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Optimization of NS-100 Membrane for Reverse Osmosis

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Synopsis

The optimization of a newly developed reverse osmosis membrane, NS-100, was studied based upon two series of statistically designed experiments. A total number of 33 experiments was run to evaluate the effects and interaction effects of five independent casting variables. With the aid of a constrained optimization method, SUMT algorithm, the optimum conditions for all casting variables were determined. Flat-sheet membranes cast under these conditions yielded a permeate flux of 10.30 ± 1.95 gal/ft^2-day (gfd) and a 99.30 ± 0.18% rejection of salt under a pressure of 600 lb/in.^{2} (psig). Tubular membranes, on the other hand, yielded a flux of 10.13 ± 3.19 gfd and a 98.51 ± 0.66% rejection of salt. These performances evidently indicate that the optimized NS-100 membrane is superior to those previously developed. The satisfactory performance of tubular membranes indicates the feasibility of applying the results found in this study for the fabrication of tubular modules.

INTRODUCTION

Reverse osmosis has become one of the major separation processes. Although it was developed initially for the desalination of brackish and sea waters, reverse osmosis has gradually found importance in water and wastewater treatments. This is especially true with the advent of new membrane materials capable of separating organics, such as the aromatic polyamide and, more recently, the crosslinked polyethylenimine, commonly known as NS-100.

The NS-100 membrane consists of an ultrathin polyethylenimine (PEI) film coated on a microporous polysulfone (PS) support and crosslinked by *m*-tolylene 2,4-diisocyanate (TDI). It was originally developed by Cadotte and Rozelle[1] and has subsequently been studied extensively by Chian and Fang[2-4] and Fang and Chian.[5,6] At room temperature, NS-100 yields a permeate containing less than one third of salt as would be obtained from the cellulose acetate membrane at the same level of permeate flux. It also rejects an average of 70% of individual low molecular weight polar organic compounds, including alcohols, acids, ketones, phenols, amines, etc., which are poorly removed by the cellulose acetate membrane. Furthermore, NS-100 is stable over a wide range of pH 2 to 12; this exceptional property gives it an uncompetitive advantage for industrial wastewater treatments.

In the previous study of NS-100 membrane,[1] the casting conditions for an optimum membrane performance were found primarily using the so-called one-variable-at-a-time method. Not only is this method time consuming, but also it often misses the overall optimum because of the negligence of the possible interaction effects among variables. These interaction effects can be determined by using experimental protocols based upon statistical design. Fahey and Grethlein[7] and Grethlein[8] have demonstrated the feasibility of using a series of designed experiments for the optimization of cellulose acetate membrane. More recently, Chian and Fang[9] have further demonstrated that by combining the method of two-level complete factorial design[10,11] and a constrained optimization technique, SUMT algorithm,[12] the optimum conditions of three casting variables of cellulose acetate membrane could be determined by using fewer experiments.

The objective of this study was to optimize the casting conditions of the NS-100 membrane which depended upon five major casting variables, as compared to three for the cellulose acetate membrane. The number of experiments, based on the complete factorial design, increases exponentially with the number of variables. Consequently, it is not practical in this study to use the complete factorial design, which has been applied successfully for the optimization of the cellulose acetate membrane.[9] Instead, an experimental protocol based upon a combination of fractional factorial design[11] and central composite rotable design[10,13] was employed in this study.

EXPERIMENTAL

The NS-100 membrane was fabricated according to the following procedures: First of all, a polysulfone (PS) supporting film of 7 mils in thickness was cast from a 12–17% solution of PS in dimethylformamide (DMF). The film was drawn out on a glass plate with a doctor blade and gelled by immersion in water containing a small amount of DMF. The gelled film was rinsed with deionized water and then coated by a diluted PEI (Tydex 12 of Dow Chemicals) aqueous solution. After 60 sec, the film was held in a vertical position to drain the excess PEI solution. Then a dilute solution of TDI in hexane was allowed to react with the PEI-coated surface. After a 60-sec reaction period, the film was again held in a vertical position to drain the excess solution from the surface. The coated membrane was finally cured in an oven for a few minutes. The ultrathin layer of the membrane is a partial reaction product of PEI and TDI; its structure is illustrated elsewhere.[6] By adjusting each variable appropriately, membranes cast following this procedure yield a permeate flux of 7–30 gal/ft^2-day (gfd) at 97–99% rejection of salt when tested with a 5000 parts per million (ppm) sodium chloride solution at 600 lb/in.^{2} (psig).

The standard testing condition for each membrane was chosen at a pressure of 600 psig, a temperature of 25°C, and a feed flow rate of 0.30 gpm. Sodium chloride aqueous solution at a concentration of 5000 ppm was chosen as a standard test solution. Fang and Chian[6] have reported that a NS-100 membrane with a higher salt rejection also removes a greater percentage of organic compounds. This relationship is independent of the characteristics of solutes, e.g., ions or molecules and organic or inorganic compounds. As a consequence, it is possible to characterize the NS-100 membrane performance from a simple test using sodium chloride solution.

Each of the membranes was tested in a small 316 stainless-steel laboratory test cell based on the design of Manjikian.[17] The effective diameter of membrane for testing is 2 in. (5.08 cm). The gap of the flow channel between the membrane surface of the test cell is ⅛ in. (0.3175 cm). In all cases, these membranes were tested at a feed flow rate of 0.3 gal/min (18.9 cc/sec). The feed solution flowed radially along the membrane surface which resulted in a Reynolds number of 140 at the outer perimeter of the test membrane using the gap of the flow channel as the characteristic length. The corresponding mass transfer coefficient k, using correlation obtained by Sourirajan and Kimura,[22] was determined to be 214×10^{-4} cm/sec. It should be noted that the average mass transfer coefficient of the test cell was much higher as k increased by an order of magnitude from the outlet (outer perimeter) to the inlet (center of the cell) of the feed. Since the flow was well within the turbulent regime, the effect of concentration polarization on membrane performance was greatly reduced as discussed later.

SELECTION OF VARIABLES

Based upon the previous work conducted by Cadotte and Rozelle[1] and Chian and Fang,[3] five major casting variables have been identified for fabricating the NS-100 membrane. These variables and their respective notations are as follows: (1) TDI concentration in hexane solution, x_1; (2) PEI concentration in coating aqueous solution, x_2; (3) PS concentration in DMF, x_3; (4) curing temperature, x_4; and (5) DMF concentration in gelling water, x_5. Five levels were selected for each variables. The midlevel, represented as 0, of each variable was chosen because a membrane cast at this level, according to the previous experience, would very likely yield an optimum performance. The lower and upper levels of each variable were represented as −1 and +1, respectively. Both levels deviated a unit interval from the midlevel. The unit interval of each variable was selected based upon the assumption that the true optimum casting conditions of each variable would fall between the lower and upper levels. The lowest and uppermost levels, represented as −2 and +2, were another unit interval deviated from levels −1 and +1, respectively. Only those experiments based upon central composite rotable design ran at level −2 or +2 for each variable.

Five major variables and their respective levels, −2, −1, 0, +1, and +2, are shown in Table I. The minor casting variables were fixed at the following conditions: the thickness of the ungelled polysulfone supporting film, 7 mils; time of draining TDI-hexane and PEI-water solutions, 60 sec; time of oven curing, 10 min.

TABLE I
Levels of Each Variable in the Designed Experiments

Variable	Level				
	−2	−1	0	+1	+2
x_1, TDI concentration in hexane solution, %	0.1	0.3	0.5	0.7	0.9
x_2, PEI concentration in aqueous solution, %	1.0	2.0	3.0	4.0	5.0
x_3, PS concentration in dimethylformamide, %	13	14	15	16	17
x_4, Curing temperature, °C	100	105	110	115	120
x_5, DMF concentration in gelling water, %	0.0	1.0	2.0	3.0	4.0

RESULTS AND DISCUSSION OF THE FIRST SERIES OF EXPERIMENTS

Sixteen sheets of membrane were first cast based upon a series of 2_{IV}^{5-1} fractional factorially designed experiments.[11] In this design, variable x_5 was designated to confound with the product of variables x_1, x_2, x_3, and x_4. Also, it presumed that multivariable interaction effects were relatively insignificant as compared to the main and two-variable interaction effects. This is usually a reasonable assumption if the response surface is smooth and continuous. Six additional sheets of membrane were also cast at the midlevel in order to examine the reproducibility of the experiments.

Two discs of membrane were cut from each sheet. The average permeate flux and rejection of salt of each sheet of membrane obtained under standard testing conditions are shown in Table II. Membranes cast at midlevel yielded an average of 10.25 gfd in permeate flux and 98.72% in rejection of salt; the standard deviations were 1.49 gfd and 0.38%, respectively. The regression equations[14,15] for permeate flux and salt rejection are found as follows:

$$Y_1\ (\text{gfd}) = 11.89 - 1.51\,x_1 - 0.35\,x_2 - 2.73\,x_3 - 5.22\,x_4 + 1.08\,x_2x_3 + 1.22\,x_3x_4 \quad (1)$$

$$Y_2\ (\%) = 97.81 + 0.72\,x_1 + 0.69\,x_3 + 0.87\,x_4 + 0.51\,x_5 + 0.32\,x_1x_2 - 0.32\,x_1x_4 - 0.46\,x_3x_4 - 0.38\,x_3x_5 - 0.34\,x_4x_5 \quad (2)$$

where each coefficient is of 95% confidence limit.

Quantitatively, both regression equations show a significant lack of fit according to the analysis of variances. This indicates that the polynomial model is inadequate. Qualitatively, there is evidence for the lack of fit when examining the residuals, i.e., the difference between the experimental observations and the corresponding predictions calculated from regression equations. At the midlevel, all the residual fluxes are negative but the residual salt rejections are positive. At all the other points of the design, on the other hand, all the residual fluxes are positive but the residual salt rejections are negative. This indicates a bias in the residuals. Such a bias is attributed to the nature of the polynomial regression equations in which the x_i^2 terms are

TABLE II

Performance of Membranes in Experiments Based upon 2_{IV}^{5-1} Design

Run	x_1	x_2	x_3	x_4	x_5	Flux, gfd	Rejection, %
1	–	–	–	–	+	24.52 ± 0.43	95.52 ± 0.31
2	+	–	–	–	–	23.91 ± 0.38	94.57 ± 0.03
3	–	+	–	–	–	22.31 ± 0.48	93.24 ± 0.74
4	+	+	–	–	+	15.89 ± 0.36	98.46 ± 0.15
5	–	–	+	–	–	15.46 ± 0.80	96.56 ± 0.18
6	+	–	+	–	+	10.72 ± 0.08	98.90 ± 0.61
7	–	+	+	–	+	17.85 ± 0.86	96.88 ± 0.75
8	+	+	+	–	–	11.05 ± 0.11	98.60 ± 0.00
9	–	–	–	+	–	10.57 ± 0.27	97.14 ± 0.29
10	+	–	–	+	+	7.60 ± 0.66	98.61 ± 0.21
11	–	+	–	+	+	9.00 ± 0.26	98.03 ± 0.12
12	+	+	–	+	–	7.94 ± 0.76	98.60 ± 0.17
13	–	–	+	+	+	5.32 ± 0.46	98.38 ± 0.27
14	+	–	+	+	–	4.66 ± 0.22	98.71 ± 0.39
15	–	+	+	+	–	6.98 ± 0.46	98.17 ± 0.27
16	+	+	+	+	+	6.07 ± 0.17	98.94 ± 0.15
17	0	0	0	0	0	9.71 ± 0.18	98.76 ± 0.13
18	0	0	0	0	0	7.47 ± 0.29	99.14 ± 0.26
19	0	0	0	0	0	10.81 ± 0.12	98.23 ± 0.23
20	0	0	0	0	0	11.41 ± 1.07	99.16 ± 0.21
21	0	0	0	0	0	10.68 ± 0.60	98.54 ± 0.19
22	0	0	0	0	0	11.39 ± 1.71	98.46 ± 0.30

omitted. It is known that the self-interaction effect of a variable becomes significant in the vicinity of the optimum; as a consequence, an adequate regression equation has to include the x_i^2 terms in this region.

In order to determine such a regression equation for permeate flux and salt rejection, a series of subsequent experiments were conducted.

RESULTS AND DISCUSSION OF THE SECOND SERIES OF EXPERIMENTS

A central composite rotable design[10,11] was developed specifically to determine the regression equation composed of x_i^2 terms. Based upon this design, ten sheets of membrane were cast under the conditions that all the variables were at their midlevels except one variable which was at its either −2 or +2 level. Finally, one additional sheet of membrane was cast at the midlevel in order to examine again the reproducibility of the experiment. Two discs of membrane were cut from each sheet. The average performance of each sheet when tested at standard conditions is shown in Table III.

All together, seven sheets of membrane were cast at the midlevel. The average permeate flux and salt rejection, and the corresponding standard deviations, are 10.53 ± 1.56 gfd and 98.63 ± 0.42%, respectively. The new regression equations for permeate flux and salt rejection become

$$\begin{aligned} Y_1(\text{gfd}) = {} & 10.600 - 1.780\,x_1 - 1.155\,x_2 - 2.571\,x_3 - 4.598\,x_4 + 0.762\,x_1^2 \\ & + 0.899\,x_2^2 - 0.071\,x_3^2 + 0.405\,x_4^2 + 1.078\,x_2x_3 + 1.217\,x_3x_4 \end{aligned} \quad (3)$$

TABLE III
Performance of Membranes in Experiments Based upon Central Composite Rotable Design

Run	x_1	x_2	x_3	x_4	x_5	Flux, gfd	Rejection, %
23	−2	0	0	0	0	18.51 ± 1.04	89.26 ± 0.27
24	2	0	0	0	0	9.23 ± 0.35	98.83 ± 0.28
25	0	−2	0	0	0	19.93 ± 4.17	97.94 ± 0.14
26	0	2	0	0	0	8.91 ± 0.53	98.16 ± 0.31
27	0	0	−2	0	0	15.06 ± 0.20	97.55 ± 0.00
28	0	0	2	0	0	6.02 ± 0.25	98.55 ± 0.01
29	0	0	0	−2	0	19.14 ± 0.49	96.97 ± 0.50
30	0	0	0	2	0	5.75 ± 0.17	97.76 ± 0.31
31	0	0	0	0	−2	11.91 ± 0.14	98.66 ± 0.02
32	0	0	0	0	2	9.86 ± 0.65	98.73 ± 0.31
33	0	0	0	0	0	12.24 ± 0.39	98.10 ± 0.05

$$\begin{aligned}Y_2\,(\%) = {} & 98.540 + 1.275\,x_1 + 0.540\,x_3 + 0.643\,x_4 + 0.345\,x_5 \\ & - 1.046\,x_1^2 - 0.045\,x_2^2 - 0.045\,x_3^2 - 0.216\,x_4^2 - 0.116\,x_5^2 + 0.318\,x_1x_2 \\ & -0.324\,x_1x_4 - 0.458\,x_3x_4 - 0.376\,x_3x_5 - 0.341\,x_4x_5 \qquad (4)\end{aligned}$$

where all the coefficients are of 95% confidence limit. An analysis of residuals indicates that the model is nonbiased. An analysis of variances indicates that there is little lack of fit in salt rejection and none in permeate flux.

The coefficient of x_i in eqs. (3) and (4) represent the main effects of the respective variable on permeate flux and salt rejection. Similarly, that of x_i^2 represents the self-interaction effect of x_i, and that of x_ix_j represents the interaction effect between x_i and x_j. By carefully examining the sign and the magnitude of each coefficient in Eqs. (3) and (4), one could conclude the following:

1. In general, the self- as well as the mutual interaction effects were slightly less significant than the main effects, but they were on the same order of magnitude. The significance of interaction effects, which is neglected by the one-variable-at-a-time method, indicates the advantages of using statistical design.

2. The self-interaction effects were indeed significant to the NS-100 membrane performance. This confirms the necessity of using central composite rotable design in the second series of experiments. This necessity is attributed, as discussed previously, to the closeness of the optimum condition and the mid-level of each variable. This closeness is also confirmed from the predicted optimum conditions to be discussed in the next section.

3. The sign of each main effect in eq. (3) is opposite to that of the corresponding main effect in Eq. (4). This is consistent with the common experience that any single effort made to increase the permeate flux always results in the decrease of salt rejection, and vice versa. A similar conclusion was also found in the study of casting cellulose acetate membranes.[9] The signs of coefficients of x_1, x_3, and x_4 in eqs. (3) and (4) indicate that the increase of TDI–hexane concentration, PS concentration in DMF, or curing temperature result in a decrease of permeate flux but an increase in salt rejection. This is attributable to the degree of crosslinkage of the ultrathin layer which in-

creases with the increase in TDI concentration and curing temperature, and to the porosity of the PS supporting film which decreases with the increase in PS concentration.

PREDICTION OF OPTIMUM CASTING CONDITIONS

Two major characteristics to be considered for a reverse osmosis membrane are its permeate flux and rejection of salt. However, making an effort to increase one of these characteristics of a membrane will always be at the expense of sacrificing the other. Hence, the optimum performance of a membrane was defined as the maximum permeate flux at a specific degree of salt rejection, which was chosen arbitrarily at 99% in this study. Also, it is risky to extrapolate a regression equation beyond the range of original experiments. The search of an optimum was thus limited to the range that each variable was within its lower and upper levels.

Consequently, the optimization of the NS-100 membrane calls for locating the maximum of permeate flux that subjected to an equality constraint (rejection of salt at 99%) and a series of inequality constraints ($-1 \leq x_i \leq +1$, $i = 1$ to 5). With the aids of the SUMT algorithm and a high-speed digital computer, the optimum casting conditions of NS-100 membrane are found as follows: x_1, TDI concentration in hexane, 0.64%; x_2, PEI concentration in water, 3.11%; x_3, PS concentration in DMF, 15.19%; x_4, curing temperature, 105°C; x_5, DMF concentration in water, 3.00%. These are very close to the midlevel selected for each variable. The corresponding performance of the membrane was predicted to yield 13.90 gfd of permeate flux at 99% rejection of salt.

Nine sheets of membrane were then cast at these conditions. Under the standard testing conditions, the average permeate flux and its standard deviation was 10.30 ± 1.95 gfd, while the average salt rejection and its standard deviation was99.30 ± 0.18%. As compared to the prediction, these membranes performed slightly higher in salt rejection but lower in permeate flux. In the previous studies, both Chian and Fang[3] and Cadotte and Rozelle[1] reported poor reproducibility of casting the NS-100 membrane. Under the same testing conditions, membranes developed by the former yielded an average flux of 9.64 gfd and a rejection of 98.9%, while those by the latter yielded 8.90 gfd and 99%. Compared to the performance of these NS-100 membranes developed previously, the optimized membranes found in this study are evidently superior in both the performance and the reproducibility.

The optimum cast conditions found in this study were also employed for casting tubular NS-100 membranes of ½ in. in diameter and 2 ft in length. After the curing process, each membrane was inserted in a porous fiberglass tube for testing. Four tubular membranes were cast and tested at standard conditions with an exception that the flow rate of test solution was increased to 3.0 gpm. The average performance was 10.13 ± 3.19 gfd and 98.51 ± 0.66%. This was in good agreement with the performance of flat sheet membranes. This agreement indicates that the optimum casting conditions developed for the flat-sheet NS-100 membrane are applicable to the production of a tubular module which is the preferred configuration in practice for handling solutions containing suspended solids.

Agrawal and Sourirajan[16] have employed a generalized capillary diffusion model for comparing reverse osmosis membrane performance using two membrane parameters, i.e., the pure water permeability constant A and the solute transport parameter $D_{AM}/k\delta$. They have shown that, under the same testing pressure and temperature, a plot of these two parameters on a log–log scale gives an unambiguous comparison among the performances of various cellulose acetate membranes. Such a plot was employed successfully by Grethlein,[8] and Chian and Fang[9] in confirming results of their optimization studies on cellulose acetate membranes. Nevertheless, results of a parallel study conducted by Chian and Aschauer[18] indicated that the generalized capillary diffusion model proposed by Kimura and Sourirajan[19] did not hold with the NS-100 membrane. For example, according to the model, the solute transport parameter should be independent of the solute concentration in the test solution and, hence, the solution flow rates. However, a linear relationship between the concentration of sodium chloride solution and the $(D_{AM}/k\delta)$ for NaCl was observed with the NS-100 membrane.[18]

Figure 1 depicts a linear increase in $(D_{AM}/k\delta)$ for NaCl with increasing

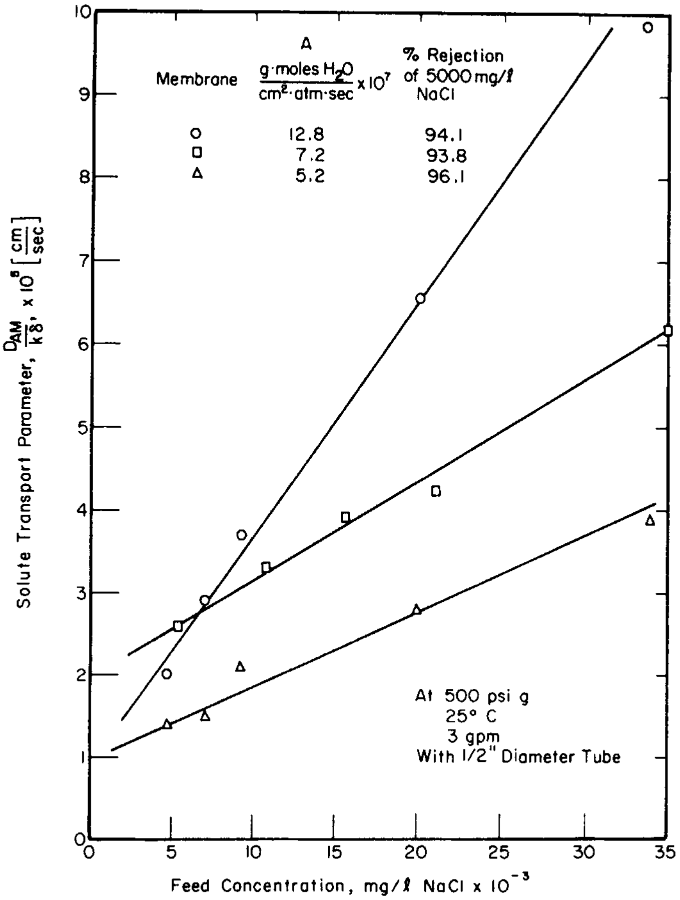

Fig. 1. Effect of feed concentration on the solute transport parameter for the system sodium chloride–water with the NS-100 membrane.

concentrations of NaCl for three NS-100 membranes having different fluxes and rejections. The differences in performance of these membranes were made possible by using different concentrations of PEI and TDI casting solutions. A general trend shows that, as the concentration of PEI in the casting solution decreases along with the increase in TDI in the casting solution, the resulting membrane gives higher sodium chloride transport parameters. This indicates strongly the dependence of the composition of the NS-100 membrane on the extent of changes in $(D_{AM}/k\delta)$ as the concentration of sodium chloride in the test solution increases. Kimura and Sourirajan[19] have also observed changes in $(D_{AM}/k\delta)$ for sucrose as the concentration of sucrose in the boundary solution varies. However, a somewhat different relationship has been obtained by these authors, e.g., the log $(D_{AM}/k\delta)$ for sucrose decreases linearly with increasing concentrations of sucrose on a square graph with the CA membrane.

Experiments of $D_{AM}/k\delta$ versus solute concentration with the NS-100 membrane were actually conducted in a tubular configuration, since the mass transfer coefficients were much better defined than those for the small test cells described previously for the membrane optimization studies. From the operating conditions given in Figure 1, the corresponding Reynolds number (Re) based on the diameter of the tube ($d = \frac{1}{2}$ in.) was calculated to be 21,000. For high Schmidt number (Sc) turbulent flow, the mass transfer coefficient k in a tube has been empirically correlated with various system parameters by Harriot and Hamilton[20] and is given by the following equation:

$$kd/D = 0.0096\ \mathrm{Re}^{0.91}\mathrm{Sc}^{0.35} \tag{5}$$

where D is the diffusivity and is estimated to be 1.5×10^{-5} cm^2/sec for an aqueous solution containing 5000 ppm of sodium chloride at 25°C.[21] The corresponding Schmidt number, Sc, is 598. From eq. (5), k was estimated to be 92×10^{-4} cm/sec for the $\frac{1}{2}$-in.-diameter tube. By using a pure water permeability constant of 5.2×10^{-7} g-mole H_2O/cm^2·atm·sec as given in Figure 1, the ratio between the concentration of sodium chloride in the membrane boundary solution and that in the bulk was determined to be 1.026, which indicated an extremely low level of concentration polarization occurring on the membrane surface under the testing conditions. As such, the concentration in the bulk is representative of that in the boundary solution. The dependence of the sodium chloride transport parameter on its concentration in the feed solution with the NS-100 membranes as shown in Figure 1 is thus valid.

To substantiate the effect of solute concentration on the $(D_{AM}/k\delta)$ for NaCl with the NS-100 membranes, the solute transport parameter was determined at various solution feed flow rates using a 5000 ppm aqueous solution of sodium chloride at 25°C. Figure 2 shows that the $(D_{AM}/k\delta)$ for NaCl increases with decreasing feed flow rates. This also gives support to the findings that the solute transport parameter is concentration dependent as the concentration of solute in the boundary solution increases with the decrease in feed flow rate.

The effect of pressure on the solute transport parameter was also studied with the NS-100 membranes.[18] Figure 3 shows an increase in the $(D_{AM}/k\delta)$ for NaCl with increasing pressure. A linear relationship was obtained on a log–log plot (Fig. 3). The latter was first observed by Sourirajan and Kimura[22] with the cellulose acetate membrane. However, a negative slope on the plot of log $(D_{AM}/k\delta)$ versus log P was reported by Sourirajan and Kimura.[22] The positive slope (Fig. 3) observed with the NS-100 membrane, i.e., the $(D_{AM}/k\delta)$ for NaCl increases with increasing pressure on a log–log plot, can be explained partially with the result of Figure 1. Since the permeation flux increases with pressure and the concentration polarization becomes more severe at higher permeation flow as predicted by the theory of mass transfer in the membrane process,[22] values of $(D_{AM}/k\delta)$ tend to increase with increasing flux and, therefore, pressure.

As estimated previously, the actual mass transfer coefficient of the small stainless test cells was much greater than 214×10^{-4} cm/sec, which in turn was already larger than the value of 92×10^{-4} cm/sec as calculated for the tubular system under the prevailing testing conditions. As such, the concentration polarization effect on the membrane surface in the small test cells would be much smaller than that for the tubular system described above. The optimum membrane performance determined with the small test cells, therefore, represents the true characteristics of the membrane.

CONCLUSIONS

By combining the method of experimental design and a constrained optimization technique, SUMT algorithm, the optimum casting conditions of the NS-100 membrane were studied. The experimental design differed from the

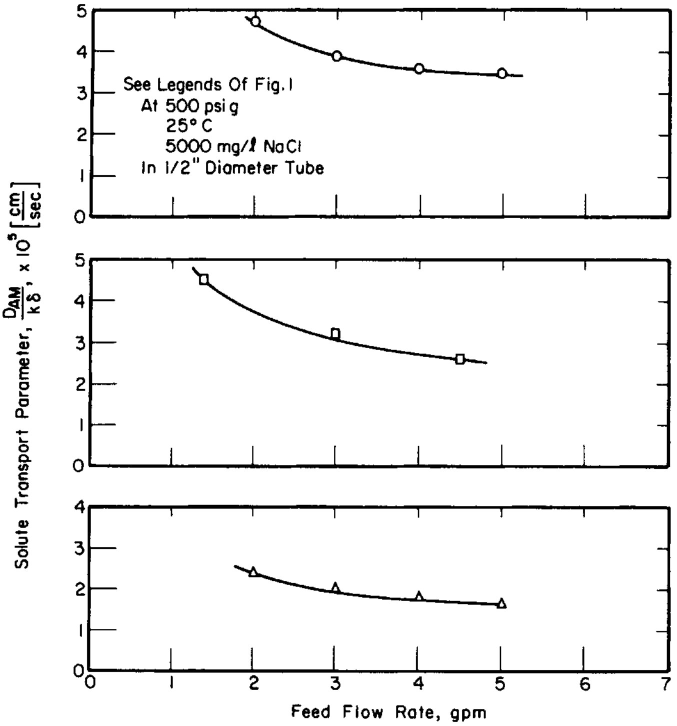

Fig. 2. Effect of feed flow rate on the solute transport parameter for the system sodium chloride–water with the NS-100 membrane.

previous study[9] because of a larger number of variables involved in the casting of NS-100 membranes.

Regression equations describing two main membrane characteristics, i.e., permeate flux and salt rejection, were determined from two series of experiments including 33 runs. The coefficients in the regression equations depict the effects and interaction effects of five major casting variables. Based on an analysis of these coefficients the following conclusions can be drawn: (1) The significance in the magnitude of the interaction effects confirms the necessity of the study using statistically designed experiments. (2) The significance in the magnitude of the self-interaction effects confirms the necessity of the second series of experiments based upon central composite rotable design. (3) The main effect of each variable shown in both regression equations indicates agreement with a common experience, i.e., any single effort to increase the permeate flux always results in the decrease of salt rejection, or vice versa; a similar conclusion was also drawn from a study of casting cellulose acetate membranes.[9]

With the aid of a digital computer, the casting conditions required for obtaining a maximum permeate flux at 99% rejection of salt was predicted from the regression equations. Both the flat-sheet and the tubular membranes cast at the optimum conditions gave permeate fluxes and salt rejections comparable to the predicted ones.

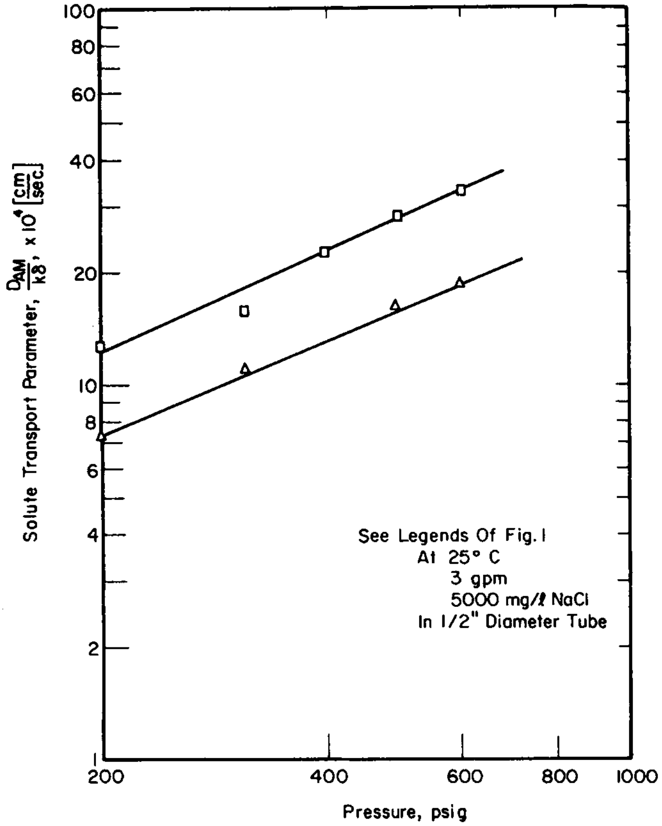

Fig. 3. Effect of pressure on the solute transport parameter for the system sodium chloride–water with the NS-100 membrane.

Compared to the NS-100 membrane previously developed, these optimized membranes were evidently superior in both the performance and the reproducibility. Also, the satisfactory performance of the tubular NS-100 membrane indicates the feasibility of applying the results of this study for the production of the tubular modules.

The solute transport parameter for sodium chloride in the NS-100 membrane was found to be both concentration and flow rate dependent. The effect of pressure on the solute transport parameter also reflected the concentration dependence of sodium chloride transport parameter in the NS-100 membrane.

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References

1. J. E. Cadotte and L. T. Rozelle, OSW Progress Report, Contract No. 14-30-2883, U.S. Dept. of the Interior, 1972.
2. E. S. K. Chian and H. H. P. Fang, *A.I.Ch.E. Symposium Series,* **136,** 497 (1974).
3. E. S. K. Chian and H. H. P. Fang, Second Annual Report to U.S. Army Medical R & D Command, Contract No. DADA 17-73-C-3025, Ft. Detrick, Md., 1974.
4. E. S. K. Chian, W. N. Bruce, and H. H. P. Fang, *Environ. Sci. Technol.,* **9,** 52 (1975).
5. H. H. P. Fang and E. S. K. Chian, Presented at the A.I.Ch.E. 67th Annual Meeting, Washington, D.C., December 1–5, 1974.
6. H. H. P. Fang and E. S. K. Chian, *J. Appl. Polym. Sci.,* **19,** 1347 (1975).
7. P. M. Fahey and H. E. Grethlein, *Desalination,* **9,** 297 (1971).
8. H. E. Grethlein, *Proc. Fourth International Symposium on Fresh Water from the Sea, Heidelberg,* **4,** 47 (1973).
9. E. S. K. Chian and H. H. P. Fang, *J. Appl. Polym. Sci.,* **19,** 251 (1975).
10. W. G. Cochran and G. M. Cox, *Experimental Designs,* 2nd ed., Wiley, New York, 1957.
11. G. E. P. Box and J. S. Hunter, *Technometrics,* **3,** 311 (1961).
12. A. V. Fiacco and G. P. McCormick, *Nonlinear Sequential Unconstrained Minimization Technique,* Wiley, New York, 1968.
13. G. E. P. Box and J. S. Hunger, *Ann. Math. Stat.,* **28,** 195 (1957).
14. A. M. Mood and F. A. Graybill, *Introduction to the Theory of Statistics,* 2nd ed., McGraw-Hill, New York, 1963.
15. N. R. Draper and H. Smith, *Applied Regression Analysis,* Wiley, New York, 1966.
16. J. Agrawal and S. Sourirajan, *Ind. Eng. Chem., Process Des. Develop.,* **8,** 439 (1969).
17. S. Manjikian, *Ind. Eng. Chem. Prod. Res. Develop.,* **6,** 23 (1967).
18. E. S. K. Chian and M. N. Aschauer, Quarterly Report to the U.S. Army Medical R & D Command, Contract No. DADA 17-73-C-3025, Ft. Detrick, Md., March 1975.
19. S. Kimura and S. Sourirajan, *Ind. Eng. Chem., Process Des. Develop.,* **7,** 548 (1968).
20. P. Harriott and R. M. Hamilton, *Chem. Eng. Sci.,* **20,** 1073 (1965).
21. S. Sourirajan, *Reverse Osmosis,* Academic Press, New York, 1970, p. 563.
22. S. Sourirajan and S. Kimura, *Ind. Eng. Chem., Process Des. Develop.,* **6,** 504 (1967).

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