

Performance of Cellulose Acetate Butyrate Membranes in Hyperfiltration of Sodium Chloride and Urea Feed Solution

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Synopsis

Cellulose acetate butyrate (CAB) membranes gave high salt and urea rejection with a water flux of about 3 gfd (gallons/ft²·day) during hyperfiltration at 600 psig. Evidence was obtained which indicated that the CAB membranes used in this work were asymmetric. Membrane heat treatment increased urea rejection significantly while salt rejection was invariant, and water flux decreased. An increase in feed solution temperature caused a significant increase in water flux and a small decrease in urea and salt rejection. Increasing the pressure increased water flux and urea and salt rejection. During a 400-hr life test, the water flux decreased by about 25% while urea rejection increased and salt rejection was invariant. The influence of pressure, membrane heat treatment, and compaction during CAB membranes life testing on urea and salt rejection provided evidence that these two solutes were rejected by somewhat different mechanisms. Salt rejection was consistent with a solution-diffusion mechanism for membrane transport and uncoupled flow while changes in urea rejection with pressure, membrane heat treatment, and compaction during life testing suggested that urea was at least partially rejected by membrane exclusion resulting from geometric factors.

INTRODUCTION

Purification of spacecraft waste water, i.e., wash water, humidity condensate, and urine by hyperfiltration or reverse osmosis requires that the hyperfiltration membrane be capable of rejecting both organic and inorganic molecules. Of the organic molecules to be rejected, urea is both one of the smallest and most abundant, its concentration in human urine being 9,300 to 23,300 ppm.¹ A review of the literature revealed that very few hyperfiltration membranes being developed for domestic or industrial water purification were effective for urea rejection. For example, the widely studied asymmetric cellulose acetate (CA) membrane is effective for salt rejection but poor for urea rejection² (see Table I). It was found that some of the more effective membranes for urea rejection were porous glass, cellulose acetate butyrate (CAB),^{3,4} and an aromatic polyamide⁵ (see Table I). Porous glass, the best urea rejector, however, has very low water flux and, as discovered earlier,^{6,7} different batches of porous glass had widely different rejection capabilities. The CAB membrane exhibits the best

TABLE I
Hyperfiltration Characteristics of Some Polymeric Membranes and Porous Glass^a

Membrane type ^b	Membrane code no.	Flux, ^c gfd	Rejection, ^d %	
			NaCl	Urea
Cellulose acetate butyrate	CAB-1	2.86	99.1	75.5
	CAB-2	2.59	99.7	76.7
Asymmetric cellulose acetate	CA-80	17.5	94.7	31.1
Polyterephthalamide of 1,3-bis(3-aminobenzamide)-benzene	Polymer II-A	2.24	99.1	65.5
	Polymer II-B	2.34	98.9	70.5
Porous glass	Batch A-5	0.259	95.4	91.6

^a Test conditions: pressure, 600 psig for polymeric membranes, 1200 psig for porous glass; feed composition, 10 g/l. NaCl + 10 g/l. urea; temperature, 19°–20°C; pH, 6.4.

^b The cellulose acetate butyrate and asymmetric cellulose acetate membranes (heat treated at 80°C) were obtained from Universal Water Corp. The aromatic polyamide membranes were from Chemstrand and the porous glass capillaries from Corning Glass Works.

^c gfd = gallons/ft²·day.

^d Per cent rejection = $\left(\frac{C_\alpha - C_\omega}{C_\alpha} \right) \times 100$, where C_α = concentration of solute in feed, mole·liter⁻¹; and C_ω = concentration of solute in effluent, mole·liter⁻¹.

combination of water flux and urea rejection. In this paper, the effects of various parameters on the flux, salt rejection, and especially urea rejection of membranes cast from cellulose acetate butyrate solutions will be reported.

EXPERIMENTAL

Casting Solution Materials and Preparation. Cellulose acetate butyrate powder was obtained from Eastman Chemical Products, Inc. (Eastman identification code EAB171-15). Other starting materials were triethyl phosphate (TEP) (K. & K. Laboratories, Inc.), glycerol (J. T. Baker AR Grade), N-propyl alcohol and acetone (Mallinckrodt AR Grade), and 40% glyoxal solution (J. T. Baker Technical Grade). All chemicals except the glyoxal solution were used without further purification. The glyoxal solution was filtered before use. After a solvent solution of the desired composition was prepared, a weighed amount of cellulose acetate butyrate powder was slowly added while the solution was continuously stirred with a motor-driven stirrer. Stirring was continued for about 1 hr before the solution was filtered under pressure through a Millipore 10-micron Mitex filter. The filtered solution was allowed to stand in a sealed vessel overnight before being used for casting.

Casting Procedure. Films 6½ in. wide and 11 in. long were cast on clean, dry glass plates with a Gardner knife having an adjustable blade. Dust particles were removed from the plate just prior to casting with a Static-master brush. The casting speed was in excess of 6 ft/min to minimize

voids and wavemarks in the cast film.⁸ Casting was done in a clean box located inside a laminar flow hood. Unless otherwise stated, the atmosphere in the casting box was saturated with solvent vapor at 22°C by placing Petri dishes containing the solvent mixture around the casting table. After casting, the membranes were dried by removing the casting box from around the casting table and allowing the filtered air from the hood to flow over the film at 148 ft/min for a known period of time. The cast films were gelled and floated free from the glass plate by quenching in ice water for 45 min. Films were stored in distilled water.

Wet Film Thickness Measurement. Equation (1) was used to calculate the wet membrane thickness:

$$t = \frac{1}{A} \left(\frac{W_{\text{H}_2\text{O}}}{D_{\text{H}_2\text{O}}} + \frac{W_{\text{CAB}}}{D_{\text{CAB}}} \right) \quad (1)$$

where A = wet membrane area, t = wet membrane thickness, $W_{\text{H}_2\text{O}}$ = weight of water in the wet membrane = weight of wet membrane minus weight of dry membrane, $D_{\text{H}_2\text{O}}$ = density of water, W_{CAB} = weight of cellulose acetate butyrate, and D_{CAB} = density of cellulose acetate butyrate. In this method of determining wet membrane thickness, it is assumed that the volumes of water and dry CAB are additive.⁹ A 5.54-cm² section of membrane was weighed before and after drying in vacuo (<10⁻³ torr) overnight. Excess water was blotted from the surface of the wet membrane before weighing in an atmosphere saturated with water vapor on a Cahn electrobalance. The density of cellulose acetate butyrate used for calculating the wet film thickness from the weight and area measurements was 1.25 g/cm³.¹⁰

Hyperfiltration Test Apparatus and Procedure. Membranes were tested for water flux and rejection using the recirculating hyperfiltration system described previously.⁶ The test cell with an adjustable gap (distance between cell wall and feed side of the membrane) was obtained from Universal Water Corp., Del Mar, California, and the cell could accommodate a 5.08-cm-diameter flat circular membrane. Membranes were backed with Whatman 41 filter paper and supported by a 5-micron porous stainless steel disk. Unless otherwise stated, the average linear feed flow rate over the membrane surface was 18 cm/sec; feed temperature, 18° to 20°C; pressure, 600 psig; and feed pH, 6.5 to 8.5. The feed composition was 10 g/l. sodium chloride plus 10 g/l. urea dissolved in distilled water. Increasing the linear feed flow rate from 18 to 36 cm/sec did not improve the flux or sodium chloride rejection of CAB membranes. Therefore, an 18 cm/sec flow rate was used in this work to prevent working near the upper flow rate limit of the high-pressure pump.

Analysis. Water flux was determined gravimetrically, urea was determined colorimetrically,¹¹ and sodium chloride was determined either with a sodium ion electrode or, when a continuous record of effluent salt concentration was desired, with a conductivity meter.

RESULTS AND DISCUSSION

It was of initial interest in this work to investigate the effect of membrane thickness on water flux, rejection, and structural integrity of CAB membranes.

Table II shows the effect of wet film thickness on water flux and NaCl and urea rejection for CAB membranes cast from the "standard formulation" of Manjikian and co-workers³ (22 g CAB powder, 2 g glycerol, 6 g N-propanol, 25 g TEP, and 45 g acetone). From a comparison of the water flux for the different films in Table II, it is apparent that the flux is not inversely proportional to the total wet membrane thickness as expected for a homogeneous solution-diffusion membrane.⁹ The 5-mil and 10-mil films have practically the same flux (there is always some difference even between identically cast membranes), and the 20-mil film has $\frac{2}{3}$ the flux of the 5-mil film. If the membranes were homogeneous, 10- and 20-mil membranes should have $\frac{1}{2}$ and $\frac{1}{4}$ the flux of the 5-mil membrane. These results suggest that the CAB films are not homogeneous and that a "skin," or a more dense layer on the surface of the membrane, and not the total membrane thickness controls water flux. Results similar to those shown in Table II were also obtained with CAB films cast from a formulation containing glyoxal (formulation to be given later in this paper), suggesting that films cast from this formulation also have a skin.

The compaction of CAB films during hyperfiltration also indicated the presence of a skin. For a nonhomogeneous membrane with a skin, it is expected that a 20-mil film would have a thicker spongy substructure beneath the skin than a 10-mil film with the same skin thickness. Therefore, a 10-mil film should compact less than a 20-mil film assuming the spongy layer contributed most to compaction by an increase in density and also assuming the skin thickness is a significant fraction of the total CAB membrane thickness (unlike asymmetric CA membranes that have a very thin skin⁹). This expected compaction effect is borne out by the data in

TABLE II
Effect of Membrane Thickness on Hyperfiltration Characteristics
of Cellulose Acetate Butyrate Membranes^a

Membrane code no.	Casting thickness ^b		Measured wet membrane thickness, μ		Decrease in mem- brane thick- ness, %	Flux, gfd	Rejection, %	
			Before	After			NaCl	Urea
	μ	mils	RO	RO				
CAB-3	127	5	47	— ^c	—	1.96	98.3	41.8
CAB-4	254	10	82	69	16	2.11	99.5	72.1
CAB-5	508	20	164	112	32	1.35	98.9	68.6

^a Membrane drying time, 60 sec.

^b Gap between the spreader blade and glass plate.

^c Film could not be cleanly separated from Whatman filter paper.

TABLE III
Effect of Drying Time on the Hyperfiltration Performance of CAB Membranes Cast from the "Standard Formulation"

Membrane code no.	Drying time, sec	Flux, gfd	Rejection, %	
			NaCl	Urea
CAB-6 ^a	0	2.09	98.5	—
CAB-7	0	3.40	98.4	—
CAB-8	15	2.48	99.2	—
CAB-9	30	2.35	98.9	56.0
CAB-10	60	2.11	99.5	72.1

^a No solvent dishes in casting box.

Table II. The 20-mil film thinned by 32% as a result of compaction at 600 psig, whereas the 10-mil film thinned by only 16%.

Table II also shows that the salt rejection is independent of membrane thickness. This might be expected for either a homogeneous or asymmetric solution-diffusion membrane, see eq. (2). Although urea rejection decreased significantly for the 5-mil film compared to the 10- and 20-mil films (see Table II), this effect was not always reproducible and the decrease may be due to imperfections in these thinner films. In some cases, 5-mil films showed no decrease in urea rejection. Since the 5-mil films did not show performance superior to thicker films and since they were also more fragile and difficult to handle, the 10-mil casting thickness was chosen for the remaining films to be discussed.

In addition to studying the effect of film thickness on CAB membrane performance during hyperfiltration, the effect of drying time was also studied with films cast from the "standard formulation." It is apparent from the data in Table III that by increasing drying time from 0 to 60 sec the water flux declines slightly, the salt rejection remains almost unchanged, while the urea rejection improves significantly. Manjikian and co-workers³ reported an increase in both water flux and salt selectivity when the drying time was increased from 0 to 60 sec. However, their membranes were dried in the "open atmosphere" and not under controlled conditions in a laminar flow hood. Having the surrounding atmosphere saturated with solvent vapors while casting did appear to improve the water flux (compare flux for CAB-6 and CAB-7, Table III) and also allowed for casting under more controllable conditions.

CAB membranes were also cast from the following formulation, given by Manjikian and Foley,⁴ and reported to yield membranes with a higher water flux and lower salt rejection than those cast from the "standard formulation": 22 g CAB powder, 2 g glycerol, 6 g N-propanol, 25 g TEP, 50 g acetone, and 5 g 40% aqueous glyoxal solution.

It was of initial interest in working with this formulation to determine the effect of age of the casting solution on the hyperfiltration performance of CAB membranes. The water flux and rejection data for CAB membranes (Table IV) were cast 5 and 51 days after the casting solution was prepared.

TABLE IV
Effect of Aging the Casting Solution on the Hyperfiltration
Characteristics of CAB Membranes

Membrane code no.	Age of casting solution, days	Flux, gfd	Rejection, %	
			NaCl	Urea
CAB-G-6	5	4.65	97.4	62.8
CAB-G-7	51	3.97	98.0	63.0

TABLE V
Effect of Drying Time on Hyperfiltration Characteristics of CAB
Membranes Cast from a Formulation Containing Glyoxal

Membrane code no.	Drying time, sec	Flux, gfd	Rejection, %	
			NaCl	Urea
CAB-G-1	0	3.73	97.5	60.8
CAB-G-2	15	4.42	97.3	55.6
CAB-G-3	30	10.5	27.8	—
CAB-G-4	60	15.8	11.6	—

There was no significant difference in either water flux or rejection for the two membranes, which showed the casting solution had a shelf life of at least 50 days.

Table V shows the effect of drying time on water flux and rejection of CAB membranes cast from the formulation containing glyoxal: the water flux increased and urea and salt rejection decreased with drying time.

CAB membranes prepared from the "standard formulation," unlike the membranes prepared from the formulation with glyoxal, did not show an increase in water flux with drying time (see Tables III and V). However, films prepared from the two different formulations did exhibit comparable flux and rejection for zero drying time. The dramatic effect of drying on water flux and rejection by CAB membranes prepared from the formulation containing glyoxal allows one to tailor hyperfiltration membranes to meet the higher water flux and lower rejection requirements for certain applications. Since CAB membranes cast from the formulation containing glyoxal had the potential of being tailored and had comparable water flux and rejection (without drying) to membranes prepared from the standard formulation, it was decided to further investigate the properties of films prepared from this "glyoxal formulation." The remainder of the work to be described was done with films made from the formulation containing glyoxal and, unless stated otherwise, prepared without drying.

The effect of heat treatment on water flux and rejection of CAB membranes is shown in Table VI. Heat treatment for 5 min in 72°C distilled water caused a flux decrease that may be attributed to membrane shrinkage or a decrease in pore size. It is evident from Table VI that heat treatment caused an appreciable decrease in urea transport relative to water transport

TABLE VI
Effect of Heat Treatment on Hyperfiltration Characteristics of CAB Membranes^a

Membrane code no.	Before heat treatment			After heat treatment		
	Flux, gfd	Rejection, %		Flux, gfd	Rejection, %	
		NaCl	Urea		NaCl	Urea
CAB-G-1	3.73	97.5	60.8	1.72	96.6	81.8
CAB-G-2 ^b	4.42	97.3	55.6	1.12	95.6	79.4

^a Heat treatment conditions: 5 min in 72°C distilled water.

^b 15-Second drying time used in this membrane preparation.

and therefore improved urea rejection while salt transport relative to water, and therefore salt rejection, remained unchanged. Improved urea rejection with heat treatment may indicate some uncoupling of urea and water flux which, on a microscopic scale, may be due to increased urea exclusion from the membrane. Other authors have suggested coupled flow of urea and water (solvent drag) through biologic membranes.^{12,13} Urea exclusion could occur simply because the urea molecule was larger than some of the membrane pores. Heat treatment would cause a decrease in membrane pore size and therefore an increase in urea exclusion and rejection. Invariant salt rejection with heat treatment is consistent with a solution-diffusion transport mechanism of uncoupled flow⁹ if both the water and salt flow "paths" are affected in the same way by membrane shrinkage, i.e., both water and salt fluxes decrease proportionately and consequently salt rejection is invariant.

The effect of increasing pressure on water flux and rejection by a CAB membrane is shown in Figure 1. The slight curvature in the water flux-versus-pressure curve may be ascribed to compaction of the membrane with increasing pressure, i.e., the rate of water flux increase with pressure slows down due to increased "skin" thickness. Both urea and salt rejection increased with pressure. An increase in rejection with pressure is expected for solution-diffusion membranes. For a solution-diffusion membrane, rejection is given by⁹

$$\text{per cent rejection} = \left[1 + \frac{D_{2m}KR T c_1''}{D_{1m}c_{1m} \bar{V}_1(\Delta p - \Delta \pi)} \right]^{-1} \times 100 \quad (2)$$

where D_{1m} is the H₂O diffusion coefficient, c_{1m} is the membrane water content, D_{2m} is the salt diffusion coefficient, K is the distribution coefficient, \bar{V}_1 is the partial molar volume of water in the membrane, $(\Delta p - \Delta \pi)$ is the net pressure difference across the membrane (applied pressure less osmotic pressure), c_1'' is the concentration of water in the effluent solution, and R and T have their usual significance. It is evident from this equation that an increase in applied pressure increases rejection, as was found for urea and salt. Therefore, the mere increase in rejection with pressure (Fig. 1) does not allow a clear distinction to be made between the transport mechanism for urea and salt. However, since urea rejection increases more than

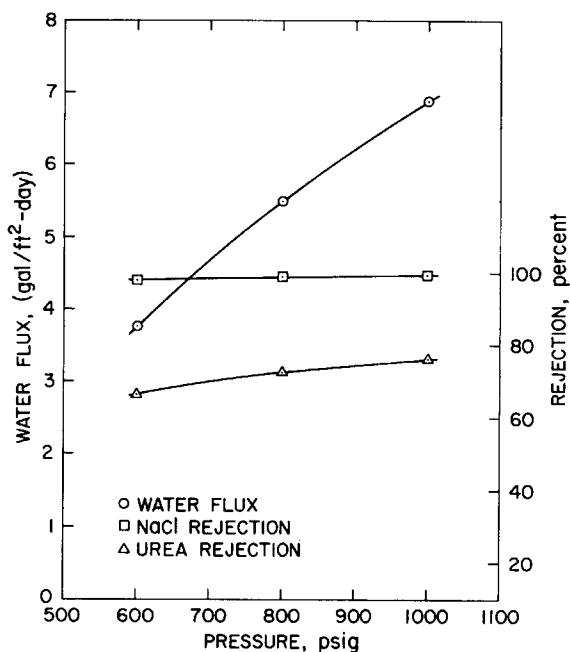


Fig. 1. Effect of pressure on the hyperfiltration performance of a CAB membrane.

sodium chloride rejection with pressure, it is possible that in the case of urea increased rejection may be due not only to the effect of pressure on the solution-diffusion mechanism but also to increased urea exclusion caused by pore shrinkage under pressure.

The improvement of urea rejection by higher pressure and by heat treatment at 72°C suggested a hyperfiltration experiment at 1000 psig with a heat-treated membrane. After running a CAB membrane for 70 hr at 1000 psig, the water flux was 3.22 gfd, salt rejection was 98.3%, and urea rejection, 85.0%. As expected, both urea rejection and water flux were higher when heat treatment was combined with operation at a pressure higher than 600 psig.

To provide additional and stronger evidence of a "skin" on the CAB membranes, the following hyperfiltration experiment was performed. First, water flux and rejection were determined with the skin side (side that contacts the casting blade during membrane fabrication) of the membrane facing the feed solution, and then the same membrane was turned over and the flux and rejection were again determined (see Table VII). It was expected that if the membrane were asymmetric, the water flux and rejection would be lower when the spongy substructure side was exposed to the feed solution. This would occur because the accumulation of solutes in the porous substructure cannot be prevented by circulating the feed solution over the membrane surface. Table VII clearly shows a significantly lower water flux and salt and urea rejection when the nonskin side of the mem-

TABLE VII
Comparison of the Hyperfiltration Characteristics of a CAB
Membrane With Skin Side Up and Skin Side Down

Membrane code no.	Skin side up			Skin side down		
	Flux, gfd	Rejection, %		Flux, gfd	Rejection, %	
		NaCl	Urea		NaCl	Urea
CAB-G-5	2.84	98.4	69.0	2.36	71.8	30.2

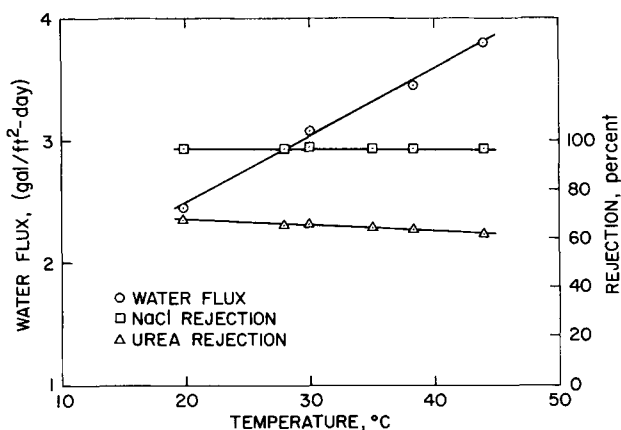


Fig. 2. Effect of temperature on the hyperfiltration performance of a CAB membrane.

brane faced the feed solution, demonstrating the asymmetry of these CAB membranes.

Figure 2 shows the effect of temperature on the hyperfiltration performance of a CAB membrane. Water flux increased significantly with temperature while both urea and salt rejection decreased. An increase in water flux with temperature is expected for a solution-diffusion membrane because of increased water diffusivity with temperature.

Urea rejection was more strongly influenced by temperature than salt rejection (Fig. 2), and this may be due to the different mechanisms by which these two solutes are rejected. If it is assumed that urea is rejected by membrane exclusion, an increase in temperature may increase the pore size of the membrane by thermal expansion, thereby allowing greater intrusion of urea into the membrane and lower urea rejection. Assuming salt is transported by a solution-diffusion mechanism, a decrease in salt rejection with increasing temperature would be predicted by eq. (2) when terms other than temperature (especially D_{1m} , c_{1m} , D_{2m} , and K) are compensating.

Figure 3 shows the hyperfiltration performance of a CAB membrane during the 400 hr of life testing. As expected, the flux decreased with time due to compaction of the membrane. Salt rejection remained constant after the initial 5 hr of testing and urea rejection slowly increased with time.

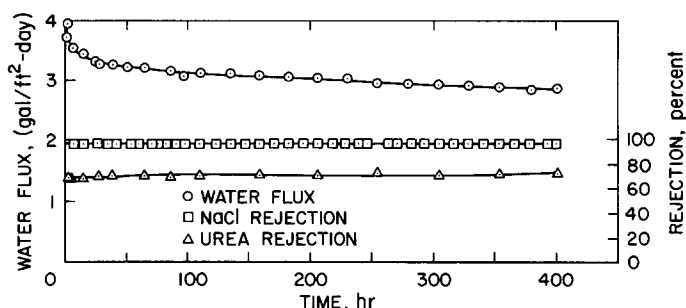


Fig. 3. Performance of a CAB membrane during life testing.

Lonsdale⁹ pointed out that for a solution-diffusion membrane, a decrease in water flux accompanied by invariant salt rejection (salt *flux* may also decrease with compaction) during compaction indicates that the thickness of the rejecting layer, or "skin," is increasing with time. Water flux and salt rejection behavior for the life test with CAB membranes are consistent with this interpretation of compaction.

The increased urea rejection with time may indicate that during compaction the membrane "skin" thickness not only increases but that the membrane pores also become smaller, thus improving urea rejection by exclusion from the membrane. This interpretation of the increased urea rejection with time during the life test is also consistent with the explanation for increased urea rejection with pressure and membrane heat treatment and decreased urea rejection with temperature.

SUMMARY

CAB membranes were found to give high salt and urea rejection with water flux of about 3 gfd at 600 psig. Membranes prepared from a formulation containing glyoxal showed a significant increase in flux and decrease in salt and urea rejection with drying time. Zero drying time gave maximum urea and salt rejection and was therefore most suitable for this work. Evidence was obtained which indicated that the CAB membranes used in this work had a skin or were asymmetric. Membrane heat treatment increased urea rejection appreciably while salt rejection was essentially invariant, and water flux decreased. An increase in feed solution temperature caused a significant increase in water flux and a small decrease in urea and salt rejection. Increasing the pressure increased water flux and urea and salt rejection. Combining membrane heat treatment with operation at 1000 psig improved urea rejection beyond that with heat treatment or pressure alone. During a 400-hr life test, the water flux decreased by about 25% while urea rejection increased and salt rejection was invariant. The effect of pressure, membrane heat treatment, and compaction during life testing on urea and salt rejection indicated that these two solutes were

rejected by somewhat different mechanisms with CAB membranes. Salt rejection was consistent with a solution-diffusion mechanism and uncoupled flow. Urea appeared to be rejected at least partially by membrane exclusion.

References

1. D. F. Putnam, Composition and Concentrative Properties of Human Urine, NASA Contractor Rept. DAC-61125-F1, June 1970.
2. H. Ohya and S. Sourirajan, *Ind. Eng. Chem., Process Des. Develop.*, **8**, 131 (1969).
3. S. Manjikian, S. Liu, M. Foley, C. Allen, and B. Fabrick, Office of Saline Water R&D Progress Rept. 534, Washington, D.C., June 1970.
4. S. Manjikian and M. I. Foley, Office of Saline Water R&D Progress Rept. 654, Washington, D.C., May 1971.
5. R. McKinney, Jr., *Polym. Preprints* **12**(No. 2), 365 (1971).
6. E. V. Ballou, T. Wydeven, and M. I. Leban, *Environ. Sci. Technol.*, **5**, 1032 (1971).
7. E. V. Ballou and T. J. Wydeven, *Colloid Interfac. Sci.*, **41**, 198 (1972).
8. W. M. King and M. L. O'Hair, Office of Saline Water R&D Progress Rept. 695, Washington, D.C., June 1971.
9. H. K. Lonsdale, in *Desalination by Reverse Osmosis*, ed. by U. Merten, M.I.T. Press, Cambridge, Mass., 1966, p. 93.
10. Eastman Chemical Products, Inc., Bulletin, *Cellulose Acetate Butyrate for Protective Coatings*, 2nd Ed., Kingsport, Tennessee, 1968.
11. G. W. Watt and J. D. Chrisp, *Anal. Chem.*, **26**, 452 (1954).
12. R. M. Hays and A. J. Leaf, *Gen. Physiol.*, **45**, 933 (1962).
13. H. H. Ussing and B. Johansen, *Nephron*, **6**, 317 (1969).

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