to be responsible for the selectivity. It is well known that the total water content of the desalting membranes is composed of capillary and bound water. The extent of bound water which is attached with the functional groups of the polymer seems to play an important role. With the increasing annealing temperature, both capillary and bound water molecules are lost, resulting in closing of rings of membrane matrix. The infrared spectral studies of annealed cellulose acetate membranes have reported the presence of largely monomeric water molecules, which have lower ability to hydrate the ions, explaining their desalting ability. The NMR and differential scanning calorimetric studies²¹⁻²³ have also demonstrated the existence of nonfreezing monomeric water molecules in cellulose acetate membranes. The morphological effects of thermal annealing of cellulose acetate membranes are also important in explaining its electrochemical and electrokinetic parameters. A correlation between these parameters and glass transition temperature of the cellulose acetate may be present. X-ray diffraction studies²⁴ have shown that cellulose 2.5 acetate with which the reverse osmosis membranes are largely prepared is mostly amorphous, with low degree of crystallinity. Typical of the behavior of the amorphous polymers, cellulose acetate undergoes second-order glass transition and the glass transition temperature (T_g) varies significantly with plasticizer content.²⁵ T_g of the wet cellulose acetate membrane is lowered to 80°C from 115°C reported for the dry state.²⁶

CONCLUSION

The membrane conductance, membrane potential, and streaming potential values change significantly for cellulose acetate membranes of various porosities. The existence as well as the decline of streaming potential for annealed cellulose acetate membranes indicate the role of surface charges on the water and solute permeation. Comparison of average pore size data with the observed conductance, membrane potential, and streaming potential values indicate that, in the pore size region of less than 3 Å, membranes annealed at 90°C, a decrease in streaming potential and membranes conductance values point out the possibility of disruption of electrical double layer at the interface, resulting in the effective exclusion of salt. In the pore size region of above 5 Å (membrane annealed at 85°C), high streaming potential and membrane conductance values indicate that the coulombic interaction be-

tween the surface charges and solution counterions facilitate formation of double layer at the interface and salt permeation through membrane pores is noticed.

It has been reported²⁷ that the ratio of bound water molecules to hydroxyl groups on the polymer matrix decreases from about six for unannealed membrane to about two at 84°C. Hence, the existence of larger molecular clusters in unannealed membranes on the one hand and the existence of monomeric and dimeric water molecules on the annealed membranes on the other hand reportedly account for their varying desalting performance.

The authors wish to thank Dr. M. P. S. Ramani, Head, Desalination Division, for his keen interest and kind encouragement throughout the course of this study.

References

1. H. K. Lonsdale, U. Merten, and R. C. Riley, *J. Appl. Polym. Sci.*, **9**, 1341 (1965).
2. O. Kedem and A. Katchalsky, *Biochem. Biophys. Acta*, **27**, 229 (1958).
3. S. Sourirajan, *Reverse Osmosis*, Logos, London, 1970.
4. E. Gluekauf, First Int. Symp. on Water Desalination, Washington, DC, 1965, Vol. 1, p. 163.
5. C. Toprak, J. N. Agar, and M. Falk, *J. Chem. Soc., Faraday Trans. I*, **75**, 803 (1979).
6. H. V. Demisch and W. Pusch, *J. Electrochem. Soc.*, **123**, 370 (1976).
7. S. G. Wong and J. C. T. Kwak, *Desalination*, **15**, 213 (1974).
8. R. C. Srivastava and A. K. Jain, *J. Polym. Sci.*, **13**, 1603 (1975).
9. V. Ramachandhran and B. M. Misra, *J. Appl. Polym. Sci.*, **27**, 3427 (1982).
10. V. Ramachandhran and B. M. Misra, *J. Appl. Polym. Sci.*, **28**, 1641 (1983).
11. V. Ramachandhran and B. M. Misra, *J. Appl. Polym. Sci.*, **30**, 35 (1985).
12. S. Prabhakar and B. M. Misra, *J. Membr. Sci.*, **29**, 143 (1986).
13. S. Prabhakar and B. M. Misra, *Radiochim. Acta*, **39**, 93 (1986).
14. S. Loeb and S. Sourirajan, *Adv. Chem. Ser.*, **38**, 117 (1963).
15. V. Ramachandhran, Ph.D. Thesis, Bombay University, 1984.
16. R. E. Lacey and S. Loeb, *Industrial Processing with Membranes*, Wiley-Interscience, New York, 1972.
17. D. N. Bennion and B. W. Rhee, *Ind. Eng. Chem. Fundam.*, **8**, 36 (1969).
18. K. S. Spiegler and J. H. Macleish, *J. Membr. Sci.*, **8**, 173 (1981).
19. N. Lakshminarayanaiah, *Transport Phenomena in Membranes*, Academic, New York, 1972, p. 325.
20. S. Sourirajan and T. Matsuura, *Reverse Osmosis/Ultrafiltration Process Principles*, National Research Council, Ottawa, Canada, 1985, p. 331.
21. M. A. Frommer, M. Shporer, and R. M. Messalem, *J. Appl. Polym. Sci.*, **17**, 2263 (1973).
22. M. A. Frommer and D. Lancet, *J. Appl. Polym. Sci.*, **16**, 1295 (1972).
23. Y. Taniguchi and S. Horigome, *J. Appl. Polym. Sci.*, **19**, 2743 (1975).
24. J. H. Daane and R. E. Barker, *Polym. Lett.*, **2**, 343 (1964).
25. U. Merten, *Desalination by Reverse Osmosis*, M.I.T. Press, Cambridge, MA, 1966.
26. R. D. Sanderson and H. S. Pienaar, *Desalination*, **25**, 281 (1978).
27. A. L. Vincent, M. K. Barsh, and R. E. Kesting, *J. Appl. Polym. Sci.*, **9**, 2363 (1965).

Received October 20, 1986

Accepted March 16, 1987