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Constrained Optimization of Cellulose Acetate Membrane Using Two-Level Factorial Design

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Synopsis

This work presents a method, the SUMT algorithm, to optimize the performance of the cellulose acetate (CA) membrane by maximizing the permeate flux subject to an equality constraint of salt rejection and a pair of inequality constraints for each variable. Three variables, i.e., (1) the concentration of formamide in the casting solution, (2) the time of evaporation of the membrane prior to gelling, and (3) the annealing temperature of the membrane, were selected for this optimization study. Experiments based on the two-level factorial design were conducted for the determination of regression equations for both premeate flux and salt rejection. At a level of 97.00% rejection of a 0.5% sodium chloride solution at 600 psig, the maximum permeate flux of the CA membrane was predicted to be 14.52 gallons per day per sq. ft (gfd). This was later confirmed by experiments. The effects of the casting variables on membrane performance concluded in this study were consistent with those reported by other researchers.

INTRODUCTION

Since Breton and Reid[1,2] discovered the cellulose acetate (CA) membrane and Loeb and Sourirajan[3] developed the casting technique, extensive investigations have been undertaken in search of improved membranes for reverse osmosis applications. Membrane equipment manufacturers have since been mainly interested in developing module configurations to house the membrane. Modules such as tubular, hollow fiber, spiral wound, plate and frame, and thin channel have been successfully developed for various applications. Although many investigators have been devoting themselves to searching for new membrane materials, e.g., substituted cellulose acetate, aromatic polyamide, poly(vinyl alcohol), crosslinked polyethylenimine, etc., most of the investigators, however, have focused their attention on improving the performance of the CA membrane by modifying the composition of the casting solution and/or the casting conditions.

Numerous efforts have been directed by various investigators toward modifying the casting solution of Loeb-Sourirajan,[3] which contains 22.2% CA, 66.7% acetone, 1.1% magnesium perchlorate, and 10.0% water. Loeb has evaluated salts of perchlorate other than magnesium perchlorate[4] and later tested solvents other than acetone.[5] Loeb and McCutchan[6] have investigated other additives to replace magnesium perchlorate. Recently, Johnson and Sourirajan[7] have studied a great variety of second additives in the casting solution. Two significant advances in the formulation of CA membrane casting solutions, however, were simultaneously reported in 1965 by Sourirajan and Govindan[8] and Manjikian et al.[9] The former found that a membrane cast from a solution of 17% CA, 68% acetone, 1.5% magnesium perchlorate, and 13.5% water at −10°C gave higher permeate flux at a given level of salt rejection than that cast from the original Loeb-Sourirajan formula.[3] Meanwhile, Manjikian et al.[9] reported a new formulation for membrane casting which contained 25% CA, 30% formamide, and 45% acetone, with casting being conducted at room temperature. Membranes cast from the latter formula gave similar performance to those reported by Sourirajan and Govindan.[8] Although there is some indication that the Sourirajan and Govindan[8] membrane is more stable, the Manjikian et al.[9] formulation has remained the membrane of choice in the field, because it is more convenient and economical to cast. Most of the commercially available modules use CA membranes fabricated with Manjikian's formula.[9]

On the other hand, many studies have been conducted to modify the casting conditions of the CA membrane. Kunst and Sourirajan[10] and later Pageau and Sourirajan[11] have found that performance of the Loeb-Sourirajan-type[3] CA membrane can be improved by suitably controlling the casting conditions, such as the evaporation time for the solvent, relative humidity, ambient temperature of the atmosphere, and temperature of the casting solution. Frommer et al.[12] have shown that the pore structure of the CA membrane is strongly dependent on the activity of water in the gelling media, i.e., the characteristics of the membrane can be controlled by adjusting the salt concentration in the gelling water. They have concluded that "salt gelling" can be used to reduce or even eliminate the need for the annealing stage. Carter et al.[13] have indicated that a similar effect can be achieved using a water-ethanol mixture as the gel medium. Lately, Mehta[14] has found that the CA membrane characteristics are also dependent on the composition of the annealing medium. Membranes annealed in a glycerin–water mixture yielded higher flux at the same level of salt rejection than those annealed in water.

Nevertheless, in all the studies mentioned above on the optimization of CA membrane, statistically designed experiments have seldom been employed. Most of the studies were conducted by first selecting one variable, say, CA concentration, then performing a series of experiments varying the value of this variable over a suitable range while maintaining the other variables, e.g., annealing temperature, time of evaporation of solvent, gelling temperature, etc., constant. Having found the optimum value of the first variable, a second variable, say, annealing temperature, was selected. A second series of experiments were conducted again while maintaining the first variable at its optimum value and the others constant. Following this pattern, the optimum values of all the variables were found.

Not only is this so called one-variable-at-a-time method time consuming, but also it often misses the overall optimum. Because of the simultaneous interactions of two or more variables, the optimum value for one variable commonly depends on the values of others. In order to consider the potential interactions among these variables, the use of experimental protocols based upon statistical design is essential. Recently, Grethlein[15] and Fahey and Grethlein[16] have reported a statistically designed method for optimization of casting the CA membrane using Manjikian's formula. In their studies, membranes cast under a given set of experimental conditions were annealed at various temperatures, and their permeate fluxes and salt rejections were measured. The flux at certain level of salt rejection, say 75%, was interpolated from the plot of flux versus rejection. The optimization of permeate flux at this level of salt rejection was then determined from 2^n series (where n is the number of variables in addition to annealing temperature) of experiments.

The objective of this study is to demonstrate yet another method for the optimization of CA membrane using a two-level factorial design and a SUMT algorithm. With the use of this method, the optimum performance of CA membrane can be predicted from a minimum number of experiments.

EXPERIMENTAL

Selection of Variables

Three major variables, i.e., (1) composition of the casting solution, (2) time of solvent evaporation prior to gelling, and (3) temperature of the annealing water, were selected for this optimization study. A Manjikian-type CA membrane was chosen because of its ease of fabrication.

The success of casting the CA membrane lies in the ability to form a highly asymmetric structure within which a densely packed active skin layer is supported by a loosely held spongy structure. It is this active skin layer which dominates both salt rejection of and water flux through the membrane. The skin layer is formed by evaporation of acetone from the freshly cast membrane resulting in precipitation of CA at the membrane–air interface. The phase diagram of CA–acetone–formamide mixtures[17] is shown in Figure 1. A casting solution having a composition close to the solubility curve on the phase diagram requires only a very short period of time of evaporation to precipitate the CA. Solutions composed of CA and acetone having a ratio of 3:5 are represented by a straight line as shown in Figure 1. This line lies very close to the solubility curve but remains soluble in the region containing 15% to 55% of formamide. Hence, only a few seconds of evaporation of acetone is needed for the precipitation of CA. On this basis, the ratio between CA and acetone was chosen as 3:5 in this study; the only variable determining the composition of the casting solution became concentration of formamide alone. This is the first variable to be considered.

Because of the close relationship between the characteristics of the skin layer to the performance of the CA membrane, the time allowed for the evaporation of acetone was selected as the second variable to be optimized in this study.

Matsuura and Sourirajan[18] have shown that during annealing of CA membranes at elevated temperature, the hydrogen bonding within the CA molecules was partially ruptured and the intermolecular bonding was formed subsequently. Such a structural change at high temperature causes the densification of the CA membrane. As a result, higher rejection of salt, accompanied by lower flux for water, has been observed after membrane annealing. Since the degree of disruption of hydrogen bonding is related to the temperature, the temperature of the annealing water was therefore selected as the third variable to be studied.

Two-Level Factorial Designed Experiments[19,20,21]

A two-level factorial design involving n variables requires 2^n combinations of two versions of each of the n variables. Two versions, i.e., the lower and the upper levels, of each variable are identified by minus and plus one. The experimental design can then be viewed geometrically. A run is represented by a point whose coordinates are the ± 1 versions for that run. The reproducibility of the experiments can be determined by the standard deviation of a number of experiments conducted at the midlevel of each variable.

In those cases that m responses ($Y_1, Y_2, \ldots. Y_m$) are observed, the regression equations for a two-level factorial design involving n variables ($x_1, \ldots. x_m$) are

$$\begin{aligned} Y_1 &= C_1^0 + \sum_{i=1}^{n} C_1^i x_i + \sum_{j=i+1}^{n} \sum_{i=1}^{n} C_1^{ij} x_i x_j + \ldots. + C_1^{1\cdots n} \prod_{i=1}^{n} x_i \\ &\vdots \\ Y_m &= C_m^0 + \sum_{i=1}^{n} C_m^i x^i + \sum_{j=i+1}^{n} \sum_{i=1}^{n} C_m^{ij} x_i x_j + \ldots. + C_m^{1\cdots n} \prod_{i=1}^{n} x_i \end{aligned} \tag{1}$$

where C_l^0 = the grand average of Y_l; C_l^i = the main effect of x_i to Y_l; C_l^{ij} = the two-variable (x_i, x_j) interaction effect to Y_l; $C_l^{1\cdots n}$ = n-variable interaction effect to Y_l; and $l = 1,2,\ldots\ldots, m$.

The grand average coefficient of Y_l, C_l^0, is obtained by dividing the sum of Y_l by the total number of experiments $2^n + n_0$,

$$C_l^0 = \frac{1}{2^n + n_0} \Sigma Y_l \tag{2}$$

where n_0 = the number of experiments running at the midlevel of each variable. $C_l^{ij\cdots k}$ is obtained by taking the sum of products between the response of Y_l and the products of $x_i x_j \ldots. x_k$ and dividing this product by 2^n,

$$C_l^{ij\cdots k} = \frac{1}{2^n} \Sigma Y_l (x_i, x_j \ldots\ldots. x_k). \tag{3}$$

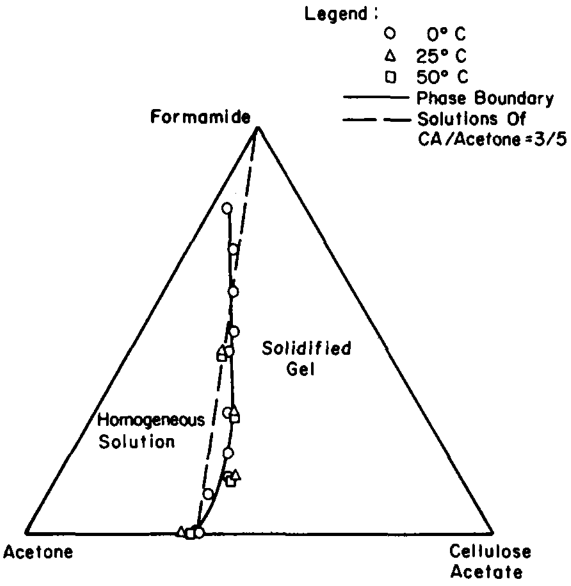

Fig. 1. Phase diagram for the cellulose acetate–acetone–formamide system.

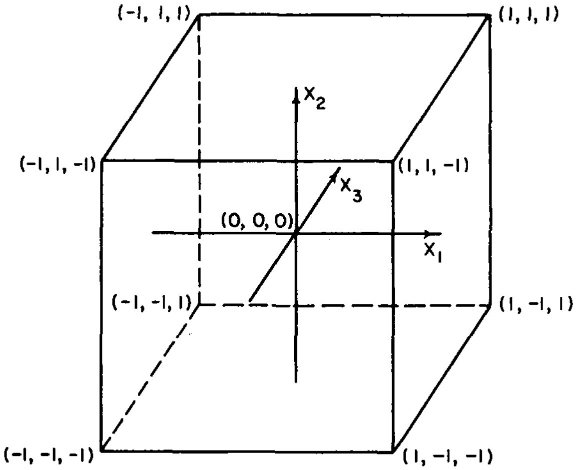

Fig. 2. 2^3 Factorial design of experiments.

The summations in both eqs. (2) and (3) are taken over all $2^n + n_0$ observations of Y_i. With the aid of digital computers, the regression equation for each response can be easily determined.

The performance of a reverse osmosis membrane is measured primarily by two responses ($m = 2$), i.e., permeate flux and salt rejection. In this study the effects of three variables ($n = 3$) on these responses were examined. Hence, eight (2^3) experiments were needed in order to determine all the possible effects. Geometrically, the regression equations, which represent responses with a cube, were determined from the responses of experiments conducted at eight corners of the cube as shown in Figure 2. Signs of plus and minus one represent the upper and lower levels of each variable and that of zero-point the midlevel of the variable.

Optimization of CA Membrane Performance

It has been found that any single effort which has been made to increase the salt rejection of the CA membrane generally has resulted in a decrease of permeate flux, or vice versa. The optimization of CA membrane, therefore, can only be conducted to optimize one response at a given level of the other response. After a series of experiments using factorial design have been conducted, both regression equations of permeate flux and salt rejection can be determined as discussed in the previous section. The optimum performance of the membrane can then be found mathematically by determining the maximum of one response subject to an equality constraint for the other response. A method commonly used in solving such a problem is to use Lagrange multipliers. The application and the procedure of such a method recently have been discussed by Luus and Jaakola.[22]

Nevertheless, in many of the optimizations of the CA membrane, the mathematical optimum was found located outside the test region ($|x_i^{\text{optimum}}| > 1$). In some cases, a physically unrealistic condition, e.g., negative value of evaporation time, was shown. Hence, in order to restrict each casting variable in a reasonable region, the optimization of the CA membrane is also subjected to two inequality constraints ($-1 \leq x_i \leq +1$) for each variable.

After both regression equations of permeate flux and salt rejection are determined, the optimization procedure encountered in this study becomes to maximize

$$Y_1\,(x_1, x_2, x_3)$$

subject to

$$Y_2\,(x_1, x_2, x_3) - Y_2^c = 0 \qquad (4)$$

and

$$-1 \leq x_i \leq +1 \qquad (i = 1, 2, 3)$$

where Y_1 and Y_2 are permeate flux and salt rejection, respectively; Y_2^c is the constrained value of salt rejection, which is arbitrarily appointed in this study as 97% rejection of sodium chloride; x_1, x_2, and x_3 are concentration of formamide, time of evaporation, and temperature of annealing, respectively.

Fiacco and McCormick[23] have developed a nonlinear sequential unconstrained minimization technique, known as SUMT algorithm, for solving such a problem. The computer code developed by Mylander et al.[24] has been used with slight modifications.

PROCEDURES

The CA resin, E 398-10 (Eastman Kodak Co., Kingsport, Tenn.) was used in this work. Reagent-grade acetone and formamide were filtered through a Whatman 4 paper (W & R Ltd., Madestone, G.B.) to remove any dust particles prior to use in preparing the casting solutions. The CA-to-acetone ratio was maintained at 3:5 in all casting solutions. Flat-sheet membranes were fabricated by casting the CA solution on a glass plate. All membranes were cast to a thickness of 5 mils (5/1000 in.) with the aid of a doctor knife. After a short period of evaporation, the membrane was gelled in an ice-cold water bath (1.5–2.5°C) for 60 min. The gelled membranes were then annealed in hot water baths at different temperatures for 20 min. Prior to testing, the membrane was compacted at 800 psig for 60 min. Three stainless steel test cells based on the design of Manjikian[25] were used for these experiments. All membranes were tested with a 0.5% aqueous solution of sodium chloride at room temperature under a pressure of 600 psig and a flow rate of 0.3 gallon per minute. A Yellow Spring conductivity bridge, Model 1485, (Cole-Parmer, Chicago, Ill.) was used for salt determination.

First Series of Designed Experiments

The zero-point, lower, and higher levels of each of the three variables are shown in Table I. The zero point of formamide concentration was chosen at 30% because the casting solution at this point has a composition similar to the Manjikian formula. Eight experiments were conducted for each variable at its lower or higher level. Four additional experiments ($n_0 = 4$) were conducted at the midlevel of each variable to estimate the standard deviation of membrane performance. The experimental results are shown in Table II. An analysis of the variance of the experiments[26] leads to the following regression equations:

$$Y_1\ (\text{gfd}) = 10.69 + 9.30x_1 - 2.88x_2 - 5.60x_3 - 0.79x_1x_2 - 6.79x_1x_3 + 1.30x_1x_2x_3 \quad (5)$$

$$Y_2\ (\%) = 97.24 - 2.41x_{.} - 0.16x_2 + 2.16x_1 - 0.16x_1x_2 + 2.66x_1x_3 + 0.34x_2x_3 + 0.17x_1x_2x_3 \quad (6)$$

where each coefficient, evaluated from eqs. (2) and (3), lies within 95% confidence limits. The standard deviations of permeate flux and salt rejection, based upon the experimental results of runs 9 to 12 (see Table II), were 0.29 gfd and 0.09%, respectively.

Under the inequality constraints, $-1 \le x_i \le 1$ ($i = 1$ to 3), the maximum permeate flux at 97.00% rejection of salt was predicted mathematically

TABLE I
Levels of Variables in the First Series of Designed Experiments

		−1	0	+1
x_1	Formamide concentration, %	20	30	40
x_2	Time of evaporization, sec	4	10	16
x_3	Annealing temperature, °C	82	86	90

TABLE II
Experimental Results of the First Series of Designed Experiments

Run no.	x_1	x_2	x_3	Permeate flux, gfd	Salt rejection, %
1	−1	−1	−1	2.45	99.47
2	+1	−1	−1	38.80	90.00
3	−1	+1	−1	0.95	99.13
4	+1	+1	−1	28.95	88.34
5	−1	−1	+1	7.50	98.14
6	+1	−1	+1	11.50	98.63
7	−1	+1	+1	0.67	98.47
8	+1	+1	+1	6.68	98.99
9	0	0	0	7.70	98.94
10	0	0	0	7.32	99.00
11	0	0	0	8.03	99.01
12	0	0	0	7.75	98.81

from both regression equations using the SUMT algorithm.[23] The optimum flux was found to be 17.82 gfd at $x_1 = 1$, $x_2 = -1$, and $x_3 = 0.4258$, namely, 40% of formamide concentration, 4 sec of evaporation time, and 87.7°C of annealing temperature.

Four membranes were then cast at the predicted optimum conditions. The average performance of these membranes were 15.89 gfd and 96.59% in terms of permeate flux and salt rejection, respectively. The experimentally determined performance of the membrane was, however, not as good as predicted by eqs. (5) and (6). The fact that two of the optimum conditions were found at their upper and lower levels ($x_1 = 1$, $x_2 = -1$) indicates a possibility that the true optimum may be located outside of the tested region. Since no conclusive result could be drawn on the basis of this first series of designed experiments, a second series of experimental study was conducted.

Second Series of Designed Experiments

The predicted optimum conditions determined from the first series of the designed experiments were selected as the zero point of the second series of experiments. The exception was made to the annealing temperature, of which the zero point was arbitrarily selected at 88.0°C instead of 87.7°C as predicted in the previous experiments. In the second series of experiments, the interval between the upper and lower levels of each variable was narrowed to 10%, 4 sec, and 4°C, respectively, for formamide concentration, evaporation time, and annealing temperature. The zero-point, higher, and lower levels of each variable are given in Table III.

Eight experiments were again conducted for each variable at its higher or lower level. Two membranes were tested under each set of experimental conditions. The average values of permeate flux and salt rejection obtained experimentally with these two membranes are shown in Table IV. The

TABLE III
Levels of Variables in the Second Series of Designed Experiments

		−1	0	+1
x_1	Formamide concentration, %	35	40	45
x_2	Time of evaporization, sec	2	4	6
x_3	Annealing temperature, °C	86	88	90

TABLE IV
Experimental Results of the Second Series of Designated Experiments[a]

Run no.	x_1	x_2	x_3	Permeate flux, gfd	Salt rejection, %
1	−1	−1	−1	14.37	96.99
2	+1	−1	−1	41.29	69.13
3	−1	+1	−1	14.75	96.98
4	+1	+1	−1	43.07	62.23
5	−1	−1	+1	7.82	97.67
6	+1	−1	+1	20.23	93.90
7	−1	+1	+1	4.62	95.25
8	+1	+1	+1	11.82	97.74

[a] An average of two membranes tested under identical experimental conditions.

corresponding regression equations having 95% confidence limits for each coefficient were found to be

$$Y_1\,(\text{gfd}) = 19.75 + 9.36x_1 - 1.18x_2 - 8.62x_3 - 0.48x_1x_2 - 4.45x_1x_3 - 1.72x_2x_3 - 0.83x_1x_2x_3 \quad (7)$$

$$Y_2\,(\%) = 88.74 - 7.99x_1 - 0.68x_2 + 7.40x_3 + 7.67x_1x_3 + 1.04x_2x_3 + 1.64x_1x_2x_3. \quad (8)$$

The optimum permeate flux was found to be 14.52 gfd at 97.00% rejection of salt. This corresponds to $x_1 = -1$, $x_2 = -0.19$, and $x_3 = -1$, namely, 35% of formamide in solution, 3.62 sec of evaporation time, and 86.0°C of annealing temperature, respectively.

Five additional membranes were then cast under the predicted optimum conditions. The averages and the standard deviations of membrane permeate flux and salt rejection were 14.51 ± 2.09 gfd and 96.99 ± 0.93%, respectively. The standard deviations were relatively large; however, the average performance agreed well with the predicted one.

The possibility that the true optimum might be located outside of the tested region also was examined. By extending the inequality constraint for each variable to $-1.5 \leq x_i \leq 1.5$, the predicted optimum became 17.59 gfd and 97.00% rejection of salt at 35.1% formamide, 2 sec evaporation time, and 85.0°C annealing temperature. However, the performance of two membranes cast under these conditions failed to confirm the prediction. The average permeate flux and salt rejection observed experimentally were

21.55 gfd and 92.92%, respectively. Two other membranes cast under conditions using 35.0% formamide, 2 sec evaporation time, and 85.5°C annealing temperature yielded a flux of 19.08 gfd at 94.5% rejection of salt. By comparing these results to those obtained from the confirmative experiments based on the predicted optimum, it is concluded that the predicted value of 14.52 gfd at 97.00% rejection of salt is a true optimum within the limits of experimental error.

DISCUSSION

It has been reported in a recent study[27] that a permeate flux of 8 gfd at 96% rejection of salt was obtained with a CA membrane, designated as KP98, manufactured by Eastman Kodak Co., while testing under the identical conditions used in this study. Under the same testing conditions, a tubular CA module, manufactured by Universal Oil Products Co. for laboratory study, yielded a flux of 10 gfd and a salt rejection of 97.3%. By comparing these data with the performance of the optimized membrane predicted in this study, i.e., 14.52 gfd at 97.00% rejection of salt, the optimized membrane is apparently improved.

Nevertheless, the most unambiguous method to compare the membrane performance is through the plot of pure-water permeability coefficient (A) versus solute transport parameter ($D_{AM}/K\delta$) as suggested by Kimura and Sourirajan.[28] Since these parameters are independent of feed concentration and feed flow conditions, equivalent membrane tested at a given pressure and temperature yields identical results regardless of other experimental conditions. Figure 3 shows results of the five confirmative tests with membranes cast under the predicted optimum conditions and those of Agrawal and Sourirajan.[29] At the same pure-water permeability coefficient, the optimized membrane shows a smaller transport parameter than that of Agrawal and Sourirajan. This indicates that higher salt rejection is obtained at a given level of pure water permeability. The improvement made in the optimized membrane and the advantage of employing a series of statistically designed experiments for the optimization study of membrane performance are thus obvious.

As discussed previously, the coefficients of x_1, x_2, and x_3 in eqs. (7) and (8) represent the main effects of the respective variables on permeate flux and salt rejection. Similarily, those of x_1x_2, x_1x_3, and x_2x_3 represent the two-variable interaction effects, and those of $x_1x_2x_3$ represent the three-variable interaction effects. By comparing the magnitudes of the coefficients in eqs. (7) and (8), three dominating effects, i.e., x_1, x_3, and x_1x_3, were determined for the optimization of membrane performance. The insensitivity of the variable x_2, i.e., evaporation time, may be attributable to either the narrow range of evaporation time studied (2 to 6 sec) or to the relatively short period of time required for acetone to evaporate to form the skin layer due to the close proximity between the solubility curve and the line of constant CA/acetone ratio. The signs of the coefficients of these

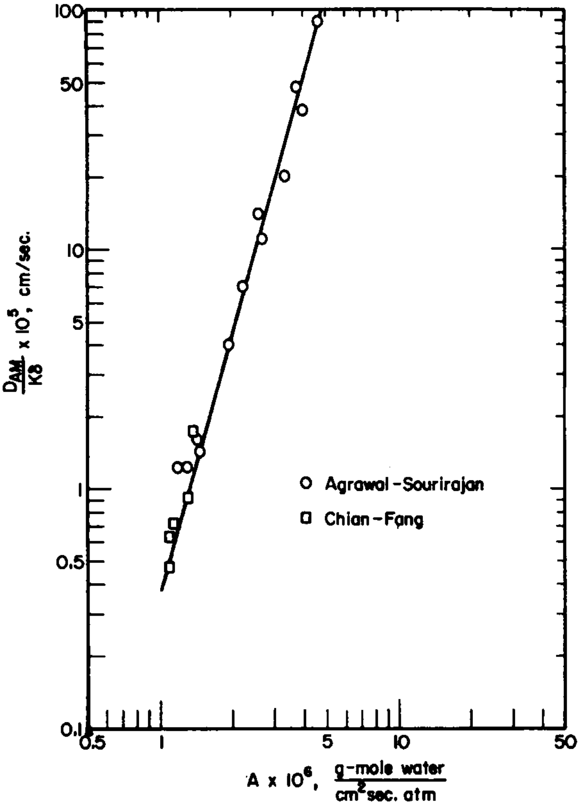

Fig. 3. Comparison of parameters of the optimized CA membranes and those of Agrawal and Sourirajan.[29]

three dominating effects in eqs. (7) and (8) are opposite to each other. This agrees well with the experience that any single effort that is made to increase the permeate flux always results in the decrease of salt rejection, or vice versa.

The effect of formamide on the performance of the CA membrane can be seen from the coefficients of x_1 and x_1x_3 in eqs. (7) and (8). If the concentration of formamide, x_1, in the casting solution is increased beyond the optimum level, where x_1 and x_3 are both equal to -1, an increase in flux and decrease in salt rejection will result. This appears to be due to the presence of an increased amount of formamide in the skin layer which will in turn be leached out during the gelling step.

Matsuura and Sourirajan[19] have postulated that, during the stage of annealing, the intramolecular hydrogen bonding of the CA molecules are disrupted, and the two neighboring CA chains are brought closer together to form a stronger intermolecular bonding. Such a structural change results in a densification of the porous structure of the CA membrane. Therefore, if the annealing temperature is raised, a lower flux or a higher rejection will result. The same conclusion may be drawn from the negative sign of the coefficient of x_3 in eq. (7) and its positive sign in eq. (8). Moreover, the signs of the coefficients of the interaction x_1x_3 in eqs. (7) and (8) clearly indicate that the higher the concentration of formamide (i.e., the more positive the value of x_1), the greater effect the annealing temperature has on the performance of the CA membrane. In other words, the structural change due to annealing is more sensitive to a looser membrane than to a denser one.

CONCLUSIONS

In this study, another method, which differs from those reported in the literature[15,16] for optimizing CA membrane casting, has been illustrated. The optimized CA membrane found in this study gives a water flux of 14.52 gfd at 97.00% rejection of salt when tested at 600 psig and room temperature with a feed containing 0.5% sodium chloride. These values have been predicted by using the method of constrained optimization and a series of statistically designed experiments.

Based on the statistically designed experiments and the resulting regression equations, the main effects and the interaction effects of variables on the performance of the CA membrane have been estimated. Conclusions drawn from these effects are in good agreement with both the experiments made in this study and the data reported in the literature.

The optimization method employed in this study is of great interest to the optimization of new membrane materials in which more variables may be involved.

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