

Parameters for Prediction of Reverse Osmosis Performance of Cellulose Acetate Propionate Membranes

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Synopsis

Data on reverse osmosis separations have been obtained for 12 alkali metal halide solutes and 24 organic solutes (including eight alcohols, four aldehydes, seven ketones, and five ethers) with cellulose acetate propionate (CAP) membranes using single-solute dilute aqueous feed solutions at 250 psig. From the analysis of these data, the parameters and correlations needed to calculate the values of solute transport parameter $D_{AM}/K\delta$ for the above classes of inorganic and organic solutes for a CAP membrane of any surface porosity from data on $D_{AM}/K\delta$ for NaCl only have been generated. These parameters and correlations enable one to predict reverse osmosis separations of different solutes included in the classes of compounds studied in this work, from a single set of experimental data on membrane specifications given in terms of pure water permeability constant and $D_{AM}/K\delta$ for NaCl. The reverse osmosis characteristics of CAP material lie intermediate between those of cellulose acetate and aromatic polyamide materials reported in the literature.

INTRODUCTION

Cellulose acetate propionate (CAP) membranes have been shown to be useful for reverse osmosis applications.¹ Hence, the predictability of the performance of such membranes is of practical interest. This work is concerned with the generation of numerical data for the parameters needed for the prediction of reverse osmosis separations of some inorganic and organic solutes using membranes made of CAP material. This work is restricted to single-solute systems and dilute aqueous solutions involving alkali metal cations and halide anions, or nonionized polar organic solutes containing no more than three straight-chain carbon atoms not associated with a polar functional group in their molecular structure.

In order to predict the performance (i.e., solute separation and membrane-permeated product rate) of a reverse osmosis membrane of any given porosity at any point in the system, data are needed on the applicable values for the three quantities, namely, pure water permeability constant A (in g-moles H_2O/cm^2 sec atm), solute transport parameter $D_{AM}/K\delta$ (treated as a single quantity, in cm/sec) and the mass transfer coefficient k (in cm/sec) on the high-pressure side of the membrane.² With reference to a given membrane under a specified set of experimental conditions, the quantity A is independent of any solute under consideration, and the quantities $D_{AM}/K\delta$ and k are different for different so-

lutes. From a single set of experimental reverse osmosis data with aqueous sodium chloride feed solutions, the values of A , and $D_{AM}/K\delta$, and k for NaCl can be calculated.² From the latter two quantities, if one can obtain the applicable $D_{AM}/K\delta$ and k values for other solutes, then one can predict membrane performance for other feed solutions involving such solutes. The possibility of such prediction has been demonstrated with respect to cellulose acetate and aromatic polyamide membranes and the type of inorganic or organic solutes with which this paper is concerned.³⁻⁵ This earlier work is extended here with respect to CAP membranes.

When the feed solution is sufficiently dilute so that its osmotic pressure is negligible compared to the operating pressure, the product rate is essentially the same as the pure-water permeation rate expressed by the quantity A . But applicable data on k and $D_{AM}/K\delta$ are needed to predict reverse osmosis separations for different solutes. When k for NaCl (k_{NaCl}) is known, k for other solutes in dilute solutions can be obtained from the relation⁶

$$k = k_{\text{NaCl}}[D_{AB}/(D_{AB})_{\text{NaCl}}]^{2/3} \quad (1)$$

where D_{AB} and $(D_{AB})_{\text{NaCl}}$ represent the diffusivities of the solute under consideration and sodium chloride solute, respectively, in water. The problem, then, is with respect to the calculation of $D_{AM}/K\delta$ values for different solutes from the corresponding data for NaCl solute only.

The concept of free-energy parameter ($-\Delta\Delta G/RT$) for different inorganic ions and nonionized organic solutes has been discussed.³⁻⁵ This parameter is a function of the chemical nature of the solute, the solvent, and the membrane material, and independent of the porous structure of the particular membrane used. With respect to completely ionized inorganic solutes in aqueous solutions, it has been shown³ that $D_{AM}/K\delta$ for the solute is related to the free-energy parameter for the ions by the expression

$$\ln (D_{AM}/K\delta) = \ln C^* + \Sigma(-\Delta\Delta G/RT)_i \quad (2)$$

where $\ln C^*$ is a constant and the subscript i represents the ion involved. It may be recalled that $\ln C^*$ is a function of the porous structure of the membrane surface and independent of the nature of the solute. With reference to NaCl solute, eq. (2) can be written as follows:

$$\ln \left(\frac{D_{AM}}{K\delta} \right)_{\text{NaCl}} = \ln C^*_{\text{NaCl}} + \left\{ \left(-\frac{\Delta\Delta G}{RT} \right)_{\text{Na}^+} + \left(-\frac{\Delta\Delta G}{RT} \right)_{\text{Cl}^-} \right\} \quad (3)$$

If data on $(-\Delta\Delta G/RT)$ for Na^+ and Cl^- ions are available, the value of $\ln C^*_{\text{NaCl}}$ can be calculated from eq. (3) using experimental data on $(D_{AM}/K\delta)_{\text{NaCl}}$. If, in addition, data on $-\Delta\Delta G/RT$ for other monovalent cations and anions are also available, one can then calculate $D_{AM}/K\delta$ for solutes involving such ions from eq. (2) expressed in the form

$$\ln \left(\frac{D_{AM}}{K\delta} \right)_{\text{M}^+\text{X}^-} = \ln C^*_{\text{NaCl}} + \left\{ \left(-\frac{\Delta\Delta G}{RT} \right)_{\text{M}^+} + \left(-\frac{\Delta\Delta G}{RT} \right)_{\text{X}^-} \right\} \quad (4)$$

where M^+ and X^- represent the monovalent cation and the monovalent anion, respectively.

Earlier work⁵ has shown that for nonionized polar aliphatic and alicyclic organic solutes in aqueous solutions, where (i) reverse osmosis separations are

governed by polar and/or steric effects *and* preferential sorption of water at the membrane-solution interface, and (ii) the contribution of nonpolar effect to solute transport parameter is assumed equal to zero for solute molecules containing no more than three straight-chain carbon atoms *not* associated with a polar functional group (this paper is concerned with such solutes only), the quantity $D_{AM}/K\delta$ can be estimated from the relation

$$\ln \left(\frac{D_{AM}}{K\delta} \right) = \ln C_{NaCl}^* + \ln \Delta^* + \left(-\frac{\Delta\Delta G}{RT} \right) + \delta^* \Sigma E_s \quad (5)$$

With reference to the quantities on the right side of the above equation, the quantity $\ln C_{NaCl}^*$ arises from eq. (3); the quantity $\ln \Delta^*$, which represents a scale factor, is a function of $\ln C_{NaCl}^*$; the polar free-energy parameter $-\Delta\Delta G/RT$ is a function of the molecular structure of the solute under consideration; the quantity ΣE_s is Taft's steric parameter for the substituent group in the solute molecule⁷; and the coefficient δ^* is a function of $\ln C_{NaCl}^*$. Therefore, in order to use eq. (5) for CAP membranes, one must know, in addition to $\ln C_{NaCl}^*$, the correlations of $\ln \Delta^*$ and δ^* with $\ln C_{NaCl}^*$, and also the data needed to compute the values of $-\Delta\Delta G/RT$ for different solute molecules.

The object of this work is to generate the free-energy parameters for alkali metal cations and halide anions for use in eqs. (3) and (4), and the correlations and data needed to make use of eq. (5) with respect to CAP membranes and aqueous solutions.

EXPERIMENTAL

The cellulose acetate propionate membranes were prepared by a method similar to that used for cellulose acetate membranes.⁸ Details on composition of film casting solutions and casting conditions for the films used are given in Table I. Each film was subjected to a pure-water pressure of 300 psig for 24 hr. The membrane was then depressurized and allowed to relax for a period of 24

TABLE I
Film Details

	Film no.					
	1 and 6	7	2 and 8	3 and 9	4 and 10	5 and 11
Composition of film casting solution, wt-%						
CAP ^a	15.5	15.5	15.5	14.5	15.5	14.5
acetone	70.6	70.6	70.6	72.5	70.6	72.5
aqueous Mg(ClO ₄) ₂ ^b	13.9	13.9	13.9	13.0	13.9	13.0
Temperature of casting solution, °C	10	10	10	10	10	10
Temperature of casting atmosphere, °C	30	30	30	30	30	30
Solvent evaporation period, sec	5	5	5	5	30	45
Film shrinkage temperature, °C	95	90	60	60	60	60

^a Cellulose acetate propionate (acetyl content 30.6%, propionyl content 14.5%) supplied by K & K Laboratories Inc., Jamaica, N. Y.

^b Mg(ClO₄)₂:H₂O = 1:5.

TABLE II
Film Characterization (at 250 psig Pressure)

	Film no.										
	1	2	3	4	5	6	7	8	9	10	11
Pure-water permeability constant A , (g-mole H_2O/cm^2 sec atm) $\times 10^6$	0.329	0.902	1.193	1.560	2.289	0.323	0.503	0.741	1.256	1.638	2.280
Solute transport parameter ^a $(D_{AM}/K\delta)_{NaCl} \times 10^5$	0.57	4.36	14.05	23.17	69.61	0.27	1.63	4.74	15.20	24.17	71.34
for 0.06 molal feed solution	0.56	3.01	10.95	14.63	46.66	—	—	—	—	—	—
for 0.005 molal feed solution	93.0	80.8	62.2	54.7	36.8	94.8	88.8	81.0	63.1	56.1	38.1
Solute separation, %	3.91	10.73	14.75	19.39	29.72	3.95	6.22	11.63	15.92	20.77	29.73
Product rate, g/hr											

^a $X_{A2} = 1.36 \times 10^{-3}$ corresponding to 0.06 molal feed solution, and 0.117×10^{-3} corresponding to 0.005 molal feed solution.

^b Area of film surface: 13.2 cm²; feed concentration: 3500 ppm (0.06 molal) NaCl-H₂O; mass transfer coefficient k : 10.76×10^{-4} cm/sec.

TABLE III
List of Solutes Used with Some Physicochemical Data

Solute no.	Solute	$D_{AB} \times 10^5$, cm ² /sec	$k \times 10^4$, cm/sec
2	LiCl	1.3667	9.64
3	LiBr	1.3777	9.69
5	NaF	1.4008	9.80
9	NaCl	1.6110	10.76
12	NaBr	1.6263	10.82
15	NaI	1.6159	10.78
17	KF	1.6828	11.08
18	KCl	1.9948	12.41
19	KBr	2.0182	12.50
23	RbCl	2.0516	12.64
25	CsCl	2.0453	12.62
26	CsBr	2.0700	12.72

hr. After this period, it was subjected to an aqueous isobutyl alcohol solution (containing 400 ppm isobutyl alcohol) at a pressure of 250 psig for another 24 hr prior to all reverse osmosis experiments. The above pretreatment helped to stabilize the porous structure of the membrane surface.⁹

The apparatus and experimental procedure employed were the same as those used in the earlier studies.³⁻⁵ The operating pressure used in all reverse osmosis experiments in this work was 250 psig. The data on film specifications² given in Table II were based on reverse osmosis results obtained with aqueous sodium chloride feed solutions. Eleven other inorganic salts, listed in Table III, and 24 organic solutes including eight alcohols, four aldehydes, seven ketones, and five ethers listed in Table IV, were used as solutes. The solute concentrations used were in the range of 0.001–0.006 g-mole/l., so that in each case the osmotic pressure of the feed solution was negligible compared to the operating pressure. All experiments were carried out at the laboratory temperature (23–25°C).

In all experiments, the terms “product” and “product rate” refer to membrane-permeated solutions. In each experiment, solute separation f , defined as

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

and product rate (PR) and pure water permeation rate (PWP) in grams per hour per given area of film surface (13.2 cm² in this work) were determined under the specified experimental conditions. The solute concentrations in the feed and product solutions were determined using either conductivity measurements (for NaCl), an atomic absorption technique (for the other inorganic salts), or a total carbon analyzer (for the organic solutes).

The PR and PWP data used in calculations were those corrected to 25°C using the relative viscosity and density data for pure water. The available data indicated that the temperature effect on PWP and PR was slightly more than that given by the above correction factor; the latter factor, however, was found to give PWP and PR values sufficiently close to experimental data within the very narrow temperature range (23°–25°C) involved in this work.

The solute transport parameter ($D_{AM}/K\delta$) is treated as a single quantity in

TABLE IV
 Physicochemical Data on Solutes Studied

No.	Solute		Mol. wt	$k \times 10^4$, cm/sec	σ^* or $\Sigma\sigma^*$	E_s or ΣE_s	$-\Delta\Delta G/RT$
	Name	Formula					
<i>Alcohols</i>							
R in ROH							
1	<i>t</i> -Butyl alcohol	<i>t</i> -C ₄ H ₉	74.1	8.06	-0.300	-1.54	2.67 ^a
2	<i>s</i> -Butyl alcohol	<i>s</i> -C ₄ H ₉	74.1	8.06	-0.210	-1.13	3.59
3	Isopropyl alcohol	<i>i</i> -C ₃ H ₇	60.1	8.87	-0.190	-0.70	3.58
4	<i>n</i> -Butyl alcohol	<i>n</i> -C ₄ H ₉	74.1	8.06	-0.130	-0.39	3.70
5	Isobutyl alcohol	<i>i</i> -C ₄ H ₉	74.1	8.06	-0.200	-0.93	3.59
6	<i>n</i> -Propyl alcohol	<i>n</i> -C ₃ H ₇	60.1	8.87	-0.115	-0.36	3.71
7	Ethyl alcohol	C ₂ H ₅	46.1	10.08	-0.100	-0.07	3.72
8	Methyl alcohol	CH ₃	32.0	12.16	0	0	5.91 ^a
<i>Ethers</i>							
R ₁ , R ₂ in R ₁ -O-R ₂							
1	<i>t</i> -Butyl isopropyl ether	<i>t</i> -C ₄ H ₉ , <i>i</i> -C ₃ H ₇	116.2	6.55	-0.490	-2.24	3.25
2	<i>t</i> -Butyl ethyl ether	<i>t</i> -C ₄ H ₉ , C ₂ H ₅	102.2	6.92	-0.400	-1.61	3.38
3	Diisopropyl ether	<i>i</i> -C ₃ H ₇ , <i>i</i> -C ₃ H ₇	102.2	6.92	-0.380	-1.40	3.26
5	Di- <i>n</i> -propyl ether	<i>n</i> -C ₃ H ₇ , <i>n</i> -C ₃ H ₇	102.2	6.92	-0.230	-0.72	3.49
7	Anisole	CH ₃ , C ₆ H ₅	108.1	7.40	0.600	-0.06	2.12
<i>Ketones</i>							
R ₁ , R ₂ in R ₁ -C(=O)-R ₂							
1	Diisopropyl ketone	<i>i</i> -C ₃ H ₇ , <i>i</i> -C ₃ H ₇	114.2	6.73	-0.380	-1.40	4.34
3	Cyclopentanone	cyclo-C ₄ H ₈	84.1	7.75	-0.250	-0.51	4.71
4	Methyl isopropyl ketone	CH ₃ , <i>i</i> -C ₃ H ₇	86.1	7.64	-0.190	-0.70	4.48
5	Methyl isobutyl ketone	CH ₃ , <i>i</i> -C ₄ H ₉	100.2	7.13	-0.200	-0.93	4.48
6	Methyl ethyl ketone	CH ₃ , C ₂ H ₅	72.1	8.30	-0.100	-0.07	4.62
8	Benzyl methyl ketone	C ₆ H ₅ (CH ₂), CH ₃	134.2	6.50	0.215	-0.38	5.02
9	Acetophenone	C ₆ H ₅ , CH ₃	120.1	6.84	0.600	-0.06	5.02
<i>Aldehydes</i>							
R in RCHO							
2	Isovaleraldehyde	<i>i</i> -C ₄ H ₉	86.1	7.64	-0.200	-0.93	3.93
3	<i>n</i> -Butylaldehyde	<i>n</i> -C ₃ H ₇	72.1	8.30	-0.115	-0.36	4.07
4	Propionaldehyde	C ₂ H ₅	58.1	9.22	-0.100	-0.07	4.08
6	Benzaldehyde	C ₆ H ₅	106.1	7.65	0.600	-0.06	4.48

^a $-\Delta\Delta G/RT$ was calculated from experimental $\Delta G_I/RT$.

all calculations. From the experimental f and PR data, values of $D_{AM}/K\delta$ for the solutes used were obtained from the expression¹⁰

$$D_{AM}/K\delta = \frac{PR}{3600Sd} \frac{1-f}{f} \left[\exp \left\{ \frac{PR}{3600Skd} \right\} \right]^{-1} \quad (6)$$

where S = effective film area (= 13.2 cm²) and d = density of solution (\approx density of pure water). All data presented are for 25°C.

RESULTS AND DISCUSSION

Free-Energy Parameter ($-\Delta\Delta G/RT$)_{*i*} for Alkali Metal Ions and Halide Ions

The free-energy parameter involves (besides the gas constant R and the absolute temperature T) the quantity $\Delta\Delta G$ defined as

$$\Delta\Delta G = \Delta G_I - \Delta G_B \quad (7)$$

TABLE V
Free-Energy Parameters of Alkali Metal Cations and Halide Anions for Cellulose Acetate Propionate Material

Ion	Ionic radius Å	ΔG_I^a kcal/mole	$\Delta\Delta G$, kcal/mol	$\left(\frac{-\Delta\Delta G}{RT}\right)_i$
Alkali Metal Cations				
Li ⁺	0.60	-121.41	0.74	-1.25
Na ⁺	0.95	- 98.14	0.77	-1.30
K ⁺	1.33	- 81.23	0.75	-1.27
Rb ⁺	1.48	- 76.06	0.73	-1.23
Cs ⁺	1.69	- 69.84	0.70	-1.18
Halide Anions				
F ⁻	1.36	-104.13	-0.25	0.42
Cl ⁻	1.81	- 75.49	-0.65	1.10
Br ⁻	1.95	- 69.54	-0.68	1.15
I ⁻	2.16	- 62.19	-0.71	1.20

^a ΔG_I values are based on $(E_I)_{c^+} = 179.2$ kcal·Å/mole; $(\Delta_I)_{c^+} = 0.876$ Å; $(E_I)_{a^-} = 123.5$ kcal·Å/mole; $(\Delta_I)_{a^-} = -0.174$ Å.

where ΔG represents the free energy of hydration (in kcal/mole) and the subscripts I and B represent the membrane-solution interface and the bulk solution phase, respectively. The following relationships have already been derived and discussed³:

$$\frac{1}{\Delta G_B} = -\frac{1}{E_B} r_i - \frac{\Delta_B}{E_B} \quad (8)$$

$$\frac{1}{\Delta G_I} = -\frac{1}{E_I} r_i - \frac{\Delta_I}{E_I} \quad (9)$$

$$\therefore \Delta\Delta G = \left(-\frac{E_I}{r_i + \Delta_I}\right) - \left(-\frac{E_B}{r_i + \Delta_B}\right) \quad (10)$$

The quantities E and Δ are constants for each class of ions; with respect to the bulk solution phase, these constants (E_B and Δ_B) can be determined from the slope and intercept of the linear plot of $1/\Delta G_B$ versus the ionic radius r_i (in angstrom units). It is already known³ that the values of E_B are 182.0 and 120.5 for the alkali metal cations and the halide anions, respectively; the corresponding values of Δ_B are 0.89 and -0.20, respectively. These values, together with those of r_i listed in Table V, are used in this work.

Using eq. (10), the free-energy parameter for a specific cation (M^+) or anion (X^-) can be expressed as

$$\left(-\frac{\Delta\Delta G}{RT}\right)_{M^+} = \frac{1}{RT} \left\{ \left(\frac{E_I}{r_{M^+} + \Delta_I}\right)_{c^+} - \left(\frac{E_B}{r_{M^+} + \Delta_B}\right)_{c^+} \right\} \quad (11)$$

and

$$\left(-\frac{\Delta\Delta G}{RT}\right)_{X^-} = \frac{1}{RT} \left\{ \left(\frac{E_I}{r_{X^-} + \Delta_I}\right)_{a^-} - \left(\frac{E_B}{r_{X^-} + \Delta_B}\right)_{a^-} \right\} \quad (12)$$

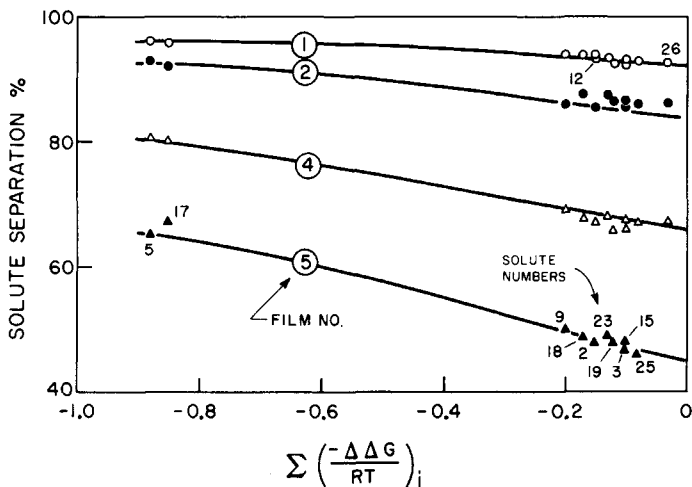


Fig. 1. Effect of $\sum(-\Delta\Delta G/RT)_i$ on solute separation of alkali metal halides: (—) predicted; (\odot \bullet \blacktriangle) experimental; film type, cellulose acetate propionate; operating pressure, 250 psig; feed concentration, 0.005 g-mole/l.; flow rate, 400 cc/min; membrane area, 13.2 cm²; solute numbers, same as in Table III.

where the subscripts c^+ and a^- represent the alkali metal cations and halide anions, respectively. Equation (4) can then be written as

$$\ln(D_{AM}/K\delta)_{M^+X^-} = \ln C_{NaCl}^* + \frac{1}{RT} \left\{ \left(\frac{E_I}{r_{M^+} + \Delta_I} \right)_{c^+} - \left(\frac{E_B}{r_{M^+} + \Delta_B} \right)_{c^+} \right\} + \frac{1}{RT} \left\{ \left(\frac{E_I}{r_{X^-} + \Delta_I} \right)_{a^-} - \left(\frac{E_B}{r_{X^-} + \Delta_B} \right)_{a^-} \right\}. \quad (13)$$

With respect to the application of eq. (13) to a given membrane, the quantity $\ln(D_{AM}/K\delta)_{M^+X^-}$ can be obtained from experimental reverse osmosis data using eq. (6); the unknown quantities are $\ln C_{NaCl}^*$, $(E_I)_{c^+}$, $(\Delta_I)_{c^+}$, $(E_I)_{a^-}$, and $(\Delta_I)_{a^-}$. In order to determine these five unknowns, a minimum of five values of $D_{AM}/K\delta$ for different alkali metal halide solutes are needed.

In this work, 12 different alkali halides, listed in Table III, were used in 0.005 molal feed solutions to determine their $D_{AM}/K\delta$ values. Using these values in eq. (13), the best fitting values for the five unknowns mentioned above were determined for a particular film sample (film number 3 specified in Table II). Of these five quantities, only $\ln C_{NaCl}^*$ is a function of the porous structure of the membrane, and the other four quantities depend only on the chemical nature of the membrane material. The values for the latter four quantities were then used in eqs. (11) and (12) to determine the free-energy parameters for each of the alkali metal cations and the halide anions. The data so obtained are given in Table V.

Using the experimental $D_{AM}/K\delta$ data for NaCl given in Table II for 0.005 molal feed solution, and the data on $(-\Delta\Delta G/RT)_i$ for Na⁺ and Cl⁻ ions given in Table V, the values of $\ln C_{NaCl}^*$ for four other films (numbers 1, 2, 4, and 5, specified in Table II) were calculated from eq. (3). Using these values of $\ln C_{NaCl}^*$ in eq. (4), and the data on $(-\Delta\Delta G/RT)_i$ for different ions given in Table V, the values of $D_{AM}/K\delta$ for the 11 other inorganic solutes were calculated for each membrane.

Using these values of $D_{AM}/K\delta$ in eq. (6), the values of f (solute separation) for different solutes were calculated and compared with the actual experimental data for each film. The excellent agreement between the calculated and experimental data on solute separation shown in Figure 1 confirm the practical validity of the free-energy parameter given in Table V for the CAP membrane material.

Parameters for Prediction of $D_{AM}/K\delta$ for Organic Solutes

Correlations of $\ln C_{NaCl}^*$ Versus δ^* for Alcohols, Aldehydes, Ketones, and Ethers. For solutes whose reverse osmosis separations are governed by polar and steric effects, the following relationship is applicable:¹¹

$$\ln (D_{AM}/K\delta) = \ln C^* + \rho^* \Sigma \sigma^* + \delta^* \Sigma E_s \quad (14)$$

or

$$\ln (D_{AM}/K\delta) - \rho^* \Sigma \sigma^* = \ln C^* + \delta^* \Sigma E_s \quad (15)$$

where $\ln C^*$ is a constant, $\Sigma \sigma^*$ represents Taft's polar parameter for the substituent group in the organic molecule,⁷ and ρ^* is the coefficient associated with $\Sigma \sigma^*$. On the basis of eq. (15), for any given membrane (i.e., given $\ln C_{NaCl}^*$), one can obtain a numerical value for δ^* from the slope of the linear plot of $\ln (D_{AM}/K\delta) - \rho^* \Sigma \sigma^*$ versus ΣE_s with reference to each class of solutes. In order to do so, one needs the applicable values of ρ^* for use in eq. (15); these values of ρ^* were estimated in this work as follows:

A plot of $\Sigma \sigma^*$ versus $\ln (D_{AM}/K\delta)$ for the eight alcohols listed in Table IV showed a linear relationship with respect to C_3 and C_4 alcohols (in the $\Sigma \sigma^*$ range of -0.3 – -0.115) for all the films tested. With each film, however, the data for methyl and ethyl alcohols ($\Sigma \sigma^* = 0$ and -0.1 , respectively) showed an abrupt increase in $\ln (D_{AM}/K\delta)$ with increase in $\Sigma \sigma^*$ similar to that found in the case of aromatic polyamide membrane material studied earlier.¹² On the basis of the earlier work on cellulose acetate and aromatic polyamide membranes,^{6,12} it is reasonable to consider that in the case of CAP membranes also, the reverse osmosis separation of C_3 and C_4 alcohols are governed primarily by polar effects, that the value of δ^* for alcohols is practically negligible when the average pore size on the membrane surface is sufficiently large, and that the value of ρ^* for alcohols is independent of the average pore size on the membrane surface.

Therefore, from least-squares analysis of experimental $D_{AM}/K\delta$ data for C_3 and C_4 alcohols, the values of ρ^* were calculated on the basis of eq. (14) for the condition $\delta^* = 0$. The values of ρ^* thus obtained were 14.39, 12.11, 12.44, 8.08, 8.55, and 7.74 for films 6, 7, 8, 9, 10, and 11 (Table II), respectively. Since the values of ρ^* for the last three relatively larger pore-size membranes are not too different from each other, an average value of 8.12 was assigned to ρ^* for the alcohol solutes with respect to the CAP membrane material used. It may be recalled⁶ that the corresponding value of ρ^* for the cellulose acetate material is 15.5. In view of the small number of compounds involved in each of the aldehyde, ketone, and ether class of solutes used, a rigorous regression analysis to generate the applicable values of ρ^* was not considered meaningful. Therefore, it was assumed that the ratio of ρ^* values for CAP and cellulose acetate membranes was constant for each of the above classes of solutes. This assumption is rea-

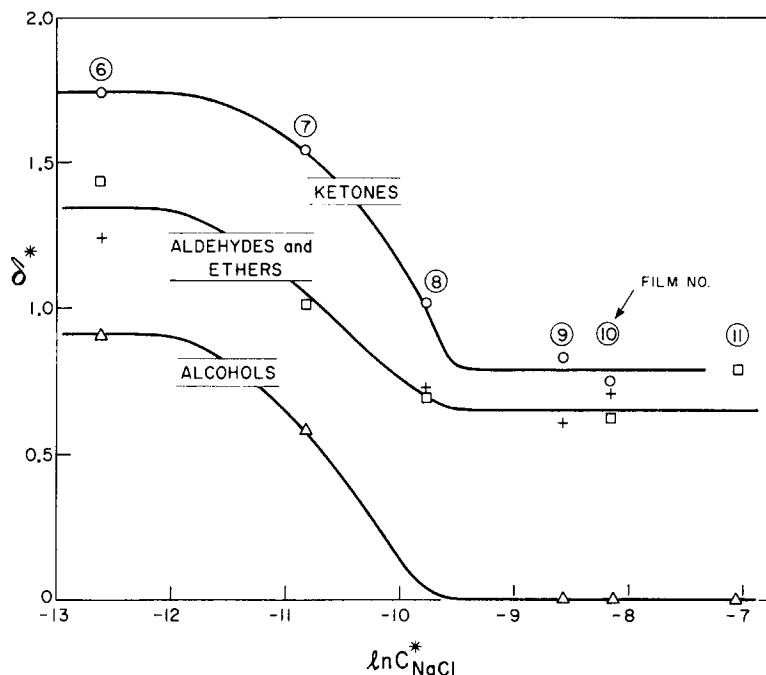


Fig. 2. Effect of pore size on membrane surface on δ^* for alcohols, ethers, aldehydes, and ketones: film type, cellulose acetate propionate; operating pressure, 250 psig; (Δ) alcohols; (\square) ethers; (+) aldehydes; (\odot) ketones.

sonable on the basis of the chemical similarity of CAP and cellulose acetate materials. Since the values of ρ^* for the cellulose acetate material are 1.7, 2.5, and 0 for aldehydes, ketones, and noncyclic ethers, respectively,¹³ the corresponding values of ρ^* for CAP material are 0.89, 1.31, and 0, respectively. These values of ρ^* were used in eq. (15).

From the linear correlation of $\ln(D_{AM}/K\delta) - \rho^*\Sigma\sigma^*$ versus ΣE_s , for membranes of different surface porosities, the values of δ^* for each class of solutes applicable to the CAP material used were obtained, and the results are plotted in Figure 2 as a function of $\ln C_{NaCl}^*$ following the format of similar correlations given earlier⁵ for cellulose acetate and polyamide membranes. For the purpose of these correlations, $\ln C_{NaCl}^*$ values were calculated on the basis of the $D_{AM}/K\delta$ data for NaCl for 0.06 molal feed solutions given in Table II.

Structural Group Contributions to ΔG_I and the Correlation of $\ln C_{NaCl}^*$ Versus $\ln \Delta^*$. Referring to eq. (7), at any given temperature the quantity ΔG_B depends on the chemical nature of solute and solvent only, and the quantity ΔG_I depends on the chemical nature of solute, solvent, and membrane material, but is independent of the porous structure of the membrane surface. As before,⁵ both ΔG_B and ΔG_I may be expressed as

$$\Delta G_B = \Sigma\gamma_B(\text{structural group}) + \gamma_{B,0} \quad (16)$$

and

$$\Delta G_I = \Sigma\gamma_I(\text{structural group}) + \gamma_{I,0} \quad (17)$$

where $\gamma_B(\text{structural group})$ and $\gamma_I(\text{structural group})$ represent the structural

TABLE VI
Structural Group Contributions for ΔG_B and ΔG_I at 25°C

Structural group	$\gamma_{B,0} = -12.04$	Cellulose acetate propionate, $\gamma_{I,0} = 8.17$
	γ_B	γ_I
—CH ₃	11.07	-0.11
>CH ₂	0.17	0.17
->CH	-10.62	0.64
$\begin{array}{c} \\ -C- \\ \end{array}$	-21.50	0.95
Cyclic	20.49	-1.93
—C ₆ H ₅	8.41	-3.00
—OH	3.99	-7.25
>O	-4.03	-3.98
—CHO	5.80	-5.65
>C=O	-5.80	-6.39

group contribution to the free energy of hydration of the solute molecule with respect to the bulk solution phase and the membrane-solution interface, respectively; and $\Delta_{B,0}$ and $\Delta_{I,0}$ are the corresponding characteristic constants common to all the structural groups involved. Ten structural groups (namely, —CH₃, >CH₂, >CH, >C<, cyclic, —C₆H₅, —OH, >O, —CHO, and >CO) are involved in the solute molecules studied in this work. The values of γ_B (structural group) and $\gamma_{B,0}$ for all the above structural groups are already available in the literature,⁵ and they are listed in Table VI. The values of γ_I (structural group) and $\gamma_{I,0}$ for the CAP material used were determined in this work as follows:

Combining eqs. (5), (7), and (17),

$$(-RT)\{\ln(D_{AM}/K\delta) - \ln C_{NaCl}^* - \delta^* \Sigma E_s\} + \Delta G_B = \Sigma \gamma_I(\text{structural group}) + \gamma_{I,0} + (-RT) \ln \Delta^* \quad (18)$$

Again, following earlier work,⁵ $\ln C_{NaCl}^*$ values were calculated from $D_{AM}/K\delta$ data for NaCl using 0.06 molal feed solutions, and the quantity $\ln \Delta^*$ was assigned a value of zero when $\ln C_{NaCl}^*$ was less than -12.0. Using 103 experimental reverse osmosis data involving 22 different solutes and six membranes of different surface porosities (including one whose $\ln C_{NaCl}^*$ was less than -12.0), eq. (18) was

TABLE VII
Comparison of ρ^* and δ^* Values of Cellulose Acetate Propionate with Cellulose Acetate and Aromatic Polyamide

Polar functional group	Cellulose acetate		Cellulose acetate propionate		Aromatic polyamide	
	ρ^*	δ^*	ρ^*	δ^*	ρ^*	δ^*
Alcohols	15.5	0	8.12	0-0.91	5.6	0.16-0.7
Aldehydes	1.7	0	0.89	0.61-1.24	0.65	1.28-2.48
Ketones	2.5	0.19-0.49	1.31	0.42-1.74	0.55	0.86-2.14
Ethers (noncyclic)	0	1.02-1.64	0	0.45-1.44	0	0.98-2.16

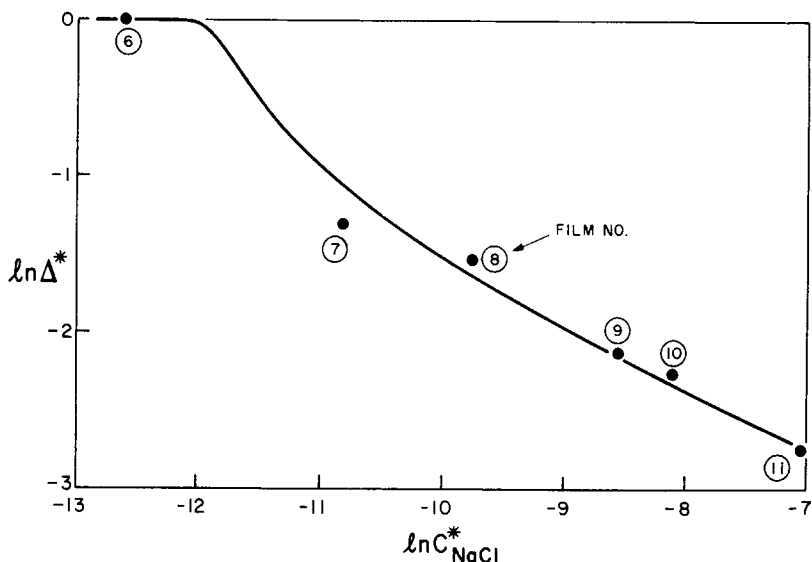


Fig. 3. Correlation of $\ln \Delta^*$ vs. $\ln C_{\text{NaCl}}^*$: film type, cellulose acetate propionate; operating pressure, 250 psig.

subjected to multiple regression analysis to solve for 16 unknowns (ten γ_I (structural group) values, one $\gamma_{I,0}$ value, and five $\ln \Delta^*$ values corresponding to five (larger than -12.0) $\ln C_{\text{NaCl}}^*$ values). The results obtained had a multiple coefficient of determination of 0.999. The values of γ_I (structural group) and $\gamma_{I,0}$ so obtained are given in Table VI, and those of $\ln \Delta^*$ are plotted in Figure 3 as a function of $\ln C_{\text{NaCl}}^*$.

The data on the free-energy parameters ($-\Delta\Delta G/RT$) for the organic solutes

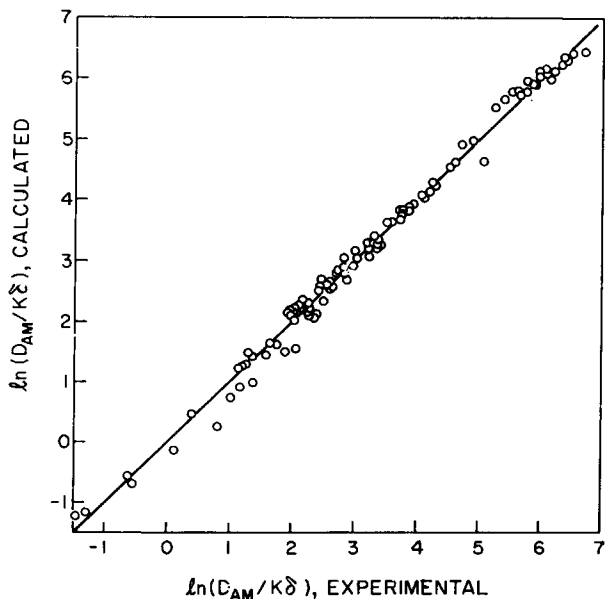


Fig. 4. Comparison of calculated $\ln(D_{AM}/K\delta)$ and experimental $\ln(D_{AM}/K\delta)$.

TABLE VIII

Comparison of Solute Separations by Cellulose Acetate, Cellulose Acetate Propionate, and Polyamide Membranes with Comparable Average Pore Size on Membrane Surface

No.	Solute Name	Solute separation at 25° C		
		Cellulose acetate ^b	Cellulose acetate propio- nate ^a	Poly- amide ^b
<i>Alcohols</i>				
1	<i>t</i> -Butyl alcohol	80.6	80.7	86.9
2	<i>s</i> -Butyl alcohol	48.1	61.5	77.8
3	Isopropyl alcohol	43.0	57.7	72.0
4	<i>n</i> -Butyl alcohol	20.6	31.3	66.3
5	Isobutyl alcohol	45.0	61.4	70.1
6	<i>n</i> -Propyl alcohol	19.1	36.4	57.3
7	Ethyl alcohol	15.3	16.2	16.7
8	Methyl alcohol	1.0	6.4	8.4
<i>Ethers</i>				
1	<i>t</i> -Butyl isopropyl ether	86.8	91.5	99.9
2	<i>t</i> -Butyl ethyl ether	80.2	87.7	99.0
3	Diisopropyl ether	72.1	82.2	99.9
5	Di- <i>n</i> -propyl ether	39.1	70.6	98.3
7	Anisole	29.7	51.6	80.3
<i>Ketones</i>				
1	Diisopropyl ketone	38.9	64.1	97.1
3	Cyclopentanone	25.7	34.6	82.6
4	Methyl isopropyl ketone	35.8	45.1	83.0
5	Methyl isobutyl ketone	33.1	43.2	88.5
6	Methyl ethyl ketone	7.7	13.6	76.6
<i>Aldehydes</i>				
2	Isovaleraldehyde	45.3	48.5	89.4
3	<i>n</i> -Butyraldehyde	33.6	37.3	71.9
4	Propionaldehyde	29.7	34.1	71.0
6	Benzaldehyde	11.8	13.8	53.8

^a Data for film 7 (Table II).^b Data from Table V in ref. 4.

calculated on the basis of the data on structural group contributions given in Table VI are included in Table IV.

Comparison of Calculated and Experimental Data. Two sets of comparisons were made. The values of $\ln(D_{AM}/K\delta)$ for several organic solutes were calculated for membranes of different surface porosities on the basis of eq. (5) using data on membrane specifications (Table II) and the data on the other parameters given in Table VI and Figures 2 and 3. Figure 4 gives a comparison of $\ln(D_{AM}/K\delta)$ data so obtained with the corresponding experimental data. Using the data on $\ln(D_{AM}/K\delta)$ calculated from eq. (5) and the applicable values of k calculated from eq. (1), together with data on A (assuming $PR \approx PWP$), the values of f (solute separation) were calculated for different solutes from eq. (6).

Figure 5 gives a comparison of solute separation data so calculated with the corresponding experimental values for films 6, 7, 10, and 11. The comparisons shown in Figures 4 and 5 involve all classes of solutes studied in this work. The

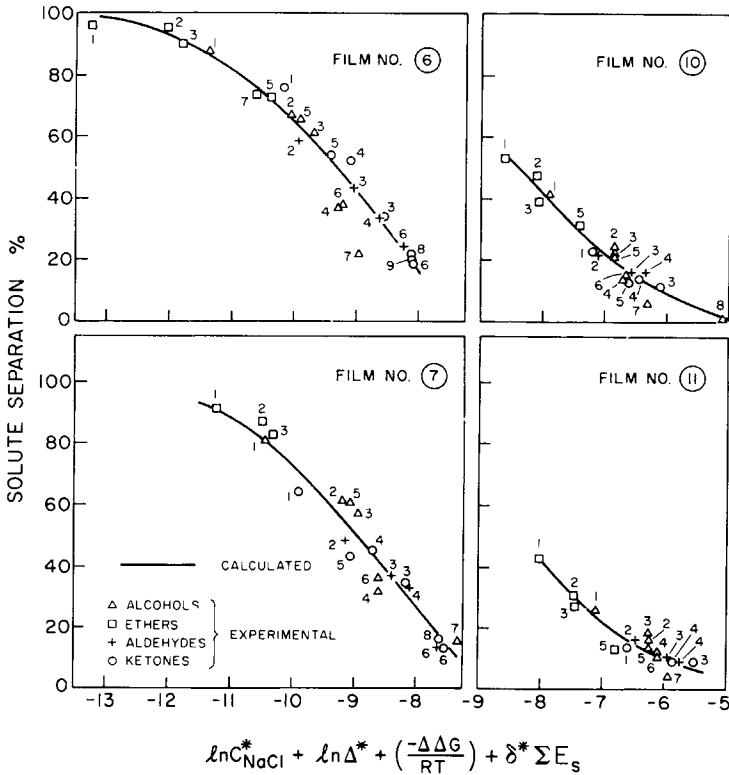


Fig. 5. Effect of $(\ln C_{\text{NaCl}}^* + \ln \Delta^* + (-\Delta\Delta G/RT) + \delta^* \Sigma E_s)$ on separation of undissociated polar organic solutes: (—) predicted; (Δ), (\square), ($+$), (\circ) experimental data for alcohols, ethers, aldehydes, and ketones, respectively; film type, cellulose acetate propionate; operating pressure, 250 psig; feed concentration, 0.001 ~ 0.006 g-mole/l.; flow rate, 400 cc/min; membrane area, 13.2 cm²; solute numbers, same as in Table IV.

agreement between the calculated and experimental data is reasonably good in all cases, which testifies the practical validity of the data on parameters and correlations generated in this work for predicting the reverse osmosis performance of CAP membranes of different surface porosities.

Comparison of Properties of Different Membrane Materials

The numerical values of the polar coefficient ρ^* and the steric coefficient δ^* represent the chemical properties of the membrane materials with respect to their performance in reverse osmosis. A comparison of the available values of ρ^* and δ^* for CAP material with the corresponding values for cellulose acetate (CA) and aromatic polyamide (PA) materials studied earlier^{4,13} (Table VII) shows that the properties of CAP lie intermediate between those of CA and PA. On this basis, one may consider that the magnitude of the resultant interfacial forces governing reverse osmosis separations for CAP membranes lies between the magnitudes of the corresponding forces for CA and PA membranes. This means that solute separations with CAP membranes may be expected to be between those of CA and PA membranes under otherwise identical experimental condi-

TABLE IX
Comparison of Free-Energy Parameters for Cellulose Acetate,
Cellulose Acetate Propionate, and Aromatic Polyamide Materials

	$(-\Delta\Delta G/RT)_i$		
	Cellulose acetate ^a	Cellulose acetate propionate	Aromatic polyamide ^b
Alkali Metal Cations			
Li ⁺	5.77	-1.25	-1.77
Na ⁺	5.79	-1.30	-2.08
K ⁺	5.91	-1.27	-2.11
Rb ⁺	5.86	-1.23	-2.08
Cs ⁺	5.72	-1.18	-2.04
Halide Anions			
F ⁻	-4.91	0.42	1.03
Cl ⁻	-4.42	1.10	1.35
Br ⁻	-4.25	1.15	1.35
I ⁻	-3.98	1.20	1.33

^a From ref. 3.

^b From ref. 4.

tions, provided the membranes under comparison have the same average pore size on the membrane surface.

For testing this hypothesis, one needs a set of CA, CAP, and PA membranes with identical average pore size on the membrane surface. There is no way by which one can be certain of meeting this pore size requirement in any actual comparison. However, if one can assume, as before,⁴ that membranes which lie in the steeply changing region of the δ^* -versus-pore size correlation have essentially the same average pore size on the membrane surface, then it is reasonable to compare the data on the performance of film 7 specified in Table II with similar data for CA and PA membranes given in Table V in ref. 4. Table VIII gives such a comparison of data with respect to 22 different organic solutes; these data do confirm that the reverse osmosis properties of CAP membranes lie between those of CA and PA membranes.

Table IX gives a comparison of the numerical data on free-energy parameters for the alkali metal cations and halide anions for the CA, CAP, and PA membrane materials. These results also show that the data for the CAP material lie intermediate between those for the CA and PA materials. Further, the sign of the above parameters for the CAP material are opposite to those for the CA material and are the same as those for the PA material, which suggests that during reverse osmosis, the CAP membrane surface, just as the PA membrane surface, behaves as if it is positively charged and hence an acid (proton donor).

CONCLUSIONS

The data on free-energy parameters for alkali metal cations and halide anions given in Table V and the data on structural group contributions to ΔG_B and ΔG_I given in Table VI, together with the correlations of δ^* and $\ln \Delta^*$ -versus- $\ln C_{\text{NaCl}}^*$ values given in Figures 2 and 3, enable one to use eqs. (3), (4), and (5) for calculating the pertinent $D_{AM}/K\delta$ values with respect to CAP membranes of different

surface porosities and aqueous feed solutions involving alkali metal halides or nonionized polar organic solutes of the type studied in this work.

The available data on $D_{AM}/K\delta$ values for NaCl show that these values increase slightly with increase in feed concentration, and the following relationship holds well:

$$D_{AM}/K\delta \propto X_{A2}^{0.113} \quad (19)$$

where X_{A2} is the mole fraction of NaCl in the boundary solution on the high-pressure side of the membrane.² Under the experimental conditions used in this work, the value of X_{A2} for the 0.06 molal NaCl-H₂O feed solution was 1.36×10^{-3} . For making use of Figures 2 and 3, the values of $\ln C_{NaCl}^*$ should be calculated from $(D_{AM}/K\delta)_{NaCl}$ values corresponding to the above value of X_{A2} . This can be done from eq. (19) using the experimental $(D_{AM}/K\delta)_{NaCl}$ data for any single feed concentration.

Thus, from data on membrane specifications given in terms of A and $D_{AM}/K\delta$ for NaCl at any single feed concentration, reverse osmosis separations of all the other solutes included in this study can be predicted for CAP membranes from the parameters and correlations generated in this work and the basic transport equations.²

While this work was limited to dilute solutions and an operating pressure of 250 psig, the parameters (Tables V and VI) and the correlations (Figs. 2 and 3) generated in this work may be expected to be independent of feed concentration and operating pressure.

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