

Microporous Clay Membrane Materials for Reverse Osmosis Applications. I. Performance Characteristics from Osmotic Studies

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Synopsis

Fired clay membranes were prepared from montmorillonite clay and also by incorporating protein (lysozyme) and nylon (copolymer of 6-amino caproic acid) to clay followed by firing these membranes at different temperatures for different durations of time. Osmotic behaviors of the membranes were studied, and the results were correlated to the porosity determined by scanning electron microscope. Reverse osmosis parameters, namely, the reflection coefficient, solute permeability, and rejection coefficient, of the membranes were determined from osmosis experiments. Rejection coefficients as determined from reverse osmosis were compared with those obtained from osmosis experiments.

INTRODUCTION

Reverse osmosis or ultrafiltration technology has witnessed a tremendous growth potential in recent years since its inception in the early sixties. It has now gained acceptance as one of the most sophisticated and economic means for the preparation of water suitable for drinking, agriculture, and other, industrial purposes. The cellulosic membranes as developed by Loeb and Sourirajan¹ still continue to be the better choice for such applications due to their excellent solute selectivity and water permeability. Other polymeric membranes including polyamides and imides, polycarbonate, poly(vinyl acetate), polyethers, and polyurethanes, polytetrafluoroethylenes, etc. and some liquid membranes such as poly(vinyl methyl ether)²⁻⁴ have been tried.

Besides the synthetic polymeric membranes, there are some reports on^{5,6} rejection characteristics of compacted Wyoming bentonite clay. McKelvey & Milne⁷ studied salt filtration through compacted bentonite clay under hydraulic pressure of 10,000 psi and observed significant salt rejection. Srivastava⁸ studied osmotic and electroosmotic behaviors of compacted kaolinite and bentonite clays and made a detailed investigation with polymeric surfactants like poly(vinyl methyl ether). These studies were based on compacted clays but no report on clay membrane is available.

In this paper, the authors report a detailed investigation on the performance characteristics of completely new types of 3-dimensional microporous fired clay membranes suitable for reverse osmosis applications. As porosity⁹⁻¹¹ has an important role in controlling the RO performance of a membrane, the authors have incorporated protein (lysolyse) and nylon(co-polymer of 6-amino caproic acid) into clay particles and fired the green membranes to develop

required porosity and to reduce charge density. Synthetic polymeric membranes are associated with some shortcomings, namely, biodegradability, hydrolytic vulnerability, etc. Besides, their glass transition temperature being low, they can't function over a wide temperature range. In the case of fired clay membranes, the shortcomings could be overcome. The obvious advantages of these new membranes include easy availability and low cost of preparation.

THEORY

The phenomenon of development of osmotic pressure is a manifestation of free energy change and is associated with the chemical potential difference of solutions of different concentrations across the membrane surfaces. As a result, the solvent molecules pass from a lower to the higher concentrated solution to bring the system in a state of thermodynamic equilibrium. Reverse osmosis being an irreversible process, a pressure greater than the osmotic pressure of solution must be applied in order to reverse the flow of solvent, i.e., from higher to lower concentration side without allowing salt permeation. So solute selectivity is one of the most important factors to be reckoned with.

The knowledge of osmotic pressure which is indispensable to carry out reverse osmosis experiment can be gathered from the deduction by Michael¹² from thermodynamic consideration and that is

$$\Pi = \frac{V_s}{(V_s - \Delta\vartheta)} \cdot \frac{W}{(100 - W)} \cdot \frac{RT}{GMW} \text{ atm/cm}^2 \quad (1)$$

where V_s = original volume of brine in the reservoir, $\Delta\vartheta$ = volume of solvent transmitted for a certain period of time, W = percentage weight of salt in solution, R = gas constant, GMW = gram molecular weight of sodium chloride, and T = temperature (K). It is possible, therefore, at all stages of flow, to determine the osmotic pressure from the above expression.

At the initial stage of flow, where no transfer of solvent takes place, $\Delta\vartheta = 0$, $V_s(V_s - \Delta\vartheta) = 1$, Eq. (1) takes the form

$$\Pi = \frac{W}{(100 - W)} \frac{RT}{GMW} \quad (2)$$

But the transport process discussed so far is based on the basis of nonporous ideal membranes and therefore solvent flux and osmotic pressure are related as

$$J_v = L_p(\Delta P - \Delta\Pi) \quad (3)$$

where L_p is a phenomenological coefficient known as a filtration coefficient and ΔP and $\Delta\Pi$ stand for hydrostatic and osmotic pressures, respectively.

Fired clay membranes, like most other membranes, are not ideally semipermeable as diffusion along with osmosis constitutes the transport process through them. These membranes, therefore, should be treated as leaky membranes, and hence the mechanism of transport process demands the inclusion

of solute permeation factor (σ)¹³ for solvent as well as solute transport. Equation (3) becomes

$$J_v = L_p(\Delta P - \sigma\Delta\Pi) \quad (4)$$

and the solute flux (J_s) is related to J_v as

$$J_s = \omega\Delta\Pi + C_s(1 - \sigma)J_v \quad (5)$$

where C_s and ω are respectively average solute concentration of solutions in the two compartments and solute permeability. σ is the reflection coefficient.

When $J_v = 0$, i.e., the flow of solvent is virtually stopped, i.e., when solute diffusion overtakes solvent flow, eq. (5) takes the form

$$J_s = \omega\Delta\Pi \text{ and hence } \omega = \left(\frac{J_s}{\Delta\Pi} \right)_{J_v=0} \quad (6)$$

The three osmotic parameters, viz., L_p , σ , and ω describe the salt rejection properties of a membrane system and the values predict the efficiency of it as a hyperfilter which will be shown later.

Salt rejection performances of the membranes were assessed by using formalism developed by Johnson¹⁴ et al. The salt rejection coefficient r as described by them is

$$r = 1 - \frac{C_{\text{eff}}}{C_R} \quad (7)$$

where C_{eff} and C_R are respectively the concentrations of filtered and reservoir solutions.

At different flow rates,

$$F = \frac{(\sigma - r)}{\sigma(1 - r)} \quad (8)$$

where the flow parameter is defined as

$$F = e^{-J_v} \cdot A \quad (9)$$

and

$$A = \frac{(1 - \sigma)\Delta x}{nRT\omega} \quad (10)$$

n is the number of ions given by one mole of electrolyte on complete dissociation (e.g., for sodium chloride, $n = 2$), R is as usual the gas constant, and T is the temperature (K). The modified form of eq. (8) is

$$\frac{J_v}{2RT} = \frac{2.303\omega}{\Delta x(1 - \sigma)} \log \frac{\sigma(1 - r)}{(\sigma - r)} \quad (11)$$

where Δx is the thickness of the membrane. At high flow rate of solvent, i.e., when filtration flow overtakes diffusion of solute, $F \rightarrow 0$ and hence $r \rightarrow \sigma$ (when $J_v \rightarrow \infty$).

It is, therefore, possible to predict that, for every membrane specimen, the rejection coefficient value (r) equals its reflection coefficient value σ at a high flux rate, and, therefore, determination of σ provides an idea of the salt rejection capability.

Thus simply from osmotic experiments it is possible to determine the rejection coefficient from a plot of ΔP vs. J_v in eq. (4).

The plot of ΔP vs. J_v gives a straight line, the slope of which provides L_p , and σ can be determined from the relation

$$\sigma = \frac{\text{intercept}}{L_p \times \Delta \Pi} \quad (12)$$

It is to be mentioned here that, with the progress of reverse osmosis flow, solute concentration is increased in the vicinity of the flushing surface and as a result of development of difference in concentrations between solutions at the membrane surface and in the main bulk of feed, "concentration polarization"¹⁵ comes into play. This newly built quantity tends to create a kind of disadvantage, since the effective osmotic pressure which must be exceeded is increased. Factors which favor the development of concentration polarization are porosity¹⁶ of larger dimension, solute of higher molecular weight particularly at higher concentrations,¹⁷ and low operational pressure. The effect of concentration polarization in case of fired clay membranes was not pronounced because the pores within membranes were microporous so that a large surface area was packaged in a small volume and partly because the molecular weight of solute was not so high and concentration of brine used was smaller (decimolar). In addition, pressure as high as 10 atm/cm² was employed against required minimum pressure of 2.5 atm/cm², as calculated from eq. (2) above, to cause reverse osmosis flow. Despite all the efforts to minimize concentration polarization, there was still a trend of flux decline with time due to the absence of turbulence in the feed.

EXPERIMENTAL

Material

Protein Clay Complex

Protein clay complex was prepared by following the method of Harter and Stotzky.¹⁸ Less than 2 $\mu\mu$ fraction of montmorillonite clay was separated by following the usual process of dispersion and sedimentation and converted into hydrogen form. The hydrogen clay was dialyzed to free from soluble ions and was allowed to react with lysozyme immediately to avoid the probability of migration of aluminium from the crystal lattice to exchange sites.

The clays were centrifuged to a thick slurry (approx. 12% w/v) and stored at 5°C until use. Sufficient volume of approximately 3.3% (w/v) clay suspension to provide 10 g of clay (in dried condition) were pipetted and divided in a

number of polypropylene centrifuge tubes. Glass distilled water ($4 \times$ distilled) was added to each tube to bring the volume to the same level in each tube. The suspension from each tube was centrifuged and the supernatant discarded. The centrifugates from all the tubes were resuspended in sufficient glass distilled water. A volume of 100 mL aqueous solution of lysozyme of analytical grade (8% w/v) was added to the total aqueous clay suspension, thoroughly mixed, and allowed to stand for 1 h. Clay-protein complex thus formed was then centrifuged and the supernatant discarded. The centrifugate was stored in a refrigerator for the preparation of green membrane.

Nylon-Clay Complex

Preparation of Clay-Amino Caproic Acid Monomer. Clay-amino caproic acid complex was prepared by adopting the method of Kato and co-workers.¹⁹ Calcium clay prepared by ion-exchange reaction of the calcium form of resin with clay suspension was allowed to react with 6-amino caproic acid (AR grade) and the clay-amino caproic acid monomer was washed with methanol until free of chloride ion. Approximately 10 g of clay suspension were treated with 250 mL of methanol solution of 10% (w/v) amino caproic acid and allowed to stand for 15 days. The clay monomer complex thus formed was separated by centrifugation and dried *in vacuo*. The complex was ground to pass 100 mesh and washed with *n*-hexane in a Soxhelt extractor for 6 h to remove excess caproic acid.

Conversion of Monomer into Polymer. Polymer complex was prepared by heating the monomer in a furnace at 240–250°C for 1 h in nitrogen atmosphere. The unreacted caprolactone was removed by leaching the product several times with methanol-water mixture.

Membrane Preparation. (a) *Preparation of green membranes:* Clay-protein, clay-nylon, and simple clay were separately treated with double distilled water to get a pasty mass for each of them. The clay-water ratio was adjusted in such a manner as to impart a membrane thickness of 0.5 cm (in perfectly dried condition). Cracking of membranes during drying operation was avoided by adopting the method of Takahama.²⁰ Membranes were contacted intermittently with hot air at 130°C in a drying chamber and brought out of the furnace for several times and finally annealed.

(b) *Conversion of green membranes into porous ones (firing of membranes):* Green membranes were heated in a furnace where temperature was gradually raised to and then maintained at 100°C for 24 h. The membranes were then fired in a muffle furnace when the temperature was raised gradually to the desired limit and were maintained for a specified period. The membranes were then annealed before bringing them back to room temperature.

Scanning electron microscopic (SEM) studies for pore size and pore density: To relate flux values with the porosity of the membranes, scanning electron microscopic study is of great importance. All the membrane specimens were coated with gold, and microphotographs were taken.

Trends in the reduction of pore size was noticed above 750°C and sintering of clay particles completed at around 900°C as a result of destruction of crystal structure of clay anhydride due to the formation of SiO₄ tetrahedral linkage through all four oxygen atoms. This morphological change was con-

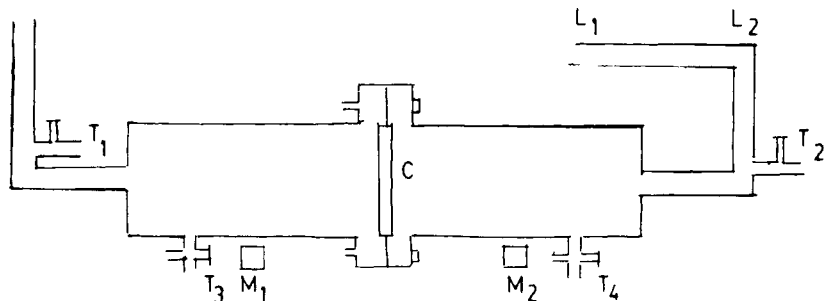


Fig. 1. Osmosis cell: (T_1, T_2, T_3, T_4) stopcocks; (M_1, M_2) magnetic stirrers; (C) membrane; (L_1, L_2) capillary tube.

firmed by X-ray measurement as well as infrared spectrum by Komarov and co-workers.²¹ It is expected, therefore, that membranes prepared by firing at 800°C should have possessed pores of smaller size and hence the authors avoided taking microphotographs of these fired membranes. SEM studies of the membranes prepared by firing green ones at 900°C, however, were done to find the degree of pore shrinkage for comparison.

Cell Assembly

Osmosis Cell

The schematic diagram of the osmosis cell used for the measurement of osmotic parameters is depicted in Figure 1.

The cell consists of two halves. Sodium chloride solution was taken on the left-hand side and double distilled water on the right-hand side of the cell. The membrane was placed into the groove of the two halves jacketed by two perforated stainless steel discs having one on each side. The membrane-disc combination was fixed into the groove by an adhesive insoluble in water. The two halves were then bolted together with the help of nuts and washers to make the system perfectly water tight.

RO Cell

A sketch of the cell designed for carrying out reverse osmosis experiments is shown in Figure 2. It consists of two halves made of gun metal. The feed half is fitted with a movable piston which is connected to a piston rod for pressure application. The lower half is provided with an outlet tube to collect filtered solution for the study of water flux and salt concentration of effluent solution. Experimental solution of strength (0.1M) was fed into the upper half, and the membrane disc combination was fixed into the grooves with the aid of an adhesive of same nature as mentioned in the case of the osmosis experiment. The two halves were then bolted to make the system water tight.

Determination of Osmotic Parameters. (*a*) L_p and σ : A solution of sodium chloride of known strength (0.01M) was taken in the left-hand compartment and distilled water ($2 \times$ distilled) in the right-hand side of the cell. The whole system was kept at $35 \pm 0.1^\circ\text{C}$ in a thermostat. The system was allowed to stand for some time in order to allow the liquid column in the

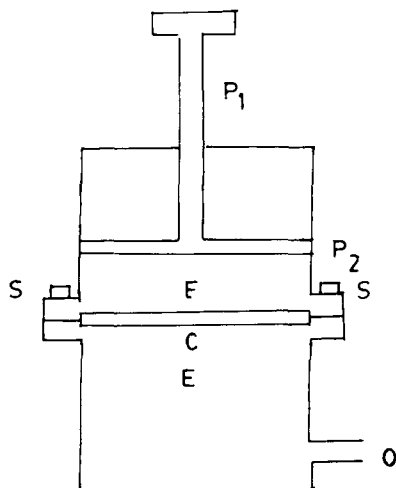


Fig. 2. RO cell: (F) feed half; (E) filtration half; (P_1) piston rod; (P_2) piston; (S) screws; (O) exit tube.

capillary L_1L_2 to stop. The water column in the tube was adjusted on the solution compartment, and the rate of advancement of liquid meniscus in the capillary was noted with time. Since the back flow of water in the solution compartment due to osmosis was negligible, the value of $\Delta\Pi$ can be taken to be more or less constant. To maintain the constancy of $\Delta\Pi$ in all such runs, the solution in the osmosis cell was replaced by a fresh stock solution of the same concentration before the measurement of volume flux for the next ΔP .

A plot of J_v vs. Δp showed a straight line, from the slope of which value of L_p was determined directly and with the knowledge of L_p and $\Delta\Pi$ [determined from eq. (2)], the value of the reflection coefficient was calculated from expression (12).

(b) *Determination of ω* : The basic condition for the determination of ω is that the solute migration through the membrane should be such as to completely stop solvent flow and under this condition it is possible to determine the value of ω by using eq. (6).

In actual experiment, a solution of sodium chloride of known concentration (0.01M) was filled, as in the previous experiment, in the left-hand side of the cell and double distilled water in the other. The condition J_v equal to zero was maintained on the system by adjusting the water column of the tube so that liquid meniscus on the capillary L_1L_2 remained stationary. The whole operation was conducted as before at a temperature of $35 \pm 0.1^\circ\text{C}$. The solutions in the two compartments were vigorously stirred with the help of magnetic stirrers M_1 and M_2 shown in Figure 1. After a period of time (10h in the present case), the solutions from the compartments were withdrawn and analyzed for sodium chloride by flame photometer. The amount of sodium chloride lost by solution compartment or that gained by the solvent compartment divided by the product of time and membrane area gave the value of J_s , the solute flux, and this divided by the osmotic pressure gave the value of solute permeability [eq. (6)].

TABLE I
Variation of Pore Size and Pore Density with Temperature and Duration of Firing for Different Types of Fired Clay Membranes as Shown by SEM

Types of membrane	Temperature of firing (°C)	Duration of firing (h)	Pore diameter (Å)	Pore density ($\times 10^{-5}/\text{cm}^2$)
Simple clay	600	1.0	3.53	0.82
		2.0	14.0	0.89
	700	1.0	7.50	2.70
		2.0	29.60	2.30
		6.0	26.25	2.03
		2.0	3.46	3.3
Protein-clay	600	1.0	3.20	1.022
		2.0	10.59	1.01
	700	2.0	31.10	1.07
		6.0	31.50	0.82
		1.0	15.88	1.34
		2.0	40.00	1.001
Nylon-clay	600	6.0	38.82	0.087
		1.0	24.70	1.135
		2.0	6.00	0.60
	700	6.0	6.80	0.67
		1.0	10.00	2.34
		2.0	16.00	1.74
900	700	6.0	18.00	1.40
		1.0	18.00	1.40
		2.0	34.80	2.14
	900	6.0	37.02	1.87
		1.0	14.0	1.60
		2.0	6.0	1.67
		6.0	6.4	1.60

RESULTS AND DISCUSSION

It was observed that, for all the membranes, pores of maximum dimension were obtained when these were fired at 700°C for a duration of 2 h (Table I). All osmotic studies, had, therefore, been confined to the membranes prepared under the above experimental condition with the expectation of better membrane performance with respect to water permeation. L_p and σ values were calculated from the curves of J_v vs. Δp (Fig. 3) and recorded (Table II).

A plot of r [calculated by using eq. (11)] vs. J_v/nRT (Fig. 4) indicates that r increased with the increase of J_v and reached a limiting value ($\sigma = r$) at higher flux rates of solvent and remained constant, in spite of increasing the rate still further.

This gave an indication that, in order to get maximum salt rejection by a particular membrane specimen in the RO experiment, the flux rate must be increased.

It was observed from osmotic data (Table II) that the performance characteristic of nylon clay membrane was superior to any other membrane, particularly when flux rates were concerned. Salt rejection behavior of simple clay, however, was better, but it showed very little promise for the poor flux rate.

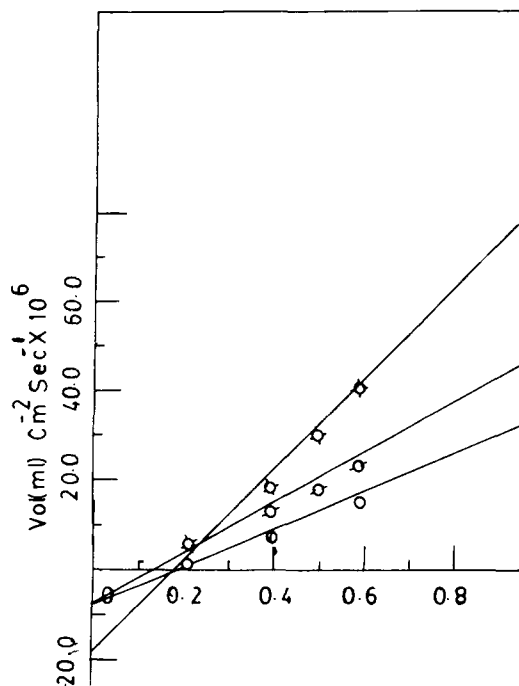


Fig. 3. Pressure applied in atm; the membranes were prepared by firing at 700°C for 2 h. The determination of L_p and σ was from eq. (4): (○) Clay membrane; (○) lysozyme-clay membrane; (◻) nylon-clay membrane.

It was also noticed that, for all the membranes, water flux increased with duration of firing and reached a constant limiting value when fired at around 2 h without further increase of the same in spite of firing for longer durations (Fig. 5).

The constancy of flux beyond 2 h of firing was supported by the constancy of pore size at and beyond 2 h of firing as determined by SEM (Table I).

TABLE II
Variation of J_v with ΔP for Membranes Prepared by Firing at 700°C for 2 h^a

Type of membrane	ΔP (atm)	J_v (mL cm ⁻² s ⁻¹ × 10 ⁶)	L_p (cm s × 10 ⁶)	σ	$\Delta \Pi$ (atm)
Simple clay	0.2	1.85	36.00	0.88	0.25
	0.4	9.00			
	0.5	13.00			
	0.6	16.00			
Protein-clay	0.2	3.00	54.34	0.54	0.25
	0.4	13.00			
	0.5	20.00			
Nylon-clay	0.2	4.00	99.64	0.72	0.25
	0.4	16.00			
	0.5	30.00			
	0.6	40.00			

^a Effective membrane area = 12.6 cm².

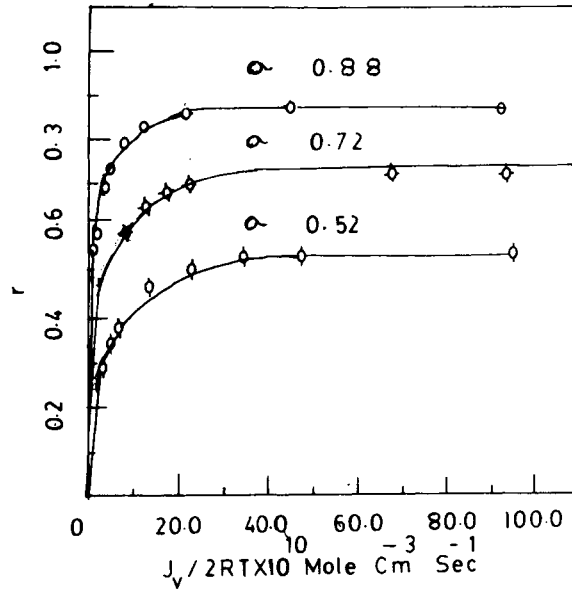


Fig. 4. Variation of r with J_v as predicted by eq. (11) membranes prepared by firing at 700 for 2 h: (○) Clay membrane; (◇) lysozyme-clay membrane; (◊) nylon-clay membrane.

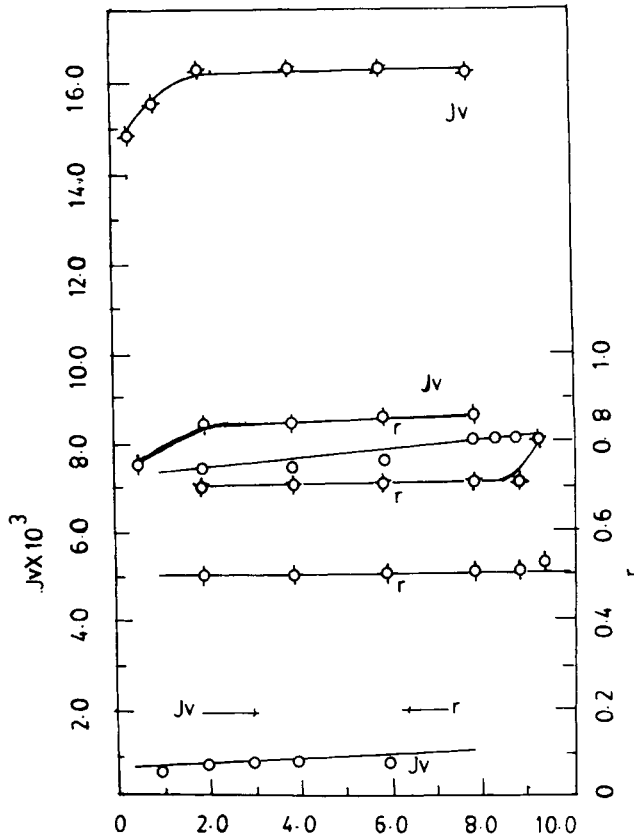


Fig. 5. Variation of J_v and r with duration of firing temperature used—700°C. Duration of firing in h; pressure applied = 10 atm/cm². (○) Clay membrane; (◇) lysozyme-clay membrane; (◊) nylon-clay membrane.

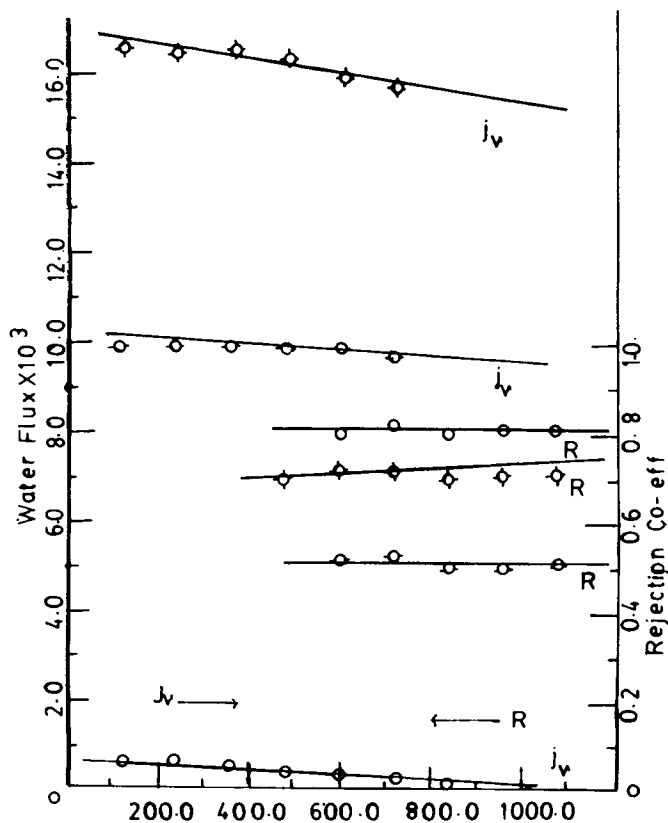


Fig. 6. Variation of flux and rejection coefficient with time. Time in s; membranes fired at 700°C for 2 h; pressure applied = 10 atm/cm². (○) Clay membrane; (◐) protein-clay membrane (lyso); (◑) nylon-clay membrane.

It is interesting to note that, although the average pore size of protein membrane was bigger than that of nylon membrane, the water flux value of protein membrane was smaller than that of its nylon counterpart. This apparent anomaly can be explained on the basis of porosity which was much greater in the case of nylon membrane than in its protein counterpart. It was noticed that a trend of flux decline with time took place because of development of concentration polarization (Fig 6) however small it might be.

CONCLUSIONS

From analysis of the above results, the following conclusions may be drawn:

1. Membranes prepared by firing green ones for about 2h showed better performance characteristics.
2. Nylon-clay membrane was considered better in performance behavior than other membranes studied.
3. Pore size in fired clay membranes plays an important role in controlling water flux and solute selectivity.

TABLE III
Comparison of r Values Predicted by Osmosis and Determined by RO Experiment^a

Type of membrane	Av. water flux [mL.s ⁻¹ cm ⁻² × 10 ³ (RO)]	r predicted by osmosis experiment	r determined by RO experiment
Simple clay	0.74	0.88	0.80
Protein- clay	8.58	0.54	0.50
Nylon- clay	16.02	0.72	0.70

^aPressure applied = 10 atm/cm²; effective membrane area = 12.6 cm² concentration of feed solution—0.1M.

4. The rejection coefficient values for all the membranes predicted by osmotic experiment were in good agreement with those determined by direct RO experiments (Table III).

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