

## Development and Performance of Some Porous Cellulose Acetate Membranes for Reverse Osmosis Desalination\*

B. KUNST† and S. SOURIRAJAN, *Division of Chemistry, National Research Council of Canada, Ottawa, Canada*

### Synopsis

The effects of casting solution composition and evaporation period on the performance of resulting porous cellulose acetate membranes have been studied, and the results are discussed in terms of casting solution structure, solvent evaporation rate during film formation, and the film shrinkage temperature profile. The development of Batch 316-type porous cellulose acetate membranes is reported. At 90% level of solute separation and feed flow conditions corresponding to a mass transfer coefficient of  $45 \times 10^{-4}$  cm/sec, the productivities of the above membranes are 21.5 gallons/day/ft<sup>2</sup> at 250 psig using 3500 ppm of NaCl in the feed, and 53.9 gallons/day/ft<sup>2</sup> at 600 psig using 5000 ppm of NaCl in the feed.

### INTRODUCTION

Since the announcement of the Loeb-Sourirajan technique in 1960 for making asymmetric porous cellulose acetate membranes for water desalination,<sup>1,2</sup> extensive investigations have been initiated in several laboratories in search for superior membranes for reverse osmosis applications.<sup>3-6</sup> Two improvements relating to casting solution composition and film casting conditions are already well known with respect to porous cellulose acetate membranes: one by Sourirajan and Govindan<sup>7</sup> and the other by Manjikian, Loeb, and McCutchan,<sup>8</sup> both reported at the same time and place in 1965. These membranes, designated here as Batch 18- and Batch 47-type membranes, respectively, have essentially the same productivity, i.e., same permeation rate (product rate) at any given level of solute separation.

One of the common features in the process of making Batch 18- and 47-type membranes is that the temperature of the casting solution and that of the casting atmosphere are the same. In a major improvement with respect to the process of making porous cellulose acetate membranes reported recently by Kunst and Sourirajan,<sup>9</sup> the above two temperatures constitute two separate variables. Batch 301-type membranes, made on the basis of the latter improvement, have a productivity twice that of Batch 18- and

\* Paper presented at the 3rd International Symposium on Fresh Water from the Sea, Dubrovnik, Yugoslavia, September 13-16, 1970.

† On leave from the Faculty of Technology, University of Zagreb, Zagreb, Yugoslavia.

47-type membranes at operating pressures of 250 psig or less.<sup>10</sup> The film casting details with respect to Batch 18-, 47-, and 301-type membranes have been reported.<sup>10</sup>

The emergence of Batch 301-type membranes is the result of a new approach to the general problem of developing more productive reverse osmosis membranes.<sup>9,11</sup> In this approach, the state or the structure of the casting solution and the rate of solvent evaporation during film formation together constitute an important interconnected variable governing the ultimate porous structure and hence the performance of the resulting membranes in reverse osmosis.

The structure of the casting solution is a function of its composition and temperature; the term "solution structure" essentially refers to the state of supermolecular polymer aggregation in the casting solution. No effective means of expressing solution structure has yet been specified. However, useful conclusions seem possible from an analysis of the polymer-solvent-nonsolvent ternary phase equilibrium diagrams. For example, the remoteness of any point representing the composition of the casting solution from the phase boundary curve is a useful measure of the state of the solution at the temperature corresponding to the boundary curve.<sup>11</sup> Supermolecular aggregation in the polymer solution is decreased by increase in temperature of the casting solution.<sup>12,13</sup>

Solvent evaporation rate during film formation refers to the rate of solvent removal from the surface which ultimately forms the dense microporous layer in the resulting asymmetric membrane. This rate is a function of solution structure, temperature of the casting atmosphere, and the ambient nature of the casting atmosphere. The solvent evaporation rate is decreased by a decrease in the temperature of the casting atmosphere and/or the presence of solvent vapor in the ambient casting atmosphere. A typical evaporation rate curve (log of solvent loss versus time) for the cellulose acetate-acetone-aqueous magnesium perchlorate system plotted on a semilog scale<sup>11</sup> consists of an initial linear part from whose slope an evaporation rate constant,  $b$ , can be determined. For a given solution structure, an optimum value of  $b$  exists for best membrane performance, and identical values of  $b$  (by whatever means they are achieved) result in the same membrane performance.<sup>11</sup>

The film shrinkage temperature versus solute separation correlation (shrinkage temperature profile) gives a relative measure of the initial size of pores on the membrane surface in the as-cast condition and of the distribution of pore size resulting from shrinkage. On the basis of the preferential sorption-capillary flow mechanism and the concept of critical pore diameters,<sup>14</sup> it is only to be expected that pore size distribution will affect membrane performance significantly. It has been shown<sup>11</sup> that constancy of both solution structure and evaporation rate will result in the same membrane performance only when the corresponding shrinkage temperature profiles are also the same. Thus, shrinkage temperature profile has emerged as an important quality control parameter in membrane development.

TABLE I  
Film-Casting Details of 5 Different Batches<sup>a</sup>

Casting solution	Concentration, wt-%				
	Batch 303	317	316	314	319
Cellulose acetate (acetyl content 39.8%)	17	17	17	17	17
Acetone	68.0	68.5	69.2	69.8	70.5
Magnesium perchlorate	1.5	1.53	1.45	1.39	1.32
Water	13.5	12.97	12.35	11.81	11.18

<sup>a</sup> Temperature of casting solution: 0°C; temperature of casting atmosphere: 24°C; casting atmosphere: ambient air in contact with aqueous solution of 30 wt-% acetone; solvent evaporation period: 6 min; duration of film setting in ice-cold water: >1 hr; nominal film thickness: 0.004 in.

The distinguishing feature of the new approach to reverse osmosis membrane development described above<sup>9-11</sup> lies in the analysis of the usual film casting variables in terms of correlating membrane performance data with the casting solution structure, solvent evaporation rate during film formation, and shrinkage temperature profile. The above approach forms the basis of this work which extends the earlier investigations<sup>9-11</sup> on the cellulose acetate-acetone-aqueous magnesium perchlorate casting solution system, with particular reference to the effect of changes in the casting solution composition on the performance of the resulting membranes. This work has led to the development of Batch 316-type porous cellulose acetate membranes which are in some respects even better than the Batch 301-type membranes for low pressure reverse osmosis desalination and other applications.

## EXPERIMENTAL

The general experimental details are the same as those reported earlier.<sup>9-11</sup> Table I gives five different compositions of the film-casting solutions used. The concentration of cellulose acetate was the same (17%) in all the casting solutions, and the acetone content increased progressively in order 68.0, 68.5, 69.2, 69.8, and 70.5 wt-% in the film-casting compositions designated as Batch 303, 317, 316, 314, and 319 respectively; the non-solvent content in each batch decreased correspondingly. The magnesium perchlorate-water ratio in the nonsolvent part was 1:9 in the Batch 303 composition and 1:8.5 in all the others. The casting solution temperature and the external conditions of solvent evaporation during film casting were identical for all the five types of films studied. The evaporation rate measurements were carried out under comparable conditions by casting the films on small aluminum plates and following the solvent loss gravimetrically.<sup>11</sup> The membrane performance data were obtained for conditions of feed concentration and feed flow rate corresponding to a mass transfer

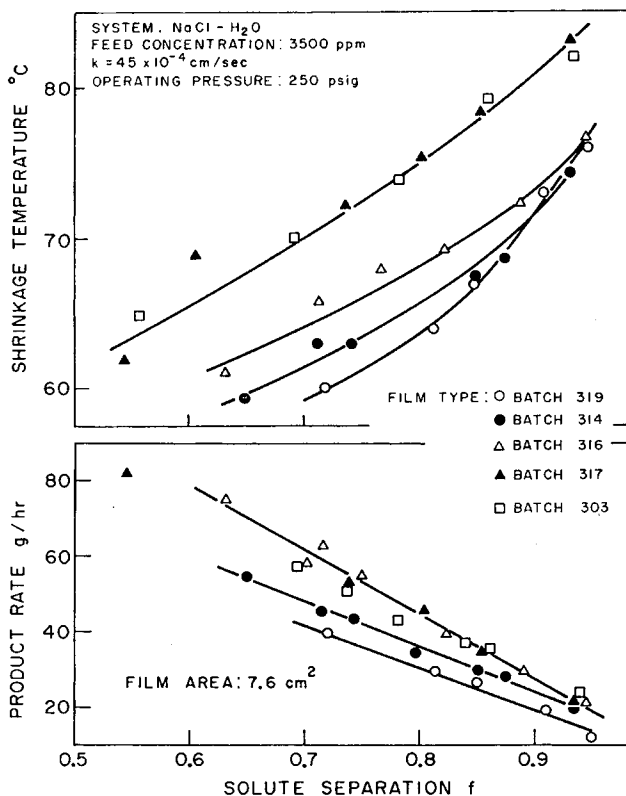


Fig. 1. Effect of casting solution composition on membrane characteristic curves.

coefficient  $k$  of  $45 \times 10^{-4}$  cm/sec on the high pressure side of the membrane, using aqueous sodium chloride feed solutions.

## RESULTS AND DISCUSSION

Figure 1 gives the performance data (solute separation versus product rate correlation) obtained with the different batches of membranes mentioned above, along with their shrinkage temperature profiles. The latter correlation shows that for the type of membranes studied, the initial average size of pores on the membrane surface (in the as-cast condition) decreases significantly and progressively with changes in acetone content in the casting solutions.

At levels of solute separation, higher than 80%, the membrane performance data fall essentially on the same curve for Batch 303-, 317-, and 316-type membranes; at lower levels of solute separation, the productivity of the membranes slightly increases in the order Batch 316 > Batch 317  $\approx$  Batch 303. The productivities of Batch 314- and 319-type membranes are lower than those of the others.

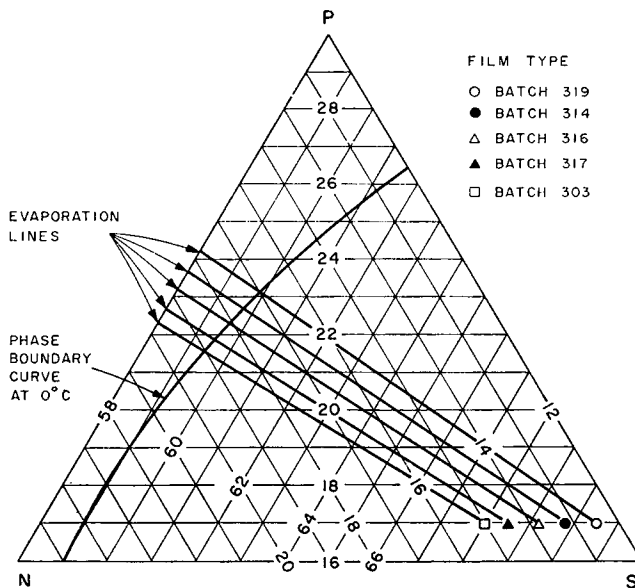


Fig. 2. Location of different compositions, their evaporation lines, and the phase boundary curve in the ternary equilibrium diagram.

Membrane performance is a function of both the average size and the effective number of pores on the membrane surface. Figure 1 also gives an indication of the changes occurring in the effective number of pores as a result of changes in the casting solution composition. The shrinkage temperature profiles and the productivities of Batch 303- and 317-type membranes are not significantly different, indicating that the average size and effective number of pores on their surfaces are not too far different from each other. The initial average pore size in Batch 316 membranes is smaller, and their productivity is better or the same as that of Batch 303 membranes. These data indicate that Batch 316-type membranes have initially more numerous pores on their surface. Batch 314- and 319-type membranes have still smaller pores in their respective as-cast conditions, but their effective numbers are insufficient to give the same productivity as the Batch 316-type membranes. Thus, from the point of view of productivity, the Batch 316-type membranes emerge as the best among the five types studied. The results clearly illustrate that even small changes in the casting solution composition affect membrane performance significantly.

The casting solution compositions used are located in the polymer-solvent-nonsolvent triangular diagram (P-S-N, Fig. 2) where the composition changes during solvent evaporation (evaporation lines) are also given. The phase boundary curve shown in Figure 2 is the same as that given earlier.<sup>11</sup> Assuming this curve to be applicable for all the casting solutions studied here, Figure 2 shows that Batch 303 and 319 compositions are the least remote and the most remote, respectively, from the phase boundary curve.

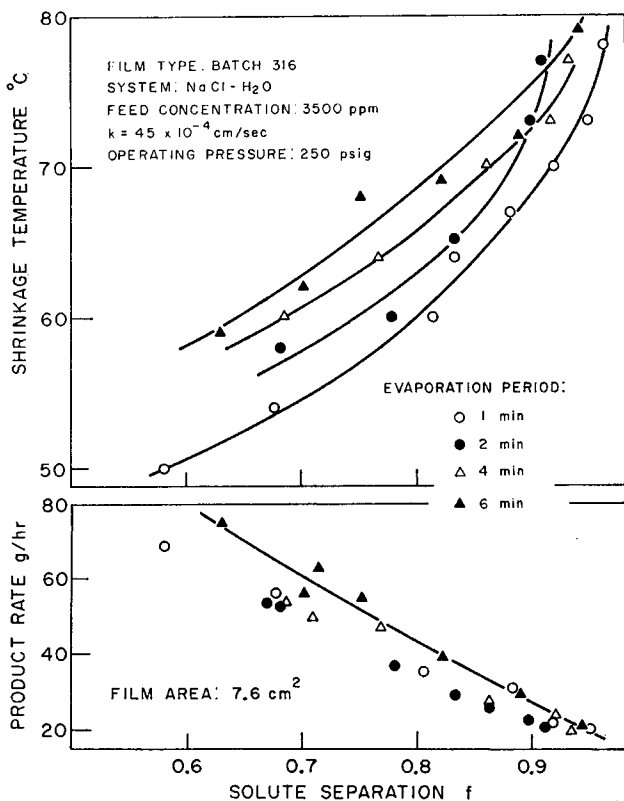


Fig. 3. Effect of evaporation periods on membrane characteristic curves.

In conjunction with the shrinkage temperature profiles given in Figure 1, Figure 2 shows that the greater the remoteness of the point representing the composition of the casting solution from the phase boundary curve, the smaller is the average size of pores produced on the membrane surface. As discussed earlier,<sup>11</sup> such greater remoteness also indicates lesser supermolecular polymer aggregation in the casting solution. Consequently, the formation of smaller pores on the membrane surface can be attributed to lesser supermolecular polymer aggregation in the casting solution. Further, it is evident that lesser supermolecular aggregation of polymer in the casting solution can be achieved either by increasing the solvent content in the casting solution or by increasing its temperature, or by both.

The experimental evaporation rate constants obtained were 0.081 and 0.098  $\text{min}^{-1}$ , respectively, for Batch 303- and 319-type membranes; intermediate values were obtained for the others. In view of the narrow range of the variations in the evaporation rate constants obtained, it is reasonable to consider that the film-casting conditions used tended toward conditions of constant evaporation rate. The evaporation rate data, along with the corresponding membrane performance data given in Figure 1, indicate that

for a constant evaporation rate there is an optimum solution structure for maximum membrane productivity. This confirms the observation made earlier that for each solution structure there is an optimum evaporation rate for maximum membrane productivity.

Figure 3 illustrates the effect of evaporation period on shrinkage temperature profile and performance of Batch 316-type membranes. The longer the evaporation period, the bigger is the average size of initial pores on the membrane surface. This is understandable on the basis of the mechanism of pore formation discussed earlier,<sup>9</sup> in which initially formed droplets in the surface region coalesce on prolongation of evaporation time, forming larger ones which result eventually in bigger size pores on the membrane surface. Similar observations have been reported before with respect to Batch 18-type membranes.<sup>9</sup> Unlike the latter-type membranes, however, evaporation period also affects the performance of Batch 316-membranes. This is only to be expected in view of the less uniform, smaller pores obtained with Batch 316 membranes. It was found that an evaporation period of 6 min resulted in best membrane performance. Further, the data indicate that, as the average size of pores on the membrane surface in the as-cast condition becomes smaller and smaller, one may expect an optimum evaporation period, and hence shrinkage temperature profile, for maximum membrane productivity.

A gradual change in the physical appearance of the Batch 316-type membranes made with different evaporation periods was immediately noticeable, as shown in Figure 4. The membranes made with an evaporation period of 1 min were opaque, and those made with an evaporation period of 6 min were transparent. For a given casting solution structure, the transparency of the resulting membranes seems closely related to the pore structure of the membrane surface. At least for the type of membranes studied in this work, it seems reasonable to conclude that membranes with a large number of small-size, less uniform pores tend to be opaque, and this opacity decreases as pores become larger and more uniform.

Figure 5 gives two sets of data on the comparative performance of Batch 18-, 47-, 301-, and 316-type membranes for the separation of salt from aqueous sodium chloride feed solutions. For example, at 90% level of solute separation and feed flow conditions corresponding to a mass transfer

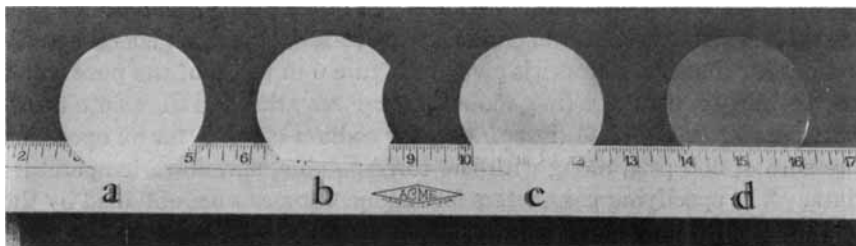


Fig. 4. Effect of evaporation period on membrane appearance: (a) 1 min; (b) 2 min; (c) 4 min; (d) 6 min.

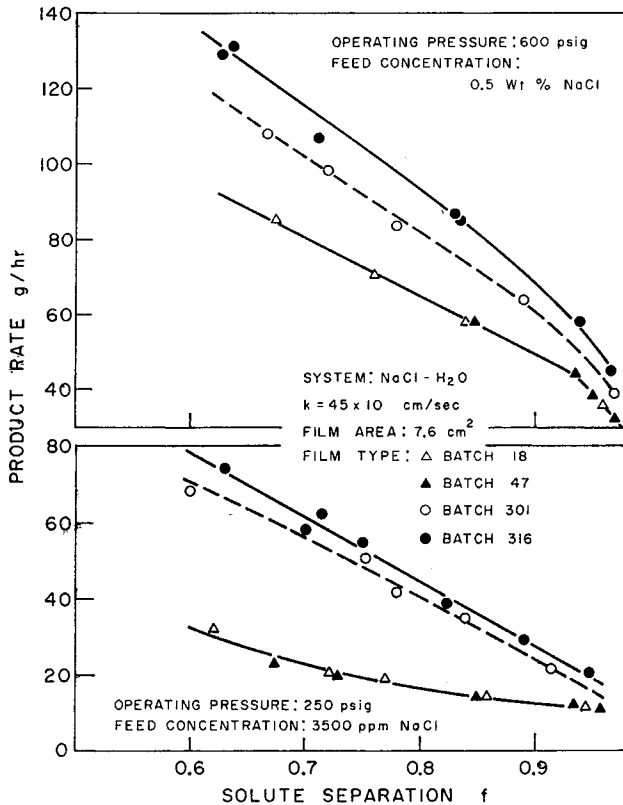


Fig. 5. Performance curves for Batch 316-type membranes at 600 and 250 psig.

coefficient  $k$  of  $45 \times 10^{-4}$  cm/sec, the productivities of Batch 18-, 47-, 301-, and 316-type membranes, in gallons per day per ft<sup>2</sup>, were 9.7, 10.8, 19.3, and 21.5, respectively, at 250 psig using 3500 ppm NaCl in the feed, and 39.2, 38.6, 47.3, and 53.9, respectively, at 600 psig using 5000 ppm NaCl in the feed. These data illustrate not only the superior performance of Batch 316-type membranes compared to the other types reported earlier, but also the success of the new approach used for the development of more productive reverse osmosis membranes.

In view of the practical importance of the Batch 316-type membranes for brackish water conversion and similar applications, a set of general specifications for these membranes is given in Figure 6 in terms of the pure water permeability constant  $A$  (in g-mole H<sub>2</sub>O/cm<sup>2</sup> sec atm) and the solute transport parameter  $D_{AM}/K\delta$  (in cm/sec), for sodium chloride for an operating pressure of 600 psig, along with the corresponding shrinkage temperature data. The specifying parameters for the membranes were obtained by the Kimura-Sourirajan analysis of the experimental reverse osmosis data,<sup>15</sup> and these specifications can be used for parametric studies on water desalination as illustrated by Ohya and Sourirajan.<sup>16</sup>



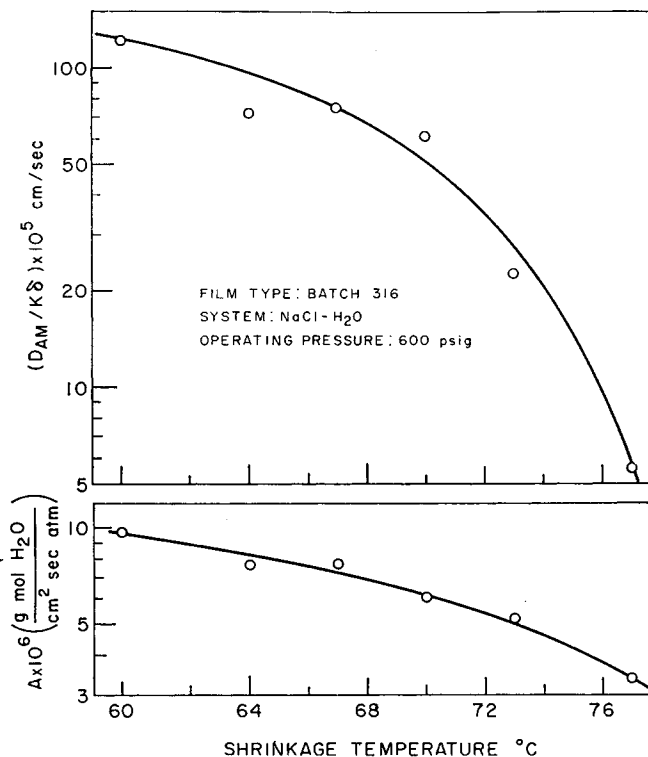


Fig. 6. General specifications for Batch 316-type membranes at 600 psig.

## CONCLUSIONS

Even small variations in the casting solution composition cause significant changes in solution structure and the properties of the resulting membranes. The results illustrate the practical utility of the general approach based on the solution structure-evaporation rate concept for creating more productive reverse osmosis membranes. The development of Batch 316-type porous cellulose acetate membranes is of great interest for a wide variety of low pressure reverse osmosis applications.

The authors are grateful to Lucien Pageau and A. G. Baxter for their valuable assistance in this work. One of the authors (B.K.) thanks the National Research Council of Canada for the award of a postdoctoral fellowship N.C.R. No. 11651.

## References

1. University of California, Office of Public Information, Press Release, New Water Desalting Process Developed at UCLA, August 23, 1960.
2. S. Loeb and S. Sourirajan, Department of Engineering, University of California, Los Angeles, Report No. 60-60, 1961.
3. S. Sourirajan, *Reverse Osmosis*, Chap. 2, Academic Press, New York, 1970.
4. C. W. Saltonstall, Research and Development Progress Report No. 434, U.S. Department of the Interior, Office of Saline Water, June 1969.

5. W. J. Subcasky and G. Segovia, Research and Development Progress Report No. 466, U.S. Department of the Interior, Office of Saline Water, October 1969.
6. R. Bloch, M. A. Frommer, O. Kedem, I. Feiner, A. Kedem, and D. Lancet, Research and Development Progress Report No. 499, U.S. Department of the Interior, Office of Saline Water, December 1969.
7. S. Sourirajan and T. S. Govindan, Proceedings of the First International Symposium on Water Desalination, Oct. 3-9, 1965, Vol. 1, U.S. Dept. of the Interior, Office of Saline Water, Washington, D.C., pp. 251-274.
8. S. Manjikian, S. Loeb, and J. W. McCutchan, Proceedings of the First International Symposium on Water Desalination, Oct. 3-9, 1965, Vol. 2, U.S. Dept. of the Interior, Office of Saline Water, Washington, D.C., pp. 159-173.
9. B. Kunst and S. Sourirajan, *J. Appl. Polym. Sci.*, **14**, 723 (1970).
10. B. Kunst and S. Sourirajan, *Desalination*, **8**, 139 (1970).
11. B. Kunst and S. Sourirajan, *J. Appl. Polym. Sci.*, **14**, 1983 (1970).
12. V. I. Klenin and N. K. Kolnibolotchuk, *Mekh. Protseessov Plenkoobrazov. Polim. Rastvorov Dispersii, Akad. Nauk SSSR, Sb. Statei*, 32 (1966).
13. V. I. Klenin and O. V. Klenina, *Mekh. Protseessov Plenkoobrazov. Polim. Rastvorov. Dispersii, Akad. Nauk SSSR, Sb. Statei*, 45 (1966).
14. S. Sourirajan, *Ind. Eng. Chem., Fund.*, **2**, 51 (1963).
15. S. Sourirajan and J. P. Agrawal, *Ind. Eng. Chem.*, **61** (11), 62 (1969).
16. H. Ohya and S. Sourirajan, *Desalination*, **6**, 153 (1969).

Received May 27, 1970.

Revised July 2, 1970.