

Studies on Ultrafiltration Membranes. I. Development of Cellulose Nitrate Membranes

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Synopsis

Ultrafiltration membranes were prepared from cellulose nitrate under different conditions and were characterized using a solution of 1.0% dextran-150 having a salinity of 1500 ppm. The role of various parameters such as polymer concentration, ratio of ether to alcohol, methanol as the solvent, and other additives is systematically studied and presented. Similarly, the effect of operational and hydraulic parameters on the membrane performance is evaluated and the minimum activation energy for the solvent permeability is experimentally deduced.

INTRODUCTION

Ultrafiltration is fast emerging as a new and versatile unit operation in separation technology. Since the time of Bechhold,¹ who coined the term "ultrafiltration" in 1906, until the middle of the century, all the research work reported was mainly associated with collodion membranes and cellophane films. With the development of asymmetric membranes in the beginning of the second half of this century, other polymeric materials have become the subject of investigation by many research workers. In particular, the work of Michaels² at Amicon Corporation, has not only revived and stimulated interest in ultrafiltration as a potential field for research, but brought this into the forefront of the separation processes.

The study of different polymeric materials for use in membrane ultrafiltration, involves (a) selection of suitable polymers, (b) membrane morphology in relation to its use as an ultrafilter, (c) characterization of these films, (d) effect of fabrication, operational, and hydraulic variables on the functional parameters namely separation efficiency and permeability, and (e) application to many of the industrial separation problems.

A detailed study of preparation and characterization of cellulose nitrate membrane is presented in this paper.

EXPERIMENTAL

Casting Solution Preparation

Cellulose nitrate, made in the U.S.S.R. was used in this study. The material analyzed gave (9–9.3)% nitrogen and 20% moisture. The casting solution was prepared by dissolving the requisite quantity of the polymer in a mixture of ether and ethanol. The bottle was occasionally shaken until all the cellulose nitrate dissolved, resulting in a clear transparent solution.

Membrane Casting

The membranes were cast in the form of flat sheets according to the method described by Loeb and Sourirajan.³ Membranes were cast by spreading the casting solution with the help of a doctor's knife on to a glass plate having a fine smooth surface of $30 \times 22 \text{ cm}^2$. The membrane thickness was adjusted by means of side runners of proper dimensions. It was rather essential to clean the glass plate thoroughly with acetone before casting the membrane so as to avoid the formation of any blisterlike impressions on the surface of the membrane. After allowing a definite time for the solvent to evaporate (evaporation time or holding time), the glass plate was immersed in a bath of water at room temperature for about 1 hr when the membrane got easily separated from the glass plate. The membrane thus obtained was generally milky white and opaque in appearance. It was preserved in distilled water till it was used for characterization studies.

Membrane Characterization

A sterile solution containing 6.0% wt/volume dextran (produced by *Leuconostoc Mesenteroides*, N.C.I.B. No. 8710) in 0.9% wt/volume NaCl solution was selected as the candidate material for characterization of the polymeric membranes. This was supplied by Tata Fison Industries, Konnagar, W. Bengal.

To study the effect of molecular weight on membrane permeability and selectivity, biochemical grade dextran of different molecular weights ranging from 10,000 to 20,000 supplied by B.D.H., England, was used.

Membrane Testing

The membrane testing was carried out in a laboratory test unit, supplied by M/s. Universal Water Corporation, California. The unit consists of a feed solution tank, a pressurizing pump, a pressure accumulator, a pressure gauge, a back pressure regulator valve, a bypass valve, and a stainless-steel high-pressure test cell.

Membrane test disks were cut easily with a simple die with a cutting edge of 2 in. diameter. The circle, together with the filter paper and the porous disk, was placed in the test cell in such a way that the air side (skin side) of the membrane always faced the feed solution. For this purpose, the membranes were always marked to distinguish the air side from the other side. The clamping nuts were uniformly tightened by hand. Permeate receivers were placed under the spouts and the pump was started with the relief valve open.

Feed solution containing approximately 1.0% dextran-150 having a salinity of about 1500 ppm was circulated by means of a stroke positive displacement diaphragm pump having an output of 12–14 gal/hr. Any pulse or shock due to pumping was eliminated by a Greer Olaer accumulator. The operating pressure in the system was controlled by adjusting the spring-loaded back pressure regulator (BPR). The relief valve was closed gradually when the system pressure built up steadily till the preset value is reached. The effluent which bleeds into the feed tank at atmospheric pressure was recirculated during the runs. Permeate was collected for analysis after 1 hr of pressurization, in all the experiments. The amount of permeate collected in a definite time was measured and the flux calculated. The presence of dextran in the permeate was qualitatively

examined by visible turbidity or coagulation, with alcohol or acetone, from time to time. Samples of permeate were preserved for analysis by polarimetry.

For each membrane a minimum of six circles were tested and the average values of flux and rejection were found.

Membrane Performance

The performance of the membranes is measured in terms of flux and rejection; where flux is the ultrafiltrate (permeate) rate calculated as gallons per square foot area of the membrane per day (gfd).

The membrane rejection is calculated as

$$R = [(C_F - C_p)/C_F] \times 100 \quad (1)$$

where R is the percent of solute rejection, C_F is the feed concentration, and C_p is the permeate (ultrafiltrate) concentration.

MEMBRANE PROPERTIES

Degree of Swelling

Degree of swelling or the swelling ratio, is the ratio of wet weight to dry weight of the membrane. The total water held up by the membrane was determined by weighing membrane samples wet, after blotting off the surface water and then weighing again after drying the samples at 105°C to constant weight. All the determinations were carried out in duplicate and the average was calculated. The degree of swelling (DS) was

$$DS = W_1/W_2 \quad (2)$$

where W_1 is the wet weight of the membrane and W_2 is the dry weight of the membrane.

Membrane Compaction

The compaction of the membrane under pressure was evaluated by measuring the membrane thickness before and after operation at a given pressure by means of a micrometer screw with a sensitivity of 0.002 mm. The ratio of the thickness of the swollen membrane to that of the pressurized membrane is taken as a measure of the degree of compaction (DC) of the membrane.

$$DC = T_s/T_p \quad (3)$$

where T_s is the thickness of the swollen membrane and T_p is the thickness of the pressurized membrane.

Membrane Water Permeability

The pure water permeability of the membranes was determined in a laboratory test unit as described earlier.

Distilled water was circulated by a high-pressure variable stroke positive displacement diaphragm pump, coupled with a 0.75 horse power motor, at the rate of 600 ml/min. Permeate was collected after 1 hr of pressurization for a

definite time. For each membrane a minimum of six circles were tested and the average permeability was calculated. The membrane permeability was then expressed as gallons per square foot of area of the membrane per day.

Water Permeability Coefficient

The permeability coefficient \bar{P} was calculated from the equation

$$\bar{P} = (J \times t)/(18 \times A \times T \times P) \quad (4)$$

where J is the quantity of water collected in time T in sec, A is the membrane area in cm^2 , t is the membrane thickness in cm, P is the operating pressure in atm, and \bar{P} is the permeability coefficient in g moles/cm sec atm.

Since flux is defined as J/AT , the above equation can be rewritten

$$\bar{P} = (F \times t)/(18 \times P) \quad (5)$$

where $F = \text{g}/\text{cm}^2 \text{ sec}$.

The permeate rate was measured as described in the "membrane water permeability" section, converted into consistent units and used in the above equation.

Average Pore Diameter of the Membranes

The average pore diameter (APD) is calculated by solvent permeability method using the Hagen-poiseuille equation.

Pore radius can be obtained by measuring the volume of water permeating in a given time at constant pressure from the following equation:

$$r = 2(8J\eta d)/(VAPT)^{1/2} \quad (6)$$

where r is the pore radius, η is the viscosity of flowing liquid, d is the length of the capillary (equal to the membrane thickness), and V is the void volume (membrane water content).

The void volume V (the membrane water content) was obtained from the difference between the wet and dry weights of the membrane after they were used in the permeability measurements at the desired pressure. The average of six circles was used in the calculation. All the terms in eq. (6) were used in consistent units and the values for ADP are represented in μm .

Analytical Methods

(a) Salt concentration in the feed and the permeate was determined by measuring the conductivity of the samples.

(b) Dextran concentration in the feed solution and permeate was determined by polarimetry by measuring the optical rotation. As the angle of rotation is directly proportional to the concentration of the optically active substance in the solution, just as the conductivity is to the concentration of salt, these are directly used in eq. (1) to calculate the percentage rejection of the macrosolutes and microsolute present in the feed solution.

The membrane casting parameters which were investigated in detail included (a) polymer concentration, (b) ether:alcohol ratio in the casting solution, (c) methanol as the solvent, (d) additives in the casting solution, and (e) evaporation

time. The operational and hydraulic parameters evaluated consisted of (1) feed flow rate, (2) feed channel length, (3) feed temperature, (4) operating pressure, (5) dextran concentration, (6) dextran molecular weight, and (7) prolonged time of operation.

RESULTS AND DISCUSSION

Variation of the Polymer Content in the Casting Solution Composition

The performance data and other properties are shown in Table I. It was observed from the results, that membranes from 10% solution gave a higher PWP flux, higher ultrafiltrate flux, and also higher dextran rejection, whereas 15% polymer membrane gave high percentage salt rejection. Degree of swelling and compaction are less for 15% membranes than for 10% membranes. It is interesting to compare these properties with those for cellulose acetate membranes.

The degree of swelling and compaction are much less for cellulose nitrate membranes.

The porosity of 15% membrane was less than half of that for the 10% membrane. Ferry⁴ has observed that the higher the concentration of cellulose nitrate in the original solution, the lower the porosity of the membrane.

Variation of Ether:Alcohol Ratio in the Solvent Mixture

Four solvent mixtures were investigated to find the effect of alcohol in the casting solution. They were 70:30, 50:50, 30:70, and 10:90 of the ether:alcohol ratio. A 15% solution was used for the preparation of the membranes. No incipient gelation was noted in the last three compositions. Hence an evaporation time of 4 min was given for the membranes from these solutions. The data are presented in Table II. It is seen from the results that 70:30 ether:alcohol membranes gave a high rejection of salt and therefore cannot be used for the separation of salt from macrosolute. Membranes from 10:90 solution gave, no doubt, maximum separation as also higher ultrafiltrate flux but their mechanical strength was quite low. Hence 30:70 ether:alcohol mixture was selected for further optimization studies as membranes from this solution gave fairly high flux and high rejection of dextran.

As the alcohol content was increased there was gradual increase in the ultrafiltrate flux, degree of swelling, and APD. The compaction also increased with the alcohol content. Hence the role of alcohol in the collodion membranes may be compared with that of formamide in the cellulose acetate membranes. Alcohol may be considered here as a swelling and pore-forming agent just as formamide is in the case of cellulose acetate membranes.

Effect of Evaporation Time on the Membrane Performance

The solution composition selected for this study was 15:30:70 (15 g cellulose nitrate, 30 ml ether, and 70 ml alcohol, respectively). Since no incipient gelation was observed with membranes cast from this composition as also in the case of other compositions containing more alcohol than ether, evaporation time ranging from 30 sec to 12 min was investigated and the data collected are represented

TABLE I
Performance of Cellulose Nitrate Membranes: Effect of Variation of Cellulose Nitrate Content in the Casting Solution^a

Polymer concentration (%)	Pure water flux (gfd)	Ultrafiltrate flux (gfd)	Percent rejection		DS	APD μm	T_s/T_p	\bar{P} ($\times 10^{-6}$)	Evaporation time for incipient gelation to occur (sec)
			Dextran	NaCl					
15	6.7	4.05	90.0	59.6	1.66	6.6	1.05	0.0037	373
10	45.0	8.10	94.0	14.8	1.99	15.34	1.35	0.0153	198
5 ^b	—	—	—	—	—	—	—	—	172

^a Solvent mixture: 70:30 ether-alcohol; operation pressure: 600 psi; feed: 1.0% dextran, 1500 ppm NaCl.

^b Membranes from 5% solution were very brittle and hence could not be tested.

TABLE II
Effect of Variation of Alcohol Proportion in the Casting Solution^a

Ether: alcohol [Evaporation time (sec)]	PWP (gfd)	Ultrafil- trate flux (gfd)	Percent rejection		APD μm	T_s/T_p	\bar{P} ($\times 10^6$)
			Dextran	NaCl			
70:30 (373)	6.7	4.1	90.0	59.0	6.6	1.06	0.0037
50:50 (240)	45.4	12.5	100.0	5.3	16.20	1.15	0.023
30:70 (240)	34.5	16.2	96.0	11.10	14.74	1.32	0.014
10:90 (240)	41.3	18.3	92.7	0.0	16.6	1.31	0.027
10:90 (600)	38.6	12.2	86.5	12.0	15.3	1.67	0.026

^a Polymer content: 15 g; pressure: 600 psi; feed: dextran, 1.0%; NaCl: 1500 ppm.

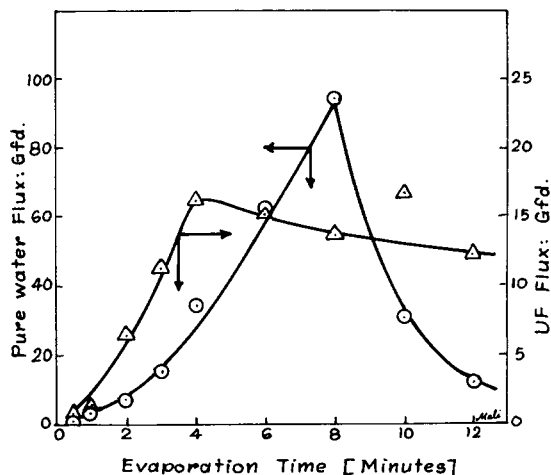


Fig. 1. Effect of evaporation time on pure water flux and ultrafiltrate flux of CN membrane.

in Figures 1 and 2. In the case of the 15:70:30 composition where there was more ether than alcohol, incipient gelation time and lower were studied and the data are presented in Table III.

It was observed, from the data presented in Table III for the membranes cast from solution containing more ether, that evaporation time lower than the incipient gelation time, did not result in productive membranes. The rejection of dextran was low (26% and 10%) the solvent flux was extremely low (2 gfd); the membrane permeability was also poor. When immersed in water there was not enough swelling of the membranes and when tested under pressure there was practically no compaction of the membranes. However, the membrane exposed to the point of incipient gelation and then immersed in water, gave fairly good permeability, solvent flux, and dextran rejection (90%), but the salt rejection was also quite high (59%). These data clearly indicate that for solutions containing more ether than alcohol, evaporation time until incipient gelation is es-

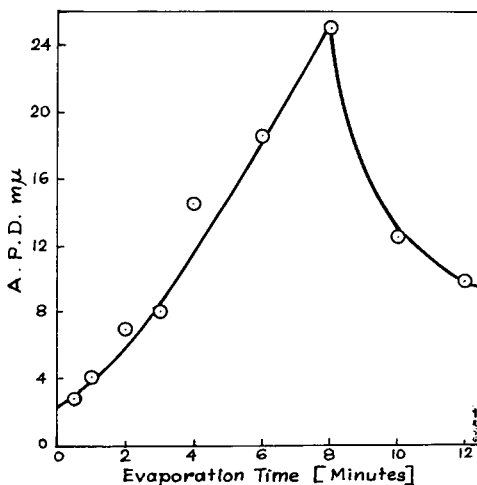


Fig. 2. Effect of evaporation time on the porosity of the CN membrane.

TABLE III
Effect of Evaporation Time on the Membrane Performance^a

Evaporation time (sec)	PWP (gfd)	Ultrafiltrate flux (gfd)	Percent rejection		APD μm	T_s/T_P	\bar{P} ($\times 10^{-6}$)
			Dextran	NaCl			
373 ^b	6.7	4.1	90.0	59.0	6.6	1.06	0.0037
202	1.9	1.3	26.0	0.0	2.94	1.02	0.0008
90	1.7	1.0	10.0	0.0	3.64	1.05	0.0005

^a Membrane: Cellulose nitrate 15% in 70:30 ether:water; pressure: 600 psi.

^b Time required for incipient gelation to occur on the glass plate.

essential in order to produce useful membranes. Ferry⁴ observed that the evaporation must proceed at least long enough to allow the collodion to set to a gel on the glass plate before immersion into a gelling bath in order to produce more highly porous membranes.

The results are entirely different for membranes cast from solutions containing more of alcohol than ether. Here no incipient gelation was observed. All the membranes (with evaporation time of $\frac{1}{2}$ to 12 min) gave good rejection of dextran (90%); the salt rejection varied from 10% to 30%. As the evaporation time was increased from 30 sec to 8 min, pure water permeability and ultrafiltrate flux steadily increased (Fig. 1). PWP reached a maximum value at 8 min and then declined with further evaporation time. Ultrafiltrate flux was almost steady between 4 and 10 min at an average value of 15 gfd after the initial rise up to 4.0 min and then fell to 10 gfd at 12 min evaporation time. The degree of swelling increased slowly up to 3 min, then remained steady up to 6 min, thereafter declining with further evaporation time. The porosity increased with evaporation time up to 8 min and then decreased with further increase in evaporation time (Fig. 2). The degree of compaction on the whole was not much and ranged from 1.0 to 1.85. Since there is an increase in permeability, DS, and APD with evaporation time up to 8 min and thereafter a decline in these properties, it may be said that 8 min may be the minimum time required for the gel to set before it is immersed in water. This has been confirmed by the observation of Elford et al.,⁵ who reported that the degree of aggregation of collodion at any point in the process depends on a highly specific manner on the composition of the solution. The composition of the solution depends in turn on the time elapsed and on the original proportions and volatilities of various solvents and nonsolvents in the solution. According to Elford et al., two processes probably occur during the evaporation: a gradual aggregation as the proportions of solvents and nonsolvents change, and a sudden gelling when the concentration of collodion becomes sufficiently high for the aggregates to lock into a rigid structure. The extent to which the aggregation has proceeded by the time gelation occurs largely determines the membrane porosity. Further evaporation from the set gel, accompanied by shrinkage of the gel when it is immersed in water, will decrease the eventual porosity.

An interesting comparison of the effect of evaporation on the behavior of membranes derived from cellulose acetate and cellulose nitrate can be made. In the case of cellulose acetate membranes⁶ the PWP, DS, and APD gradually decrease with increase in evaporation time, say up to 90 sec, and they thereafter show an upward tendency; the ultrafiltrate flux is more or less steady at 12 gfd throughout; in the case of cellulose nitrate membranes exactly the reverse trend was observed. There was an increase in these properties up to 8 min and then they showed a decline; the ultrafiltrate flux also gradually increased up to 4 min, remained steady for some time (up to 10 min), and then declined. The DS and compaction are comparatively higher for cellulose acetate than for cellulose nitrate membranes. Thus, it can be concluded that 15:30:70 (cellulose nitrate: ether:alcohol) cellulose nitrate membranes are better than 15:40:45 (cellulose acetate:formamide:acetone) cellulose acetate membrane as the former are in general more resistant to compaction and give more solvent flux than the latter.

Effect of Heat-Treatment on the Membrane Performance

Membranes were prepared from two different solution compositions, namely, 15:70:30 and 15:30:70, of cellulose nitrate:ether:alcohol. They were given different evaporation times before immersion in the gelling bath. The membranes were then heated to 95°C for 20 min before they were tested. The data are shown in Table IV. For membranes drawn from solution containing more ether, there was considerable decline in PWP, solvent flux, dextran and salt rejection, DS, and APD on giving heat treatment. This was also confirmed for another evaporation period. This was not the observation for membranes drawn from solution containing more alcohol. On heating these membranes, there was an appreciable increase in PWP, solvent flux (with less rejection of dextran and no salt rejection), DS, and APD. This is again in contrast to the observation that on heating the cellulose acetate membrane, the flux, swelling, and permeability drop to a low level, and the membrane acquires semipermeability, i.e., salt rejection increased enormously. This is another distinguishing characteristic of the cellulose acetate membrane from that of cellulose nitrate membrane. Ferry⁴ has reported that porosity of cellulose nitrate membranes is increased by heating it to 90–98°C in water bath. This is true of membranes prepared from solutions containing a greater proportion of alcohol as has been shown by the data in Table IV.

Effect on the Membrane Performance of Additives to the Casting Solution

The additives selected for this study were (1) acetone, (2) amyl alcohol, (3) formamide, and (4) a mixture of acetone and amyl alcohol. The common evaporation time in all the cases was 6 min, but some were investigated at more than one evaporation time. The additives were incorporated at the expense of ether keeping the alcohol content the same (30 ml) throughout. From the results presented in Table V, it was observed that acetone addition resulted in a membrane with decreased porosity, reduced permeability and solvent flux, low degree of swelling, and low dextran rejection. On the other hand, amyl alcohol improved the water permeability, ultrafiltrate flux, and dextran rejection to an appreciable extent as compared with the control (without any additive). Addition of water also improved, to a very great extent, the solvent flux and rejection of dextran; at the same time, the salt rejection was also high. However, the performance of membranes with water as the additive was better at 6 min evaporation than at other evaporation periods. Formamide, no doubt, increased the PWP and ultrafiltrate flux, but dextran rejection was poor. A mixture of acetone and amyl alcohol in equal proportions resulted in membranes with high water permeability and also ultrafiltrate flux, but not much rejection of dextran. The membrane possessed high porosity (23 μm) as compared to 6.66 μm for the control membranes. Thus, it can be seen that acetone and amyl alcohol alone do not give highly permeable membranes; a mixture of these two gave membranes with higher porosity and permeability. Water also increases the permeability and, by giving more evaporation times, selectivity also can be imparted to these membranes. Ferry⁴ states that addition of various nonsolvents or precipitating agents to a collodion solution was found to increase, to a limited degree, the porosity of the membranes prepared from it; among these reagents were glycerol, water, lactic acid, and ethylene glycol. He has summarized the results of adding

TABLE IV
Effect of Heat Treatment on the Performance of Cellulose Nitrate Membrane

Membrane composition	Evaporation time (sec)	PWP (gfd)	Ultrafiltrate flux (gfd)	$\frac{\text{Percent rejection}}{\text{Dextran}}$	$\frac{\text{Percent rejection}}{\text{NaCl}}$	DS	APD μm	T_s/T_p
CN:Ether:Alcohol	373 {	a	4.1	90.0	59.0	1.66	6.6	1.06
		b	0.2	80.0	23.0	1.42	1.32	1.07
15:70:30	202 {	a	1.3	26.0	0.0	1.64	2.94	1.02
		b	1.2	1.3	20.0	10.6	1.41	2.6
15:30:70	360 {	a	13.50	97.6	5.5	3.20	16.3	1.45
		b	28.80	66.0	50.0	0.0	—	18.90

^a Blank or unheated membrane.

^b Membrane heat treated at 95°C for 20 min.

various reagents to the ether:alcohol collodion solution as follows: amyl alcohol, acetone, and methanol alone decreases the porosity; amyl alcohol in the presence of acetone increases the porosity; water increases the porosity. Asheshov⁷ also prepared membranes of high porosity by adding to the collodion solution a mixture of amyl alcohol and acetone. Thus the data obtained are in complete agreement with the findings of earlier workers.

Methanol as Solvent

Individually ether and ethanol were not found to be good solvents for cellulose nitrate, whereas methanol was found to dissolve cellulose nitrate readily and give a good solution. The membranes were drawn from a 15% cellulose nitrate solution and were given definite evaporation times of 6 and 10 min. No incipient gelation was observed up to 6 min. In the case of a 10 min evaporation time, the membrane started becoming opaque at the edges after 7 min and then spread to the whole film in 10 min time. The data in Table VI show that methanol alone is a good solvent; a membrane with 6 min evaporation time gave excellent separation of dextran from salt with ultrafiltrate flux of nearly 15 gfd. Membrane compaction is also found to be less as compared to ether-alcohol collodion membrane cast with same evaporation time.

Effect of Flow and Other Operating Parameters

The membranes drawn from the optimized formula 15:30:70 of CN:ether:alcohol with a 6 min evaporation period were used in the studies to evaluate the effect of feed concentration, feed flow rate, operating pressure and temperature, mixing or turbulence at the membrane surface, and dextrans of different molecular weights.

Effect on the Membrane Performance of Feed Concentration

Feed concentrations ranging from 10% to 0.625% of dextran grade C (mole. wt. 60,000–90,000) biochemical grade, supplied by B.D.H., England were used. The operating pressure was 600 psi. Data on flux was plotted in Figure 3.

Membrane rejection for all concentrations of dextran was found to be over 99.5% for dextran and nil for NaCl. The ultrafiltrate flux was found to decrease with increase in the concentration of dextran. It could be seen from the flux vs concentration graph in Figure 3 that the decline was more rapid at lower concentration than at higher concentration of dextran. Here, as in the case of CA, concentration does not affect solute rejection but decreases the flux considerably. The flux values, as is the separation efficiency of this optimized cellulose nitrate membrane, are found to be same as those for the optimized cellulose acetate membrane. As discussed earlier, cellulose nitrate membranes are subjected to less compaction under pressure and therefore have an advantage over cellulose acetate membrane.

TABLE V
Effect on the Membrane Performance of Additives in the Casting Solution

Additive	Membrane composition and [Evaporation time (min)]	PWP	Ultrafil- trate flux (gfd)	$\frac{\text{Percent rejection}}{\text{Dextran}}$	$\frac{\text{Percent rejection}}{\text{NaCl}}$	DS	ADP μm	$\frac{T_s}{T_p}$	\bar{P} ($\times 10^{-6}$)
Acetone	CN Ethanol Alcohol 15, 50, 30 + 20 ml acetone	0.5	0.3	48.0	0.0	1.19	2.16	1.0	0.00015
Amyl alcohol	15, 50, 30 + 20 ml amyl alcohol (6)	11.2	10.2	92.5	21.5	1.39	7.64	1.7	0.0005
Water	15, 60, 30 + 10 ml water (0)	1.35	1.35	28.3	21.5	1.73	3.28	1.09	0.0012
Water	15, 60, 30 + 10 ml water (2)	63.0	56.0	44.7	27.7	3.50	17.7	1.77	0.035
Water	15, 60, 30 + 10 ml water (6)	30.5	27.1	97.2	55.3	3.04	12.0	1.05	0.018

Water	15, 60, 30 +10 ml water (10)	39.4	33.8	76.2	46.2	2.88	15.6	1.11	0.028
Acetone + amyl alcohol	15, 50, 30 + 10 ml acetone + 10 ml amyl alcohol (6)	103.0	23.6	38.0	38.0	1.48	23.0	1.21	0.0244
Acetone + amyl alcohol	15, 50, 30 + 10 ml acetone + 10 ml amyl alcohol (10)	69.0	11.5	79.0	0.0	1.95	16.4	1.14	0.0482
Formamide	15, 50, 30 + 20 ml formamide (6)	42.7	20.3	25.0	—	2.84	13.9	1.33	0.020
No additive	15, 70, 30 (6)	6.7	4.1	90.0	59.0	1.66	6.6	1.06	0.0037

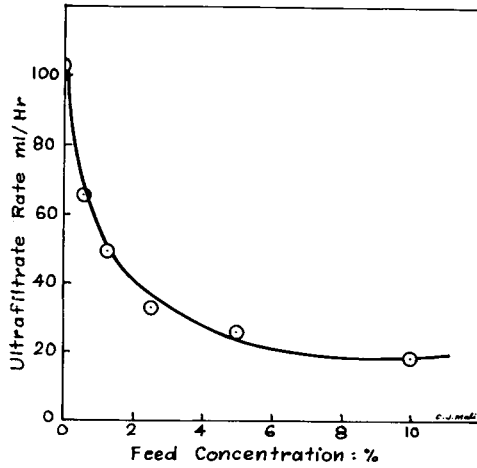


Fig. 3. Effect of feed concentration on the ultrafiltrate rate of CN membrane.

TABLE VI
Effect of Methanol as the Solvent for Cellulose Nitrate (CN) Membranes^a

Evaporation time (min)	PWP (gfd)	Ultrafil- trate flux (gfd)	Percent rejection		DS	APD μm	T_s/T_p	\bar{P} ($\times 10^{-6}$)
			Dextran	NaCl				
6	58.0	14.9	94.5	0.0	3.6	17.6	1.33	.041
10	45.0	17.6	88.0	0.0	1.42	14.5	1.8	.024

^a Membrane composition 15 g CN in 100 ml methanol; pressure: 600 psi; feed: 1.0% dextran in 1500 ppm NaCl.

Effect on the Membrane Performance of Feed Flow Rate

The data on the effect of feed flow rate varying from 900 to 6200 ml/min on the membrane performance were plotted in Figure 4. As the flow rate is in-

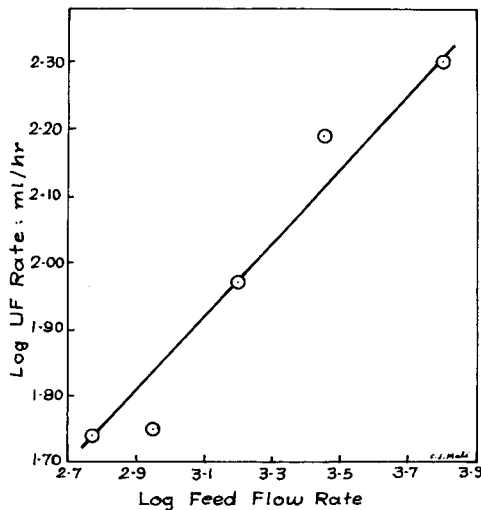


Fig. 4. Effect of feed flow rate on ultrafiltrate (UF) rate for CN membrane.

creased, the ultrafiltrate flux increased enormously (Fig. 4), and the dextran rejection also increased appreciably. The increase in dextran rejection with flow rate is more in the case of cellulose nitrate membranes than in cellulose acetate membranes. Log flow rate vs log flux shows a straight line with a slope similar to that of the cellulose acetate membranes.

Effect on the Membrane Performance of Operating Temperature

As the feed temperature increased from 32°C at the start to 46°C at the end of the experiment, the flux increased from 200 to 315 ml/hr. The average value of the percent increase in flux per degree rise in temperature was found to be 4.4. This value is somewhat more than 3.5 for cellulose acetate membrane.⁶ Log flux was plotted against $1/T$ when a straight line with negative slope was obtained (Fig. 5), thereby indicating that the data fitted in well in the Arrhenius form of equation. The activation energy of water transport as calculated from the slope was found to be 6.55 K cal/mole, a value somewhat higher than that obtained for the cellulose acetate membrane (5.58 K cal/mole).

Effect on Membrane Performance of Pressure

As in the case of cellulose acetate membranes, the effect of pressure was studied both in ascending as well as descending order. The data are shown in Table VII. The ultrafiltrate flux did not increase with operating pressure thereby confirming that the flux is independent of the transmembrane pressure drop. But in the reverse approach when the pressure on the membrane is slowly reduced from 600 to 100 psi, flux declined from 55 to 13 ml/hr, demonstrating the compaction effect under pressure. Here again the cellulose nitrate membrane suffered less compaction as compared to cellulose acetate (a decline of 68% in flux over the preceding value as against the corresponding value of 73% decline for cellulose acetate membrane).

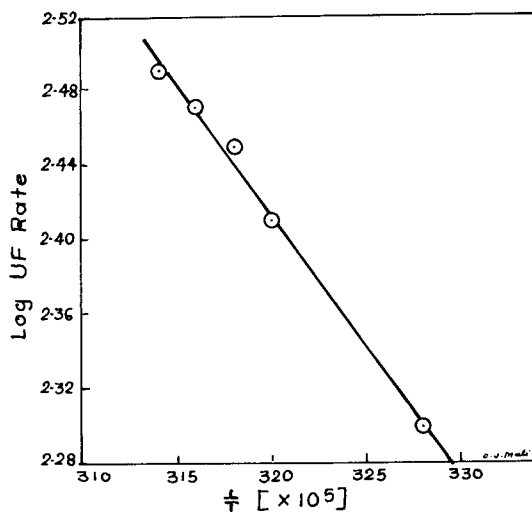


Fig. 5. Effect of feed temperature on the ultrafiltrate (UF) rate of CN membrane.

TABLE VII
Effect of Pressure on the Ultrafiltrate Flux of Cellulose Nitrate Membranes^a

Operating pressure (psi)	Ultrafiltrate rate (ml/hr) ^b	Pressure in decreasing order (psi)	Ultrafiltrate rate (ml/hr)	% decline in ultrafiltrate rate over the initial value
50	56	600	55	—
100	54.5	400	55	nil
200	55.0	200	41	25.5
400	54.5	100	13	76.3
600	55.5	—	—	—

^a Feed: 1.0% dextran; feed flow rate: 600 ml/min, membrane composition: 15 g cellulose nitrate, 30 ml ether, 70 ml alcohol.

^b ml/hr \times 0.3384 = gfd.

Variation of Ultrafiltrate Flux with Time

The long-term effect on the membrane performance when the permeate was continuously withdrawn, was investigated by starting with 3000 ml of 1.0% dextran feed. The feed was recirculated in the cell until the volume was reduced to 1500 ml. The experiment was conducted over a period of 12 hr. In one cell, the feed flow channel length was adjusted to 1.5 mm, while in the other it was maintained at 7.5 mm. There was decline in flux to the extent of about 30% percent (Fig. 6). There was total rejection of dextran till the end of the operation. The decline in flux is attributed to the increased feed concentration as a result of the removal of permeate as also due to the increased hydraulic resistance of the gel layer formed on the membrane surface.

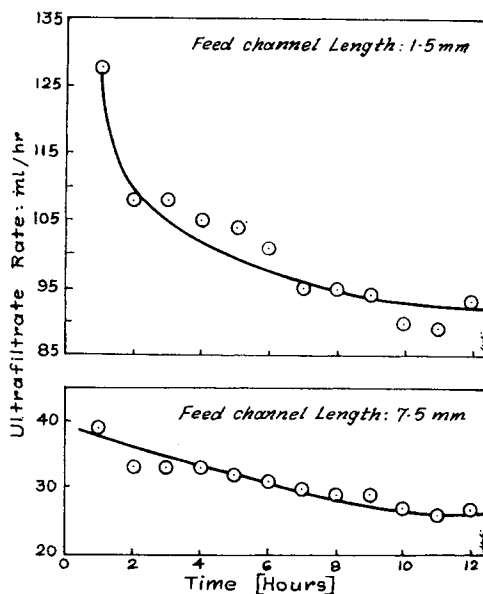


Fig. 6. Decline of ultrafiltrate rate with time for CN membrane: feed channel lengths: (a) 1.5 mm and (b) 7.5 mm.

TABLE VIII
Effect of Molecular Weight of Dextran on Flux and Rejection of CN Membranes^a

Dextran grade	Ultrafiltrate flux (gfd)	Percent rejection		Molecular weight range
		Dextran	NaCl	
A	16.9	94.3	0.0	A = 200,000–275,000
B	18.6	97.4	0.0	B = 150,000–200,000
C	18.95	92.0	0.0	C = 60,000–90,000
D	20.64	91.0	0.0	D = 40,000
E	24.40	86.0	0.0	E = 10,000

^a Membrane: CN, 15 g; ether, 30 ml; alcohol, 70 ml; pressure: 600 psi.

Effect on the Membrane Performance of Molecular Weight of the Macrosolute

As in the case of cellulose acetate membranes, the flux slowly increased with the decrease in the molecular weight of dextran (Table VIII). The rejection of 10,000 mole wt. dextran was found to be only 86% by cellulose nitrate membrane and that of 40,000 dextran, it was about 90%. Hence it appears that the "cutoff" level for this membrane is of the order of 40,000 for the solute species of the dextran type. This means that for solutes below 40,000 mole wt. the rejection is not 90%; in this respect this differs from cellulose acetate membrane which gave 97% rejection for 10,000 dextran, indicating thereby a lower cutoff level.

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