An Approach to the Development of Cellulose Acetate Ultrafiltration Membranes

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Synopsis

The film-casting solution consisted of a mixture of cellulose acetate, acetone, and aqueous magnesium perchlorate [$Mg(ClO_4)_2 : H_2O$ = 1:8.5], designated as polymer P, solvent S, and nonsolvent N, respectively. Using the composition P:S:N = 17:69.2:13.8 as reference, films were obtained from 19 different casting solutions in which the weight ratios S/P, N/S, and N/P were varied in different directions. The casting solution temperature was 0°C, and solvent evaporation period during film formation was minimum in most cases. The effects of variations of casting solution temperature and solvent evaporation period were also briefly studied. Reverse osmosis experiments with resulting membranes were carried out at 100 psig using 200 ppm $NaCl$–H_2O as the feed solution. Decrease in S/P, increase in N/S, and increase in N/P in the casting solution, decrease in temperature of the casting solution, and increase in solvent evaporation period tend to increase the size of pores on the surface of resulting membranes in the as-cast condition. Increase in S/P in the casting solution, and increase in the temperature of the casting solution tend to increase the effective number of pores on the membrane surface. These results offer definitive physicochemical criteria in terms on solution structure–evaporation rate concept for developing useful cellulose acetate ultrafiltration membranes.

INTRODUCTION

Cellulose acetate ultrafiltration membranes are of practical interest for a great variety of industrial applications such as food processing and biochemical separations. These ultrafiltration membranes may be considered simply as reverse osmosis membranes with relatively bigger average-size pores on the membrane surface. The location of the dividing line between the sizes of pores on the surfaces of ultrafiltration and reverse osmosis membranes is totally arbitrary. The solution structure–evaporation rate concept developed earlier[1-8] for controlling the porosity of cellulose acetate reverse osmosis membranes during film formation is equally relevant for the creation of similar ultrafiltration membranes. It is the object of this paper to illustrate this relevance.

The term solution structure essentially refers to the state of supermolecular polymer aggregation in the film casting solution, and it is a function of

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the composition and temperature of the casting solution. 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 porous membrane; the above rate is a function of solution structure, temperature of casting atmosphere, ambient nature of casting atmosphere including humidity, and solvent evaporation period.

Previous work[1-8] has shown that a bigger size of pores on the membrane surface in the as-cast condition is the result of larger size of supermolecular polymer aggregates in the casting solution. A similar result is also obtained by a higher rate of droplet growth and/or droplet coalescence in the interdispersed phase during film formation; the latter factors are favored by higher rates of solvent evaporation.

Since composition and temperature of the casting solution affect both the size of supermolecular polymer aggregate and solvent evaporation rate during film formation, change of casting solution structure offers a means of creating bigger average-size pores on the membrane surface in the as-cast condition. This paper is particularly concerned with this aspect of the subject.

EXPERIMENTAL

The film-casting solution used in this work consisted of a mixture of cellulose acetate (Eastman Grade 398-3), acetone, and aqueous magnesium perchlorate solution [$Mg(ClO_4)_2 : H_2O = 1 : 8.5$]. Just for convenience of discussion, the above constituents are designated in this paper as polymer P, solvent S, and nonsolvent N. The casting solution composition corresponding to Batch 316-type membranes developed earlier[3] (see Table I) was taken as the reference composition. For the purpose of this work, the casting solution compositions were chosen by systematic changes in different directions as indicated in the triangular composition (weight-%) diagram shown in Figure 1. The actual compositions used are given in Table I. The film-casting conditions used were as follows: temperature of casting solution, 0°C (unless otherwise specified); temperature of casting atmosphere, 25°C; relative humidity of casting atmosphere, 60–65%; evaporation period, minimum (2 to 5 sec) (unless otherwise specified); gelation medium, ice-cold water; and gelation period, 1 hr. The temperature of the glass plate on which the film was cast was the same as the temperature of the casting solution in each case. The membranes were not subjected to any thermal shrinkage treatment prior to reverse osmosis experiments The membranes, however, were initially subjected to pure water pressure of 150 psig for 2 hr to stabilize their porous structure.

Reverse osmosis experiments were carried out in the apparatus used before[3] at an operating pressure of 100 psig using aqueous sodium chloride feed solutions. All experiments were carried out at the laboratory temperature (23–25°C). In each experiment, the solute concentration in feed was 200 ppm, and the feed flow rate was 400 cc/min corresponding to a mass transfer coefficient of 25×10^{-4} cm/sec on the high-pressure side of the

TABLE I
Casting Solution Compositions Used

Direction	Batch no.	P	S	N
A	316	17	69.2	13.8
	350	15	69.2	15.8
	351	14	69.2	16.8
	352	13	69.2	17.8
B	316	17	69.2	13.8
	353	16	68.2	15.8
	354	15	67	18.0
	355	14	66	20.0
C	316	17	69.2	13.8
	356	16.5	67.2	16.3
	357	16.2	66.2	17.6
	358	16	65.1	18.9
D	316	17	69.2	13.8
	359	17	67	16.0
	360	17	65	18.0
	361	17	63	20.0
E	316	17	69.2	13.8
	362	18.2	67	14.8
	363	19.2	65.2	15.6
	364	20.2	63.4	16.4
F	316	17	69.2	13.8
	365	19	67.2	13.8
	366	20.6	65.6	13.8
	367	22.2	64	13.8

membrane.   Under the experimental conditions used, the osmotic pressure effects were negligible.   The effective area of film surface was 13.2 cm². In each experiment, the pure-water permeation rate PWP and membrane-permeated product rate PR, in g/hr per given area (13.2 cm²) of film surface, and the per cent solute separation f obtained from the relation f, (solute ppm in feed − solute ppm in product) ÷ (solute ppm in feed), were determined.   Since data on PWP and PR were essentially the same, the data on PWP and solute separation were considered to give a measure of the size and number of pores on the membrane surface.

The solute concentrations in feed and product solutions were determined by specific resistance measurements using a conductivity cell.   The accuracy of separation data is within 1%, and that of PWP data is within 3% in all cases.

RESULTS AND DISCUSSION

Casting Solution Compositions

With Batch 316 composition as the starting point, the composition of the casting solution was changed in six different directions, A to F, shown in Figure 1.   The actual compositions used in this study are listed in Table
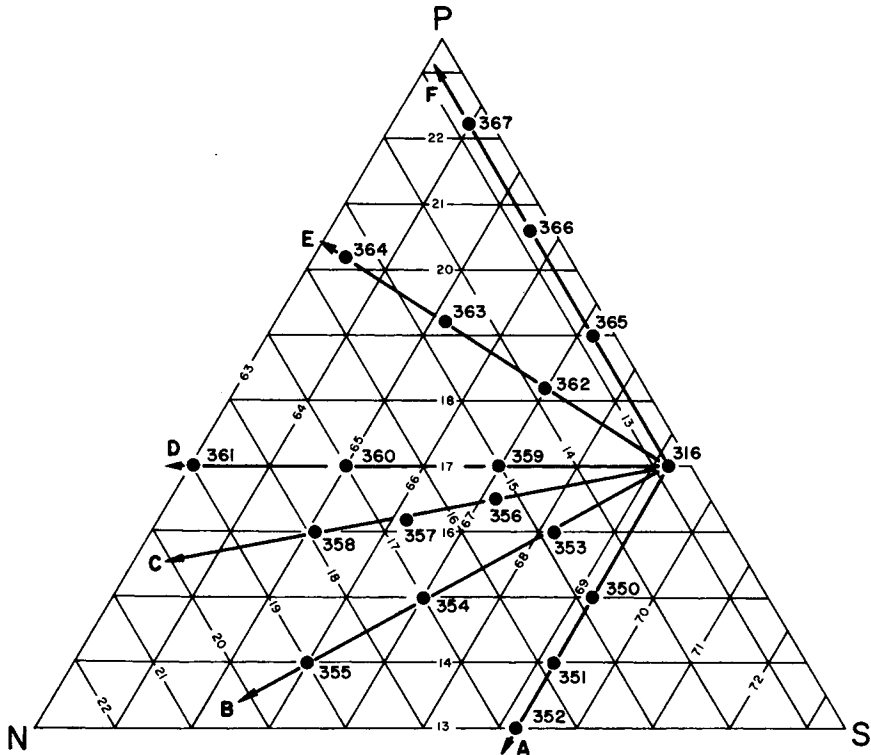
Fig. 1. Changes in casting solution compositions as seen in a triangular diagram.

I, and the changes in the composition variables in terms of weight ratios S/P, N/S, and N/P in each direction are shown in Figure 2. As the location of the casting solution composition in the triangular diagram (Fig. 1) is chosen progressively farther away from the location of the 316 composition, the following changes occur with respect to composition variables.

Polymer content (P) decreases in directions A, B, and C, remains constant in direction D, and increases in directions E and F. Solvent content (S) remains constant in direction A and decreases in directions B to F. The nonsolvent (N) content increases in directions A to E, and remains constant in direction F. The S/P ratio increases in directions A and B, remains constant in direction C, and decreases in directions D, E, and F. The N/P ratio increases in directions A to D, remains constant in direction E, and decreases in direction F. The N/S ratio increases in all the directions A to F studied.

Membrane Porosity Versus Casting Solution Composition Variables

The data on solute separation for sodium chloride and pure water permeation rate obtained with films cast from 19 different casting solution compositions (Table I) chosen from directions A to F described above are shown
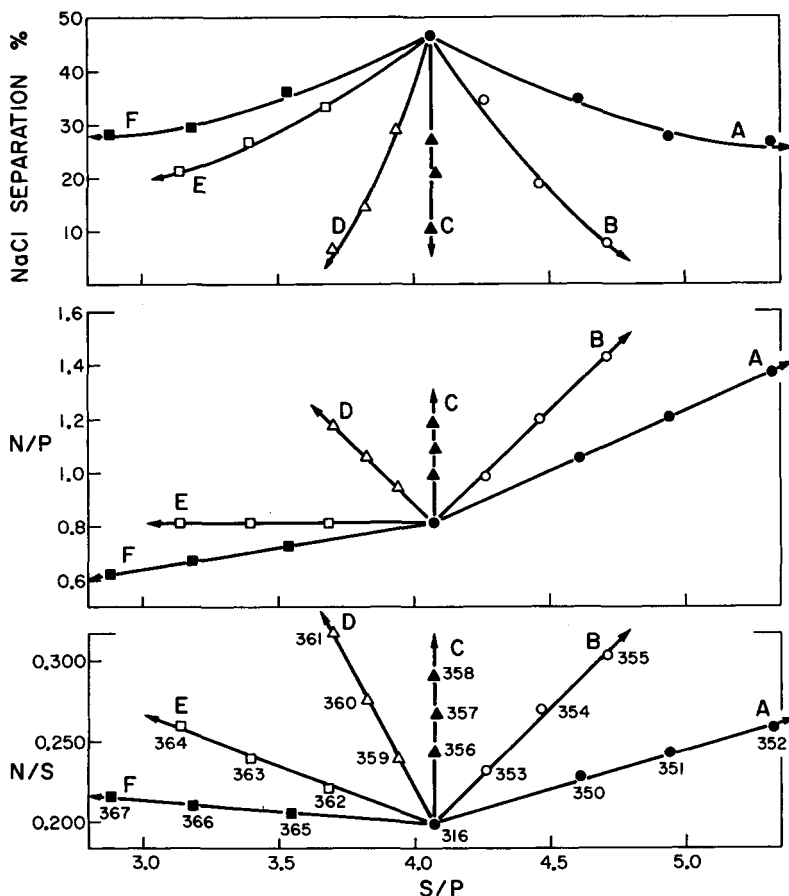
Fig. 2. Effect of variations of S/P, N/S, and N/P ratios on solute separation. Composition of casting solution, as given in Table I; temperature of casting solution, 0°C; temperature of casting atmosphere, 25°C; relative humidity of casting atmosphere, 60–65%; evaporation period, minimum (2 to 5 sec); feed solution, 200 ppm NaCl–H_2O; operating pressure, 100 psig.

in Figures 2 and 3. In these experiments, the temperature of the casting solution was 0°C, and solvent evaporation period during film formation was minimum in the range of 2 to 5 sec in all cases. With such short evaporation periods, the quantity of solvent lost by evaporation before immersion in ice-cold water could be considered practically negligible. Consequently, the change in average size of pores on the membrane surface could be considered essentially due to the change in casting solution structure. Since the membranes were not subjected to any thermal shrinkage treatment prior to reverse osmosis experiments, the data on solute separation and pure water permeation rate could be considered respectively to give relative quantitative measures of average pore size on membrane surface and overall porosity of the membrane in the as-cast condition.
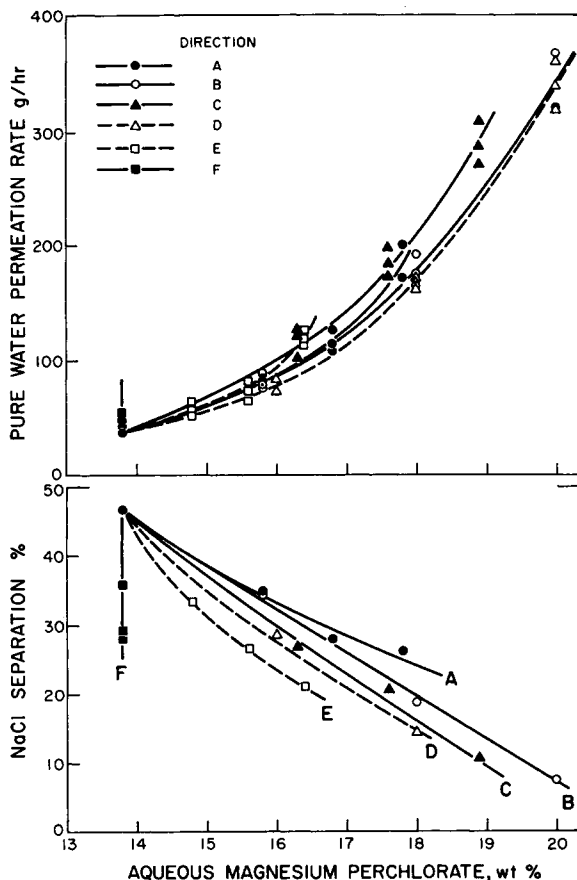
Fig. 3. Effect of casting solution composition on solute separation and pure water permeation rate. Effective film area, 13.2 cm²; other details, same as for Fig. 2.

Figure 2 illustrates the effects of S/P, N/P, and N/S ratios on the average pore size on the surface of resulting membranes. A decrease in solute separation represents an increase in average pore size on the membrane surface. The experimental data show that by systematic change of casting solution composition, one can produce bigger average-size pores on the surface of resulting membranes. The membrane obtained from the Batch 316 composition gave 46.7% separation for sodium chloride, whereas that obtained from the Batch 361 composition gave 6.5% separation for sodium chloride. These data show that the average pore size on the surface of the latter membrane was considerably bigger.

Figure 2 further shows that in each one of directions A to F, the farther away the location of the casting solution composition was from the location of the Batch 316 composition, the bigger was the average size of pores on the surface of the resulting membrane. Since the above result corresponds to an increase in N/S ratio in each case, one may conclude that, at a con-

stant temperature of the casting solution, for any given polymer concentration an increase in N/S ratio in the casting solution results in an increase in the average size of pores on the surface of the resulting membranes. This conclusion is confirmed by the results obtained with respect to casting solution compositions chosen in the direction D which corresponds to constant polymer content. Similar observations with respect to the effect of nonsolvent content in the casting solution have been made by several workers.[9-13] Solute separation data further show that an increase in average pore size on the membrane surface results also from an increase in N/P ratio in casting solutions whose S/P ratio is constant (direction C) and by a decrease in S/P ratio in casting solutions whose N/P ratio is constant (direction E). All the above results are consistent on the basis that (i) the size of supermolecular polymer aggregate in the casting solution increases with increase in N/S, increase in N/P, and/or decrease in S/P; and (ii) the presence of the larger size of supermolecular polymer aggregates in the casting solution leads to the formation of bigger-size pores on the surface of resulting membranes.

Table II illustrates the relative effects of 10% and 20% changes in the casting-solution composition variables N/P, N/S, and S/P using Batch 316 composition as the reference. The changes were assumed in the direction of greater supermolecular polymer aggregation in the casting solution (increases in N/P and N/S, and decrease in S/P), and data on solute separation obtainable on such composition changes were obtained by interpolation from experimental data given in Figure 2. The results showed that solute separations were essentially the same for the same fractional increases in N/P and N/S in the reference composition; but a decrease in S/P to the same fractional extent gave lower solute separations. These results indicate that, with respect to the reference composition considered, the same fractional increases in N/P (in direction C) and N/S (in directional D) result in essentially identical changes in the structure of the resulting casting solution, whereas a decrease in S/P (in direction E) to the same fractional extent has a greater effect on the structure of the resulting casting solution. For example, a 10% decrease in S/P in the reference composition in the

TABLE II
Effect of Change in N/P, N/S, and S/P Ratios on Pore Size on Membrane Surface

Change	Direction C		Direction D		Direction E	
	N/P	Solute sepn., %	N/S	Solute sepn., %	S/P	Solute sepn., %[b]
Reference composition[a]	0.812	46.7	0.199	46.7	4.071	46.7
10%	0.893	37.2	0.219	36.8	3.664	33.0
20%	0.974	29.0	0.239	28.9	3.257	23.0

[a] Batch-316 composition.
[b] From data in Fig. 2.

direction E increases the size of supermolecular polymer aggregates in the resulting casting solution more than a 10% increase in N/P in the direction C, or N/S in the direction D for the same reference composition. These observations probably have some general significance, even though the magnitude of changes involved should be expected to differ for different casting solution compositions and temperatures.

From a practical point of view, one is interested in creating not only bigger size of pores on the membrane surface, but also a larger number of such pores for increasing the productivity (i.e., membrane flux for a given pore size) of such membranes. The latter is a function not only of the number of pores on the membrane surface but also of the effective thickness of the membrane, which is again a function of the structure of the casting solution and conditions of film casting. There is no precise way of mutually separating the effect of changes in the number of pores on the membrane surface and that of changes in the effective thickness of the membrane. Therefore, for practical purposes, one may consider an increase in membrane flux at a given level of solute separation to represent an increase in the effective number of pores on the membrane surface.

Figure 3 gives data on sodium chloride separation and pure water permeation rate (PWP) as a function of aqueous magnesium perchlorate (nonsolvent) content in the casting solutions used. The general increase in PWP with decrease in solute separation is of course due to the increase in average size of pores on the membrane surface. The PWP data at a given level of solute separation are particularly interesting from the point of view of the effective number of pores on the membrane surface. The data show, for example, that for 30% level of solute separation, the pure-water permeation rates are 110, 99, 99, 71, 65, and 46 g/hr (per 13.2 cm^2 of film surface) respectively for casting solution compositions lying in directions A, B, C, D, E, and F. The data on PWP for lower levels of separation are in the same order in the range of available experimental data. This means that composition changes in direction A offers the possibilities of obtaining more productive ultrafiltration membranes than those obtainable from composition changes chosen from the other directions studied.

The foregoing results are significant. They are generally consistent with Kesting's conclusion[11-13] on the effect of increase in concentration of swelling agent (nonsolvent) in the casting solution. Further, referring to Figure 2, the casting solution composition variables given by the ratios S/P, N/S, and N/P all increase in direction A. An increase in S/P tends to decrease supermolecular polymer aggregation in the casting solution. It has already been shown[3,5] that lesser supermolecular polymer aggregation in the casting solution tends to generate a larger number of smaller-size pores on the membrane surface in the as-cast condition. Thus, with respect to composition changes in direction A, an increase in N/S or N/P tends to favor the formation of bigger-size pores on the membrane surface, while an increase in S/P tends to favor the formation of a larger number of such pores. These two simultaneous tendencies constitute the requirement for

the development of ultrafiltration membranes for practical applications. One may find an optimum combination of S/P and N/S with respect to casting solution composition for the creation of the largest effective number of pores of required size on the membrane surface in the as-cast condition. Thus, the effect of casting solution structure on the porosity of the resulting membranes explains the experimental data given in Figure 3 and offers a physicochemical basis for the development of useful ultrafiltration cellulose acetate membranes.

Effect of Casting Solution Temperature

The effect of temperature of casting solution on the size of pores on the surface of resulting membranes was studied using Batch-316, -350, -354, -360, and -363 compositions chosen from directions A, B, D, and E shown in Figure 2. Films were cast with casting solution temperature kept at 25°C for all the above compositions; films were also cast with casting solution temperature kept at −10°C and 10°C for the Batch-354 composition. The solvent evaporation period was again kept minimum (2 to 5 sec) in each case. The data on solute separation and PWP obtained with the above films are given in Table III along with data obtained for the corresponding films cast from solutions at 0°C (Fig. 3). The results show that, in all cases tested, solute separation increased (i.e., average size of pores on the surface of resulting membranes decreased) with increase in temperature of the casting solution. It is known[14,15] that for a casting solution of given composition, the size of supermolecular polymer aggregates decreases sharply with increase in temperature of the solution. The data given in Table III confirm the observation made earlier[3,5] that smaller supermolecular polymer aggregates in the casting solution tend to decrease the size of

TABLE III
Effect on Casting Solution Temperature on Membrane Porosity

Direction	Batch no.	Casting solution temp., °C	Solute sepn., %[a]	PWP, g/hr[a]
Reference	316	0	46.7	37.4
		25	58.4	14.7
A	350	0	34.8	78.5
		25	50.5	37.1
B	354	−10	7.3	358.1
		0	18.8	179.4
		10	24.1	137.2
		25	35.6	96.4
D	360	0	14.5	168.6
		25	36.7	68.3
E	363	0	26.6	72.2
		25	42.8	35.8

[a] Operating pressure, 100 psig; feed concentration, 200 ppm NaCl; feed flow rate, 400 cc/min; effective film area, 13.2 cm².

pores on the surface of resulting membranes. Consequently, for a given casting solution composition, a decrease in the temperature of the solution would tend to increase the size of pores on the surface of resulting membranes in the as-cast condition. This is explicitly confirmed by the data given in Table III for the Batch-354 composition in the temperature range of −10° to 25°C.

The decrease in PWP with increase in solute separation reported in Table III is primarily the consequence of the decrease in pore size on the membrane surface. The effect of temperature of casting solution on the productivity (i.e., PWP for a given pore size) of resulting membranes has been discussed in an earlier paper.[5] Since lower supermolecular polymer aggregation in the casting solution favors both droplet formation and droplet coalescence in the interdispersed phase during film formation, a change in solution structure by change in temperature of solution may be expected to lead to positive, negative, or zero change in productivity of resulting membrane depending on the particular casting solution composition under consideration.

Effect of Evaporation Period

The basis of solution structure–evaporation rate concept in reverse osmosis membrane science is that both the structure of the casting solution and solvent evaporation rate during film formation together constitute a single interconnected variable governing the porosity of resulting membrane. Even though this paper is mainly concerned with the effect of solution structure on porosity, the need for combining appropriately the effects of casting solution structure and solvent evaporation rate during film formation to give optimum results for specific applications cannot be overemphasized.

The effect of (time-independent) evaporation rate constant on the porous structure of resulting membranes has been discussed in earlier papers[2,5] primarily from the point of view of creating relatively smaller size pores on the membrane surface. Similar studies from the point of view of creating progressively bigger-size pores on the membrane surface should be rewarding in developing useful ultrafiltration membranes.

Even though the effect of evaporaion period on porosity is part of the general effect of solvent evaporation rate during film formation, the former is best treated as an independent variable in reverse osmosis membrane science. It has been shown before[3-5] that the average size of pores on the membrane surface increases with increase in evaporation time. Consequently, evaporation period is a particularly significant variable in the development of ultrafiltration membranes. This is illustrated by the data presented in Table IV for a set of membranes cast from Batch-354 casting solution at 0°C. In making these films, the evaporation period was changed from very short (2 to 5 sec) to 90 sec. Data on membrane performance in reverse osmosis showed that solute separation decreased and PWP increased progressively with increase in evaporation period. These results

TABLE IV
Effect of Evaporation Period on Membrane Porosity

Evapn. period, sec	Solute sepn., %[a]	PWP, g/hr[a]
2–5	18.8	179
20	12.5	258
40	7.8	304
60	2.9	442
90	1.1	615

[a] Operating pressure, 100 psig; feed concentration, 200 ppm NaCl; feed flow rate, 400 cc/min; effective film area, 13.2 cm².

confirm that a longer evaporation period tends to increase the size of pores on the surface of resulting membranes. Similar results have been discussed earlier[3–5] on the basis of the effect of evaporation period on the rate of droplet formation, growth, and coalescence in the interdispersed phase during film formation. These discussions led to the conclusion that there exists an optimum evaporation period for maximum membrane productivity; the experimental results reported earlier confirmed the above conclusion which should hence be valid for the development of useful ultrafiltration reverse osmosis membranes also.

CONCLUSIONS

The solution structure–evaporation rate concept developed earlier with reference to the development of cellulose acetate reverse osmosis membranes is equally valid with reference to the development of cellulose acetate ultrafiltration membranes. Decrease in S/P, increase in N/S, and increase in N/P in the casting solution, decrease in temperature of the casting solution, and increase in solvent evaporation period—each one of these factors tends to increase the size of pores on the surface of resulting membranes in the as-cast condition. Increase in S/P in the casting solution and increase in the temperature of the casting solution tend to increase the effective number of pores on the membrane surface. These results offer definitive physicochemical criteria for developing useful cellulose acetate ultrafiltration membranes for a variety of practical applications.

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