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Some Transport Characteristics of Aromatic Polyamide Membranes in Reverse Osmosis

J. M. DICKSON,* TAKESHI MATSUURA, P. BLAIS, and S. SOURIRAJAN, *Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R9*

Synopsis

The effects of solute concentration in the range of 0.0013 to 1.051 molality in the feed solution and operating pressure in the range of 100 to 900 psig on solute transport parameter $D_{AM}/K\delta$ in reverse osmosis have been studied for a class of laboratory-made aromatic polyamide membranes and aqueous sodium chloride feed solutions. The results showed that $D_{AM}/K\delta$ for NaCl increased both with increase in operating pressure and solute concentration in the concentrated boundary solution on the high-pressure side of the membrane. A general expression for $D_{AM}/K\delta$ for NaCl including the effects of both the above operating variables is given. These results are different from the corresponding results obtained for cellulose acetate membranes.

INTRODUCTION

Aromatic polyamide membranes constitute one of the newer classes of successful membranes presently being developed for water desalination and other reverse osmosis applications.[1-9] Therefore, the transport characteristics of such membranes are of practical interest.[10,11] A considerable amount of data is available in the literature indicated above on the reverse osmosis performance of different types of polyamide membranes under specific experimental conditions. However, no general transport correlation has been reported by which one can predict the effect of pressure and solute concentration in feed on membrane performance from data on membrane specifications given for a single set of experimental conditions. This paper presents such a correlation with respect to aqueous sodium chloride feed solutions and the type of aromatic polyamide membranes reported earlier.[10,11]

EXPERIMENTAL

Several samples of flat aromatic polyamide membranes of different surface porosities made in the laboratory by a method reported earlier[10] were used in this work. As stated earlier, the membrane material was essentially a ran-

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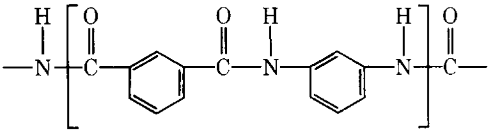
* Co-op Student, Department of Chemical Engineering, University of Waterloo, Canada.

dom copolymer consisting of the following repeat units in the molar ratio of 7 to 3, respectively:



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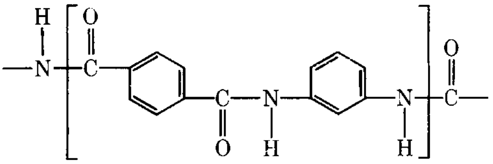

The details of the synthesis and further physicochemical characterization of the polymer used are given by Gan et al.[12] Membranes were placed in the cells and were initially exposed to a pure water feed at 1700 psig for 24 hr prior to reverse osmosis experiments. The apparatus and the experimental details used are the same as those described earlier.[13] Unless otherwise stated, sodium chloride was the solute used. A few experiments were also carried out with glucose as the solute. The effective area of film surface was 13.2 cm^2, and the feed flow rate was 400 cm^3/min in all cases.

The NaCl concentration in the feed solutions used was in the range of 0.0013 to 1.051 molal, and the operating pressures used were in the range of 6.8 to 61.2 atm (100 to 900 psig). The salt concentrations in the feed and product solutions were analyzed either through conductivity or refractive index measurements.

All experiments were carried out at the laboratory temperature (23° to 25°C). The reported permeation rates are those corrected to 25°C using the relative viscosity and density data for pure water. In all experiments, the terms "product" and "product rate" refer to membrane permeated solutions. In each experiment, the fraction solute separation f, defined as

$$f = \frac{\text{solute molality in feed} - \text{solute molality in product}}{\text{solute molality in feed}}$$

and the product rate *PR* and the pure water permeation rate *PWP* in g/hr per given area of film surface (13.2 cm^2 in this work) were determined under the specified experimental conditions.

RESULTS AND DISCUSSION

Data on Solute Transport Parameter for Sodium Chloride

These data were obtained from the basic transport equations arising from the Kimura-Sourirajan analysis of experimental reverse osmosis results under the experimental conditions used.[14]

It may be recalled that the above analysis is based on a generalized capillary flow model involving simultaneous viscous flow for water transport, pore diffusion for solute transport, and "film" theory governing mass transfer on the high-pressure side of the membrane. Thus, in this analysis, the total material transport across the membrane at any point in a given membrane–solution operating system under steady-state conditions is the sum of simultaneous water transport (proportional to the effective pressure difference) and solute transport (proportional to the effective concentration difference) across the membrane, both of which are affected by the mass transfer coefficient on the high-pressure side of the membrane. This analysis, which is applicable to all levels of solute separation, gives rise to the following basic equations relating the pure water permeability constant A, the transport of solvent water N_B, the solute transport parameter $D_{AM}/K\delta$ (treated as a single quantity for purposes of analysis), and the mass transfer coefficient k on the high-pressure side of the membrane at any point (position or time) in the system under operating conditions of constant temperature and pressure[15]:

$$A = PWP/(M_B \times S \times 3600 \times P) \tag{1}$$

$$N_B = A[P - \Pi(X_{A2}) + \Pi(X_{A3})] \tag{2}$$

$$N_B = \frac{D_{AM}}{K\delta}\left(\frac{1 - X_{A3}}{X_{A3}}\right)(c_2X_{A2} - c_3X_{A3}) \tag{3}$$

$$N_B = kc_1(1 - X_{A3}) \ln\left(\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right). \tag{4}$$

All symbols used are defined at the end of the paper.

In steady-state operation under a given set of experimental conditions, a single set of experimental data on PWP, PR, and f enables one to calculate A, X_{A2}, $D_{AM}/K\delta$, and k at any point (position or time) in a reverse osmosis system, using eqs. (1) to (4).

For very dilute feed solutions (i.e., $c_1 = c_2 = c_3 = c$ (constant), and weight of salt $\ll$ weight of water in a given quantity of solution), eqs. (3) and (4) can be written as[16]

$$D_{AM}/K\delta = \frac{PR}{3600S\rho}\frac{1-f}{f}\left[\exp\frac{PR}{3600Sk\rho}\right]^{-1} \tag{5}$$

Data on $D_{AM}/K\delta$ for sodium chloride were calculated from eq. (3) or (5) in this work using the experimental PWP, PR, and f data.

For very low solute concentrations in feed, the experimental data on PR and PWP were so close to each other that even small errors in their measurements resulted in significant differences in the calculated values of X_{A2}, $D_{AM}/K\delta$, and k. The uncertainties in such calculated values were avoided by using a constant average value of k in all the experiments. This procedure was justified on the following basis. It has already been shown that the values of k do not vary significantly even in a wide range of NaCl concentration in feed (see Fig. 3-67 in ref. 15). Therefore, the average value of k obtained for relatively high feed concentrations (average $k = 6.3 \times 10^{-4}$ cm/sec in this work) is practically valid for low feed concentrations also. Further, the values for solute separations and product rates obtained by back calculations using this average value of k in the transport equations listed above agreed well with the experimental data.

Effect of Operating Pressure on *A*

The effect of pressure P (in atm) on pure water permeability constant A (in g-mole $H_2O/cm^2 \cdot sec \cdot atm$) in the operating pressure range of 17 to 61.2 atm for three films of different surface porosities is shown in Figure 1. The results show that A tends to decrease with increase in operating pressure, and the plot of log A versus P is essentially a straight line, and the slope of this straight line is practically identical for all the three films tested. The data given in Figure 1 can be represented by the relation

$$A = A_0 \exp(-0.001264P) \tag{6}$$

where A_0 is the extrapolated value of A at $P = 0$.

The above correlation is similar to that obtained for cellulose acetate membranes.[15] The slope of the straight line representing the log A-versus-P correlation is a function of the overall porous structure of the membrane in its initial condition and the subsequent pressurization and other pretreatments on the membrane. Therefore, the numerical coefficient given in eq. (6) for the above slope should be taken to represent the characteristic only of the particular type of films tested in this work.

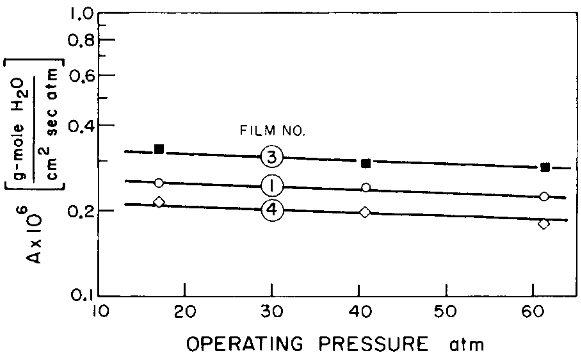

Fig. 1. Effect of operating pressure on pure water permeability constant A.

Effect of X_{A2} on $D_{AM}/K\delta$ for NaCl

In the case of cellulose acetate membranes, $D_{AM}/K\delta$ for NaCl was found to be independent of feed concentration and feed flow rate, and hence independent of the boundary solution concentration X_{A2} under the experimental conditions.[15] In the case of the aromatic polyamide membranes tested, $D_{AM}/K\delta$ was found to be dependent on X_{A2} as illustrated by the data presented in Figure 2. These data were obtained from reverse osmosis experiments using NaCl concentrations in the range of 0.054 to 1.051 molal in the feed solutions and operating pressures of 17.0, 40.8, and 61.2 atm. It was found that at each operating pressure, $D_{AM}/K\delta$ for NaCl increased with increase in X_{A2}, and the X_{A2}-versus-$D_{AM}/K\delta$ correlation was a straight line on a log–log plot; further, the slopes of the above straight lines were essentially identical for all the films and the operating pressures tested. All the data presented in Figure 2 can be represented by the general relation

$$D_{AM}/K\delta \propto X_{A2}^{0.299} \tag{7}$$

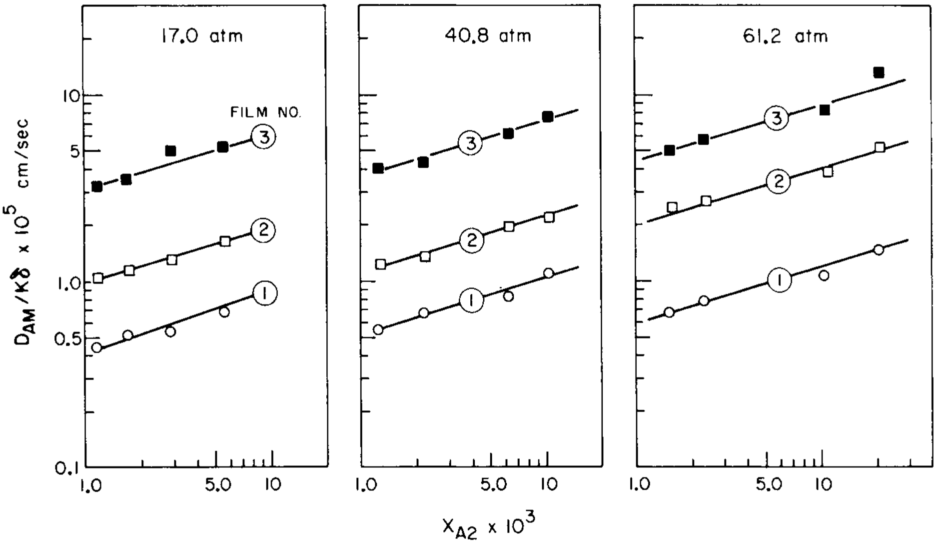

Fig. 2. Correlation between $D_{AM}/K\delta$ for NaCl and boundary concentration X_{A2} at different operating pressures. Operating pressure, 17.0 atm; feed concentration range, 0.059 to 0.30 molal. Operating pressure, 40.8 atm; feed concentration range, 0.054 to 0.51 molal. Operating pressure, 61.2 atm; feed concentration range, 0.059 to 1.05 molal.

For any given film, at any operating pressure, the value of $D_{AM}/K\delta$ for any X_{A2} can then be expressed by the relation

$$D_{AM}/K\delta = (D_{AM}/K\delta)_{\text{ref}} \left[\frac{X_{A2}}{(X_{A2})_{\text{ref}}}\right]^{0.299} \tag{8}$$

where $(X_{A2})_{\text{ref}}$ refers to any chosen X_{A2} for which the corresponding $D_{AM}/K\delta$ value is given by $(D_{AM}/K\delta)_{\text{ref}}$.

Effect of Pressure on $D_{AM}/K\delta$ for NaCl

Since $D_{AM}/K\delta$ changes with X_{A2}, it is necessary to compare $D_{AM}/K\delta$ changes with pressure at fixed values of X_{A2}. Such comparisons were made with the data given in Figure 2. Figure 3 illustrates this comparison for an arbitrarily chosen value of $X_{A2} = 6.0 \times 10^{-3}$. The results with other values

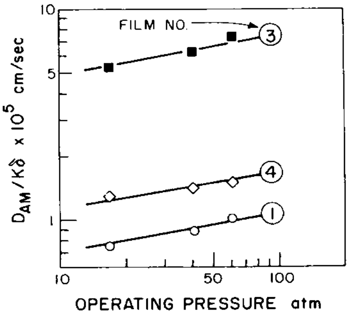

Fig. 3. Effect of operating pressure on $D_{AM}/K\delta$ for NaCl at $X_{A2} = 6.0 \times 10^{-3}$.

of X_{A2} are similar. These results show that $D_{AM}/K\delta$ tends to increase with increase in operating pressure, which is opposite of the case observed with cellulose acetate membranes. Further, log $(D_{AM}/K\delta)$-versus-log P correlations are parallel straight lines with slope = 0.176 for all the three films. Consequently, one can express the effect of pressure on $D_{AM}/K\delta$ for any membrane for a specified X_{A2} by the relation

$$D_{AM}/K\delta = (D_{AM}/K\delta)_{\text{ref}} \left[\frac{P}{(P)_{\text{ref}}} \right]^{0.176} \tag{9}$$

where $(P)_{\text{ref}}$ refers to any chosen reference pressure at which $D_{AM}/K\delta$ corresponding to the specified X_{A2} is given by $(D_{AM}/K\delta)_{\text{ref}}$.

General Correlation of $D_{AM}/K\delta$ for NaCl

Combining eqs. (8) and (9), the effect of both operating pressure P and NaCl concentration X_{A2} on $D_{AM}/K\delta$ can be expressed by the relation

$$D_{AM}/K\delta = (D_{AM}/K\delta)_{\text{ref}} \left[\frac{P}{(P)_{\text{ref}}} \right]^{0.176} \left[\frac{X_{A2}}{(X_{A2})_{\text{ref}}} \right]^{0.299} \tag{10}$$

where $(D_{AM}/K\delta)_{\text{ref}}$ and $(X_{A2})_{\text{ref}}$ refer to the data obtained from a single reverse osmosis experiment carried out at any chosen operating pressure P with any chosen NaCl concentration in the feed solution.

Predictability of Membrane Performance

Using one or more of the equations from the set of eqs. (6), (8), (9), and (10), along with the basic transport eqs. (1) to (5), one can predict solute separation and product rate for any membrane as a function of operating pressure, NaCl concentration in the feed solution, and the mass transfer coefficient k from a single set of reverse osmosis data taken as the reference condition. A comparison of the experimental data (points) with those calculated from the equations referred above (solid lines) was made, and the results are shown in Figures 4 and 5. This comparison involved three new film samples (films 10, 12, and 13) the data from which were not used in the generation of eqs. (6) to (10). The effect of NaCl concentration in the feed solution in the range of 0.0013 to 0.24 molal was studied with film 10 at the operating pressure of 17 atm; the effect of operating pressure in the range of 6.8 to 61.2 atm was studied with films 12 and 13 using 0.05 molal NaCl in the feed solution. The feed flow rate, and hence k, was kept constant in both sets of experiments. The results showed good agreement between the experimental and calculated values confirming the validity of eqs. (6) to (10) to represent the reverse osmosis transport characteristics of the type of membranes used.

Also shown in Figure 4 (dotted lines) is a comparison between the results predicted with eq. (10) and what would be expected if $D_{AM}/K\delta$ (obtained for the reference experiment) was kept constant for all concentrations. It can be seen that the solute separations obtained for the membranes used are more sensitive to concentration changes than those obtainable for the case where $D_{AM}/K\delta$ is independent of concentration. The differences in product rates, however, were small for the particular range of feed concentrations tested.

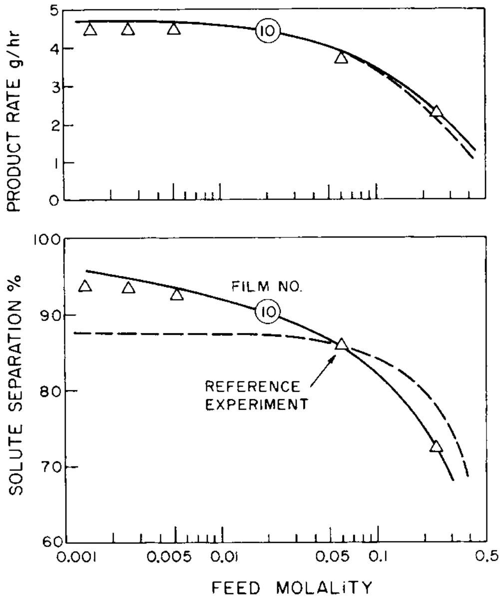

Fig. 4. Predictability of membrane performance—effect of feed concentration. Feed solution, NaCl-H_2O; operating pressure, 17 atm; feed flow rate, 400 cm^3/min; effective membrane area, 13.2 cm^2; (△) experimental; (——) predicted; (- - - -) calculated for constant $D_{AM}/K\delta$.

$D_{AM}/K\delta$ for Glucose

A set of reverse osmosis experiments was carried out with four membranes of different surface porosities (films 12 to 15) using aqueous glucose feed solutions. The operating pressure was kept at 61.2 atm in all cases. The solute

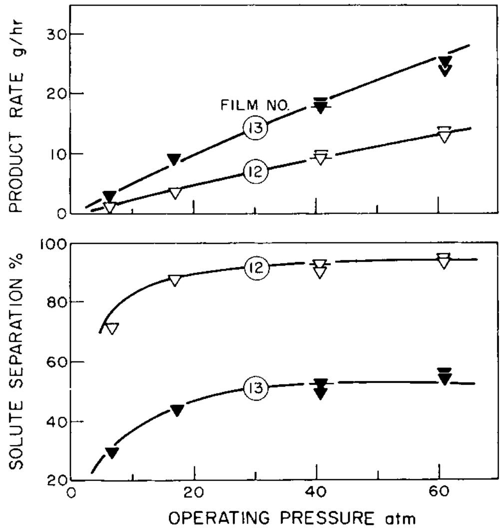

Fig. 5. Predictability of membrane performance—effect of operating pressure. Feed solution, NaCl-H_2O; solute concentration in feed, 0.05 molal; feed flow rate, 400 cm^3/min; effective membrane area, 13.2 cm^2; (▽ ▼) experimental; (-▽- -▼-) reference experiment; (——) predicted.

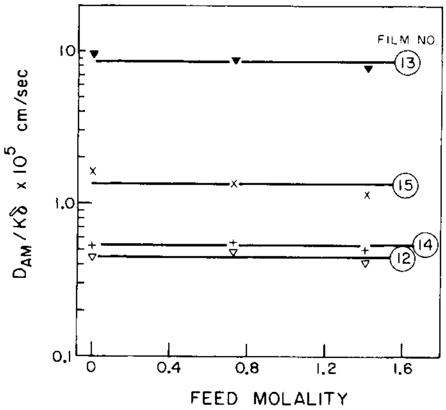

Fig. 6. Effect of solute concentration in feed on $D_{AM}/K\delta$ for glucose. Operating pressure, 61.2 atm.

concentration in the feed solution was varied in the range of 0.006 to 1.411 molal. The average value of k during the experiments was 3.8×10^{-4} cm/sec. From the reverse osmosis experimental data, the values of $D_{AM}/K\delta$ for glucose were calculated. The results, given in Figure 6, showed that $D_{AM}/K\delta$ remained essentially constant in the entire range of feed concentration studied, and the result was similar with respect to each one of the films tested. These results are similar to those observed for cellulose acetate membranes.[17]

CONCLUSIONS

The transport characteristics of aromatic polyamide membranes in reverse osmosis are different from those of cellulose acetate membranes with respect to sodium chloride. In contrast to the latter type of membranes, $D_{AM}/K\delta$ for NaCl increases both with increase in operating pressure and with increase in X_{A2} (which is determined by feed concentration and feed flow rate); therefore, separations of sodium chloride in reverse osmosis are more sensitive to feed concentrations with the polyamide membranes. That $D_{AM}/K\delta$ for glucose is independent of X_{A2} indicates that the polyamide membrane behaves differently with ionic and nonionic solutes in reverse osmosis transport. It is possible that the polyamide membrane material has some ionic character. The numerical values of the exponents governing the effects of pressure and X_{A2} on $D_{AM}/K\delta$, for example, 0.176 and 0.299, respectively, in eq. (10), may be expected to be different for different classes of ionic solutes and other aromatic polyamide membrane materials. Since the above characteristics can have significant effects on the applications of such membrane materials, more detailed studies on the transport characteristics of aromatic polyamide membranes in reverse osmosis are called for.

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Nomenclature

A	pure water permeability constant, g-mole pure water/cm^2·sec·atm
A_0	value of A extrapolated to $P = 0$
c	molar density of solution, g-mole/cm^3

$D_{AM}/K\delta$	solute transport parameter (treated as a single quantity), cm/sec
f	fraction solute separation
k	mass transfer coefficient on the high-pressure side of membrane, cm/sec
M_B	molecular weight of water
N_B	solvent water flux through membrane, g-mole/cm^2·sec
P	operating pressure, atm
PR	product rate per specified area of membrane surface, g/hr
PWP	pure water permeation rate per specified area of membrane surface, g/hr
S	effective area of membrane surface, cm^2
X_A	mole fraction of solute
$\Pi(X_A)$	osmotic pressure of solution corresponding to X_A, atm
ρ	density of solution, g/cm^3
Subscripts	
1, 2, and 3	bulk solution and concentrated boundary solution on the high-pressure side of the membrane and membrane permeated product solution on the low-pressure side of the membrane, respectively, at any point (position or time) in the reverse osmosis system.

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