

Reverse Osmosis Separations of Some Organic and Inorganic Solutes in Aqueous Solutions Using Aromatic Polyamide Membranes

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Synopsis

The reverse osmosis separations of some ethers, ketones, aldehydes, monocarboxylic acids, and inorganic salts in single-solute (55–454 ppm) aqueous solution systems using aromatic polyamide membranes have been studied at 250 psig. It was found that reverse osmosis separation was essentially a function of steric parameter for ethers, and of both polar and steric parameters for ketones, aldehydes, and alcohols. Solute separations for monocarboxylic acids passed through a minimum at a pK_a value of ~ 4.8 . The values for the free-energy parameter for Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , and F^- , Cl^- , Br^- , I^- , and IO_3^- ions have been calculated for the polyamide membranes used. The above values for cations are negative and those for anions are positive, suggesting that the polyamide membrane surface behaves as if it is positively charged. Further, the data show that the polyamide membrane material is only about 40% as polar as that of the cellulose acetate membrane material studied earlier.

INTRODUCTION

Aromatic polyamide membranes constitute one of the newer classes of successful membranes presently being developed for reverse osmosis applications.¹⁻⁷ Therefore, the physicochemical criteria governing the separation of organic and inorganic solutes in aqueous solutions using such membranes are of both scientific and practical interest. Some studies on the influence of polar and nonpolar interactions on the performance of a class of aromatic polyamide membranes have been reported⁸ with respect to the reverse osmosis separations of alcohols and phenols in aqueous solutions. This work is a similar study with respect to the reverse osmosis separations of some ethers, ketones, aldehydes, monocarboxylic acids, and inorganic solutes in single-solute aqueous solution systems involving the same class of aromatic polyamide membranes. As before, the solute concentration in the feed solution was kept very low (100 to 200 ppm) in all the experiments so that the osmotic pressure of the feed solution was negligible compared to the operating pressure of 250 psig used in this work. The results obtained were analyzed on the basis of polar, nonpolar, steric, and/or ionic character of the solute molecule concerned, and compared with similar data reported earlier⁹⁻¹¹ for the corresponding reverse osmosis systems involving cellulose acetate membranes.

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EXPERIMENTAL

Six samples of flat aromatic polyamide membranes of different surface porosities made in the laboratory by the method reported earlier⁸ were used in this work. As stated before,⁸ the membrane material was essentially a random copolymer consisting of the following repeat units in the molar ratio of 7 to 3, respectively:

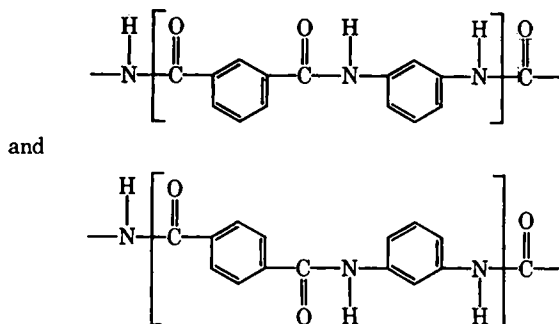


Table I gives their specifications¹² in terms of pure water permeability constant A (in g-mole H_2O/cm^2 sec atm) and solute transport parameter $D_{AM}/K\delta$ for sodium chloride (in cm/sec) at the operating pressure of 250 psig. The organic solutes used included seven noncyclic ethers, ten ketones, and seven aldehydes listed in Table II, and nine monocarboxylic acids listed in Table III. The inorganic solutes used included the halides of sodium and, in addition, the chlorides of lithium, potassium, rubidium, and cesium, and sodium iodate. The solute concentrations used were in the range of 0.0005 to 0.0076 g-mole/l. (55 to 454 ppm). The general details of the reverse osmosis experiments were the same as before.⁸ All the experiments were carried out at 250 psig and at laboratory temperature (23–25°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

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

TABLE I
Film Specifications^a

	Film					
	1	2	3	4	5	6
Pure water permeability constant A , $\frac{\text{g-mole } H_2O}{\text{cm}^2 \cdot \text{sec} \cdot \text{atm}} \times 10^6$	0.154	0.133	0.216	0.267	0.301	0.364
Solute transport parameter $(D_{AM}/K\delta)_{NaCl}$, (cm/sec) $\times 10^5$	0.109	0.398	0.752	1.24	3.07	5.04
Solute separation, %	97.6	90.9	87.4	84.1	71.6	65.6
Product rate, g/hr ^b	1.90	1.72	2.75	3.45	3.98	4.76

^a Feed concentration: 3500 ppm NaCl- H_2O ; mass transfer coefficient k : 22×10^{-4} cm/sec; operating pressure, 250 psig.




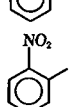
^b Area of film surface: 13.2 cm².

the product rate (*PR*) and pure water permeation rate (*PWP*) in g/hr per given area of film surface (= 13.2 cm² in this work) were determined under the specified experimental conditions. A Beckman total carbon analyzer Model 915 was used to measure the concentrations of the organic solutes in the feed and product

TABLE II
Physicochemical Data on Solutes Studied

No.	Name	Formula	Mol. wt.	σ^* or $\Sigma\sigma^*$	E_s or ΣE_s
Ethers					
		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	-0.490	-2.24
2	<i>t</i> -Butyl ethyl ether	<i>t</i> -C ₄ H ₉ , C ₂ H ₅	102.2	-0.400	-1.61
3	Diisopropyl ether	<i>i</i> -C ₃ H ₇ , <i>i</i> -C ₃ H ₇	102.2	-0.380	-1.40
4	Butyl ethyl ether	<i>n</i> -C ₄ H ₉ , C ₂ H ₅	102.2	-0.230	-0.46
5	Di- <i>n</i> -propyl ether	<i>n</i> -C ₃ H ₇ , <i>n</i> -C ₃ H ₇	102.2	-0.230	-0.72
6	Phenetole	C ₂ H ₅ , C ₆ H ₅	122.2	0.500	-0.13
7	Anisole	CH ₃ , C ₆ H ₅	108.1	0.600	-0.06
Ketones					
		R_1, R_2 in $R_1-\overset{\text{O}}{\parallel}{\text{C}}-R_2$			
1	Diisopropyl ketone	<i>i</i> -C ₃ H ₇ , <i>i</i> -C ₃ H ₇	114.2	-0.380	-1.40
2	Diisobutyl ketone	<i>i</i> -C ₄ H ₉ , <i>i</i> -C ₄ H ₉	142.2	-0.400	-1.86
3	Cyclopentanone	cyclo-C ₄ H ₈	84.1	-0.250	-0.51
4	Methyl isobutyl ketone	CH ₃ , <i>i</i> -C ₄ H ₉	100.2	-0.200	-0.93
5	Methyl isopropyl ketone	CH ₃ , <i>i</i> -C ₃ H ₇	86.1	-0.190	-0.70
6	Methyl ethyl ketone	CH ₃ , C ₂ H ₅	72.1	-0.100	-0.07
7	Acetone	CH ₃ , CH ₃	58.1	0	0
8	Benzyl methyl ketone	C ₆ H ₅ (CH ₂), CH ₃	134.2	0.215	-0.38
9	Acetophenone	C ₆ H ₅ , CH ₃	120.1	0.600	-0.06
10	Cyclohexanone	cyclo-C ₅ H ₁₀	98.1	-0.180	-0.79
Aldehydes					
		R in $RCHO$			
1	Isobutyraldehyde	<i>i</i> -C ₃ H ₇	72.1	-0.190	-0.70
2	Isovaleraldehyde	<i>i</i> -C ₄ H ₉	86.1	-0.200	-0.93
3	<i>n</i> -Butyraldehyde	<i>n</i> -C ₃ H ₇	72.1	-0.115	-0.36
4	Propionaldehyde	C ₂ H ₅	58.1	-0.100	-0.07
5	Acetaldehyde	CH ₃	44.1	0.0	0.0
6	Benzaldehyde	C ₆ H ₅	106.1	0.600	-0.06
7	Hexanal	<i>n</i> -C ₅ H ₁₁	100.2	-0.133	-0.40

TABLE III
Acidity Parameters for Monocarboxylic Acids

Solute no.	Name	R in RCOOH	Mol. wt.	pK _a
1	Pivalic acid	<i>t</i> -C ₄ H ₉	102.1	5.05
2	Propionic acid	C ₂ H ₅	74.1	4.87
3	Isobutyric acid	<i>i</i> -C ₃ H ₇	88.1	4.86
4	Valeric acid	<i>n</i> -C ₄ H ₉	102.1	4.86
5	Acetic acid	CH ₃	60.1	4.75
6	Anisic acid		152.1	4.47
7	Benzoic acid		122.1	4.20
8	<i>o</i> -Chlorobenzoic acid		156.6	2.94
9	<i>o</i> -Nitrobenzoic acid		167.1	2.17

solutions. The concentrations of the inorganic solutes were obtained using a conductivity bridge. The mass transfer coefficient k (in cm/sec) obtained in each experiment was calculated using the diffusivity (D_{AB}) data for different solutes^{9,11} and sodium chloride as the reference solute ($k = 22 \times 10^{-4}$ cm/sec). From the experimental PR , f , and k data, the solute transport parameter ($D_{AM}/K\delta$) for each solute was then calculated following the method described earlier.¹³

RESULTS AND DISCUSSION

Separations of Ethers, Ketones, and Aldehydes

Analysis of Data. On the basis of the work reported earlier,⁹ the data on solute transport parameter ($D_{AM}/K\delta$) for the above classes of solutes may be analyzed in terms of one of the following equations:

$$\ln (D_{AM}/K\delta) = \rho^* \Sigma \sigma^* + \ln C^* \quad (1)$$

$$\ln (D_{AM}/K\delta) = \delta^* \Sigma E_s + \ln C^* \quad (2)$$

$$\ln (D_{AM}/K\delta) = \rho^* \Sigma \sigma^* + \delta^* \Sigma E_s + \ln C^* \quad (3)$$

where $\Sigma \sigma^*$ and ΣE_s are the polar and steric parameters, respectively, given by Taft¹⁴ for substituent groups in the organic molecule; ρ^* and δ^* are the coefficients associated with $\Sigma \sigma^*$ and ΣE_s , respectively, appropriate for each functional group under the experimental conditions used; and C^* is the corresponding proportionality constant depending on the porous structure of the membrane. Equations (1) to (3) have been discussed.⁹ Equation (1) is applicable where steric effects are small or negligible; eq. (2), where polar effects are small or negligible; and eq. (3), where both polar and steric effects are not either small or negligible. It has also been pointed out⁹ that among the four functional groups —OH, —CHO, C=O, and C—O—C, alcohols are the most polar and ethers are the least polar, and the polar character of aldehydes and ketones is intermediate between that of alcohols and that of ethers. The applicability of eq. (1) for the correlation of $D_{AM}/K\delta$ data for alcohols has been established with respect to both polyamide⁸ and cellulose acetate¹⁵ membranes. The $D_{AM}/K\delta$ data for ethers and ketones have been successfully correlated on the basis of eqs. (2) and (3), respectively, for cellulose acetate membranes⁹; the possibility of developing similar correlations with respect to polyamide membranes was hence tested in this work. The polar ($\Sigma \sigma^*$) and steric (ΣE_s) parameters for all the ether, ketone, and aldehyde solutes tested are included in Table II.

The $D_{AM}/K\delta$ data obtained for different ethers with six different film samples (polyamide membranes) were subjected to least-squares analysis for correlation in terms of eq. (2) which involves only the steric parameter ΣE_s with respect to the solutes. Figure 1 illustrates the plots of ΣE_s versus $\ln (D_{AM}/K\delta)$ for three of these films; the correlations obtained with the other films tested were similar. Figure 1 includes both the experimental data and the corresponding straight lines for the least-squares fit of such data with respect to each film. The values for the correlation coefficient $R_{\Sigma E_s}$ obtained from the least-squares analysis of data were 0.94 and higher for all the films tested, indicating that the values of $D_{AM}/K\delta$ for the ethers considered are well represented by the linear correlation expressed by eq. (2). The values of δ^* and $\ln C^*$ for each film can be obtained

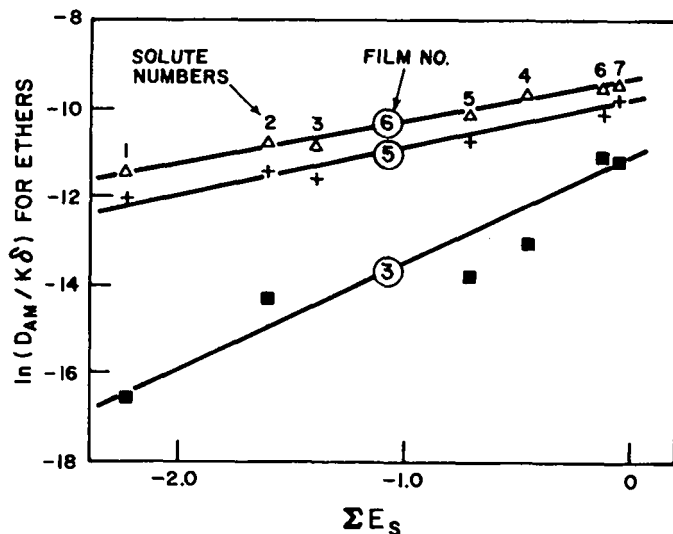


Fig. 1. ΣE_s vs. $\ln(D_{AM}/K\delta)$ correlation for ethers at 250 psig. Solute numbers same as in Table II: (■+Δ) experimental data; (—) least-squares straight line.

from the slope and intercept of the corresponding least-squares straight lines, and the above values are different for different films made of the same material.

The $D_{AM}/K\delta$ data obtained for the ketone solutes with the above polyamide membranes were subjected to multiple regression analysis¹⁶ for correlation in terms of eq. (3) involving both polar ($\Sigma\sigma^*$) and steric (ΣE_s) parameters. The results obtained with three membranes are illustrated in Figure 2, which gives the correlations of $\ln(D_{AM}/K\delta)$ versus $(\rho^*\Sigma\sigma^* + \delta^*\Sigma E_s + \ln C^*)$. Figure 2 includes both the experimental data and the straight lines representing them in terms of eq. (3); the correlations obtained with the other membranes were similar. The values for the coefficients of determination obtained from regression analysis with respect to the polar parameter (i.e., $R^2_{\Sigma\sigma^*}$) were in the range 0.061 to 0.181, and those with respect to the steric parameter (i.e., $R^2_{\Sigma E_s}$) were in the range 0.783 to 0.900 with an average value of 0.97 for the sum $R^2_{\Sigma\sigma^*} + R^2_{\Sigma E_s}$. These results show that both polar and steric parameters govern solute separation in reverse osmosis, and hence it is appropriate to express $D_{AM}/K\delta$ for the ketone solutes by the linear correlation given by eq. (3); the results also show that the governing influence of the steric parameter is significantly more than that of the polar parameter.

For cellulose acetate membranes, the $D_{AM}/K\delta$ data obtained for the different aldehyde solutes were correlated satisfactorily in terms of eq. (1) involving only the polar parameter for the solute⁹; such correlation, however, proved unsatisfactory for the data obtained with the polyamide membranes used in this work. Therefore, the latter data also were subjected to multiple regression analysis for correlation in terms of eq. (3) involving both polar and steric parameters. The results obtained with three membranes are illustrated in Figure 3, which gives the correlation of $\ln(D_{AM}/K\delta)$ versus $(\rho^*\Sigma\sigma^* + \delta^*\Sigma E_s + \ln C^*)$ for each film. Figure 3 includes both the experimental data and the straight lines representing them in terms of eq. (3); the correlations obtained with the other films tested were similar. The values obtained for $R^2_{\Sigma\sigma^*}$ in the regression analy-

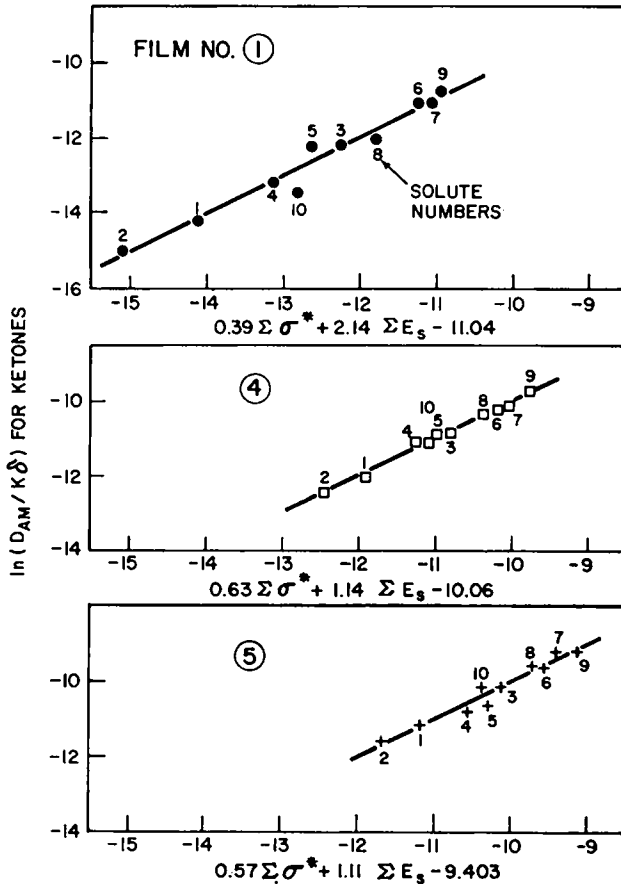


Fig. 2. ($\rho^* \Sigma \sigma^* + \delta^* \Sigma E_s + \ln C^*$) vs. $\ln (D_{AM}/K\delta)$ correlation for ketones at 250 psig. Solute numbers same as in Table II: (●□+) experimental data; (—) linear correlation by multiple regression analysis.

sis were in the range 0.103 to 0.153, and those for $R^2_{\Sigma E_s}$ were in the range of 0.675 to 0.789 with an average value of 0.86 for the sum $R^2_{\Sigma \sigma^*} + R^2_{\Sigma E_s}$. These data show that both polar and steric effects govern reverse osmosis separations of aldehydes using polyamide membranes. Further, the somewhat low value for the sum $R^2_{\Sigma \sigma^*} + R^2_{\Sigma E_s}$ indicates that the nonpolar parameter for the solute may also have a significant influence on the separation of aldehyde solutes; however, the number of solutes involved in this work is insufficient for a meaningful analysis including all the three (polar, steric, and nonpolar) parameters for the solutes concerned.

Effect of Average Pore Size on Membrane Surface on ρ^* and δ^* . On the basis of the foregoing analysis, the values of ρ^* and δ^* obtained with different films for the ether, ketone, and aldehyde solutes are plotted in Figure 4 as a function of the average pore size on the membrane surface. The latter pore size is expressed arbitrarily in terms of NaCl separation at 250 psig using a 3500-ppm NaCl-H₂O feed solution. A higher value for NaCl separation represents a smaller average size of pores on the membrane surface.

Figure 4 shows that the values of ρ^* are essentially independent of average pore size on membrane surface for both aldehydes and ketones, the value of ρ^*

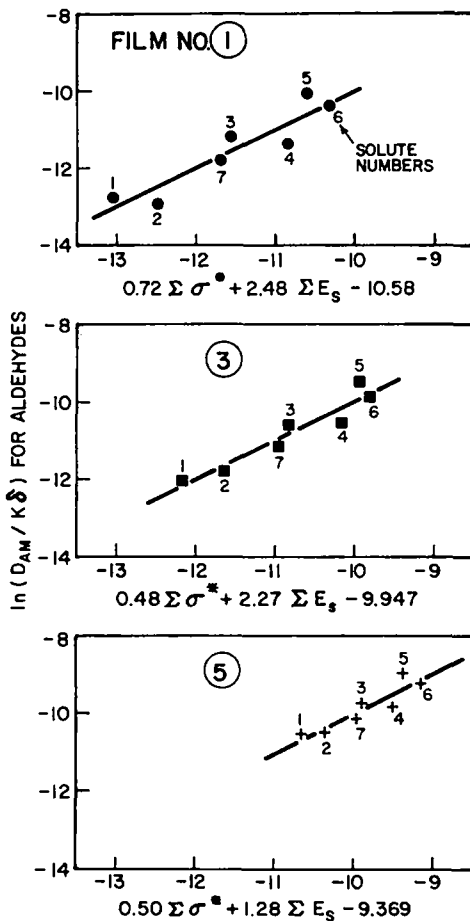


Fig. 3. ($\rho^*\Sigma\sigma^* + \delta^*\Sigma E_s + \ln C^*$) vs. $\ln(D_{AM}/K\delta)$ correlation for aldehydes at 250 psig. Solute numbers same as in Table II: (●■+) experimental data; (—) linear correlation by multiple regression analysis.

for ethers being zero. The values of δ^* are essentially the same for both ethers and ketones, and those for aldehydes are generally higher than the corresponding values for ethers and ketones. For each class of solutes, the values of δ^* remain constant above a particular average pore size on the membrane surface, at which pore size δ^* starts to increase sharply with further decrease in pore size and then tends to reach a limiting value with still further decrease in pore size. The form of correlations of δ^* versus average pore size on the membrane surface appears general for all classes of solutes tested with both polyamide and cellulose acetate membranes. The above form of correlations makes sense. It is only reasonable to expect that when the pore sizes on the membrane surface remain sufficiently big, the change in δ^* should be negligible. Further, when the pore sizes become sufficiently small, δ^* should increase with decrease in pore size, and the above increase in δ^* must reach a limiting value at some small value for the pore size.

It was reported earlier³ that the ρ^* value obtained for alcohol solutes with the above polyamide membranes remained constant at ~ 5.6 up to a particular pore size on the membrane surface, and then increased to a limiting value of 10.1 with further decrease in pore size. This result was attributed to the possible in-

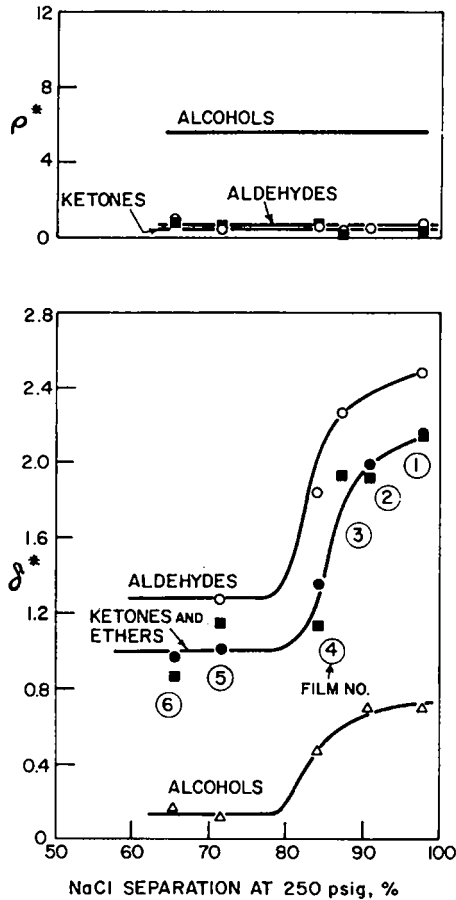


Fig. 4. Effect of pore size on membrane surface on ρ^* and δ^* for alcohols, aldehydes, ketones, and ethers. Film type, aromatic polyamide; operating pressure, 250 psig. Solute numbers same as in Table II: (●) ethers; (○) aldehydes; (■) ketones; (Δ) alcohols.

fluence of steric effects. The $D_{AM}/K\delta$ data for the alcohol solutes reported earlier were reanalyzed on the basis of eq. (3) (which involves both polar and steric parameters for the solute) assuming a constant value of 5.6 for ρ^* . The δ^* values obtained in such analysis are also included in Figure 4, which shows again that the δ^* -versus-pore size correlation for the alcohol solutes is similar to those obtained for the other classes of solutes studied.

Predictability of Solute Separations. The data on polar ($\Sigma\sigma^*$) and steric (ΣE_s) parameters given in Table II and the correlations of ρ^* and δ^* given in Figure 4, together with eqs. (2) and (3), offer a means of predicting $D_{AM}/K\delta$ values, and hence solute separations, for ethers, ketones, and aldehydes. For such predictions, data on sodium chloride separation (under the same conditions reported in Fig. 4) representing the average pore size on the membrane surface, and reverse osmosis data for only one reference solute for each class of compounds are needed. The data on sodium chloride separations are used to find the applicable value of δ^* for ethers, ketones, and aldehydes. The values of ρ^* for the above class of compounds, in the range of $\Sigma\sigma^*$ and ΣE_s values tested in this work, may be taken to be 0, 0.55, and 0.65, respectively. The $D_{AM}/K\delta$

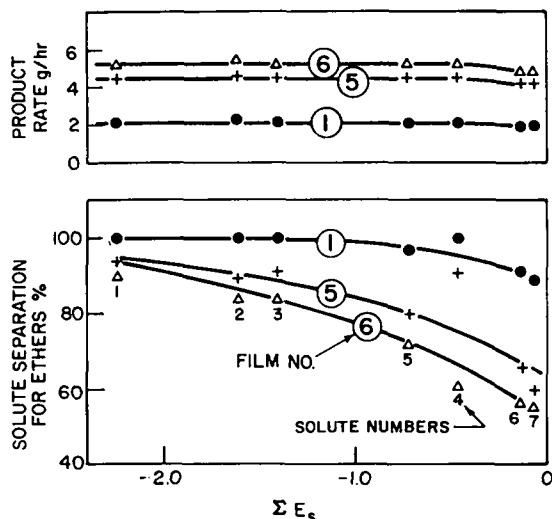


Fig. 5. Effect of ΣE_s on solute separation of ethers for films 1, 5, and 6: (—) predicted; (●+Δ) experimental. Film type, aromatic polyamide; operating pressure, 250 psig; feed concentration, 0.0005 ~ 0.0011 g-mole/l.; flow rate, 400 cc/min; membrane area, 13.2 cm²; solute numbers, same as in Table II.

data for the reference solutes may be used to calculate the values of C^* for the film concerned from eq. (2) applicable for ethers, and eq. (3) applicable for ketones and aldehydes. The values of $D_{AM}/K\delta$ for solutes other than the reference solutes can then be calculated using eq. (2) or eq. (3) and the known values of $\Sigma\sigma^*$ and ΣE_s . The values of $D_{AM}/K\delta$ so calculated may then be used to obtain data on solute separation f , using the applicable value of mass transfer coefficient k on the high-pressure side of the membrane and the following equation as before⁹:

$$D_{AM}/K\delta = \frac{(PR)}{3600 S d} \frac{(1-f)}{f} \left[\exp \left\{ \frac{(PR)}{3600 S k d} \right\} \right]^{-1}. \quad (4)$$

The above technique was used to back calculate solute separations for the ether, ketone, and aldehyde solutes and some of the polyamide membranes used in this work. Phenetole, cyclopentanone, and benzaldehyde were used as the reference solutes in these calculations. The results obtained are given in Figures 5 (ethers), 6 (ketones), and 7 (aldehydes) where the calculated values (solid lines) are compared with the experimental data (points). The satisfactory agreement between calculated and experimental results confirm the validity of the prediction technique and the numerical values of ρ^* and δ^* used in this technique.

Performance of Polyamide and Cellulose Acetate Membranes—A Comparison.

Table IV gives a summary of ρ^* and δ^* values obtained with the polyamide membranes studied in this work and the cellulose acetate membranes studied earlier⁹ with respect to alcohol, aldehyde, ketone, and ether solutes in the given ranges of $\Sigma\sigma^*$ and ΣE_s . The results show that while ρ^* was zero for both types of membranes with respect to ethers, the values of ρ^* were generally much lower for the polyamide membranes than those for the cellulose acetate membranes with respect to ketones, aldehydes, and alcohols. This lesser dependence of membrane performance on the polar parameter $\Sigma\sigma^*$ for solutes indicates that

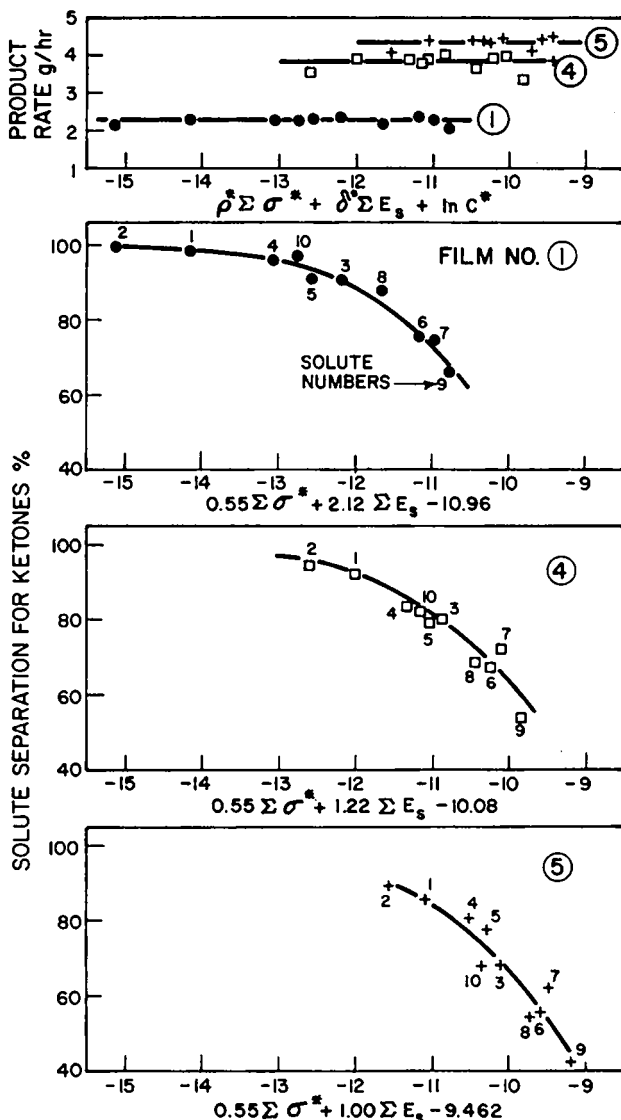


Fig. 6. Effect of $(\rho^* \Sigma \sigma^* + \delta^* \Sigma E_s + \ln C^*)$ on solute separation of ketones for films 1, 4, and 5: (—) predicted; (\bullet +) experimental. Film type, aromatic polyamide; operating pressure, 250 psig; feed concentration, 0.0006 ~ 0.0026 g-mole/l.; flow rate, 400 cc/min; membrane area, 13.2 cm²; solute numbers, same as in Table II.

the polyamide membrane material itself is less polar than the cellulose acetate membrane material. This aspect of the subject will be discussed later.

Table IV also shows that δ^* values for the ethers are in the same range for both polyamide and cellulose acetate membranes; and for ketones, aldehydes, and alcohols, the δ^* values for the polyamide membranes are significantly higher than those obtained for the cellulose acetate membranes. Since an increase in δ^* is generally associated with a decrease in ρ^* , the relatively higher values of δ^* obtained for polyamide membranes are attributable to their lesser polar character.

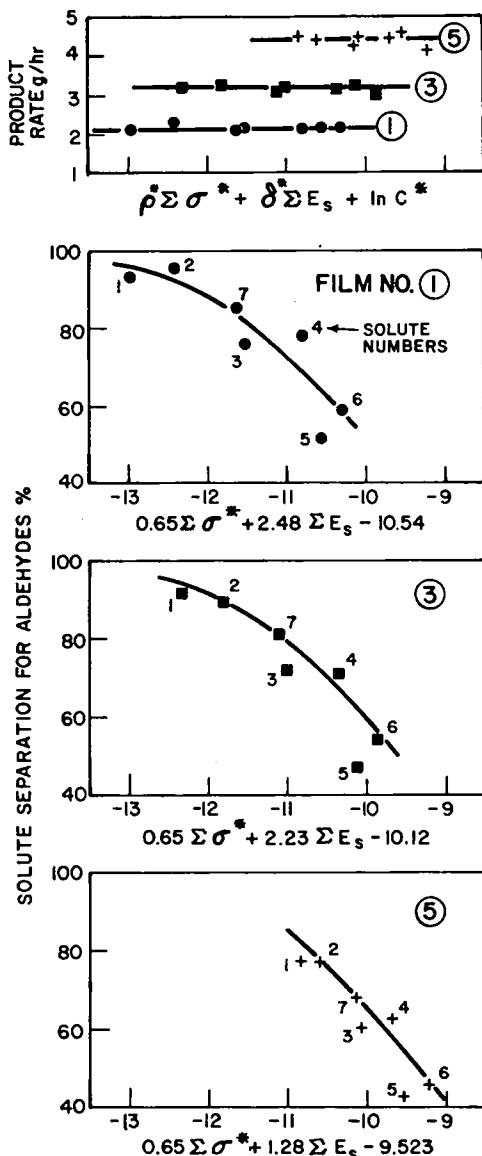


Fig. 7. Effect of $(\rho^* \Sigma \sigma^* + \delta^* \Sigma E_s + \ln C^*)$ on solute separation of aldehydes for films 1, 3, and 5: (—) predicted; (●■+) experimental. Film type, aromatic polyamide; operating pressure, 250 psig; feed concentration, 0.0009 ~ 0.0030 g-mole/l.; flow rate, 400 cc/min; membrane area, 13.2 cm²; solute numbers, same as in Table II.

A comparison of data on solute separations obtained with a polyamide membrane and a cellulose acetate membrane has meaning only if the average pore size on the membrane surface is the same for both membranes and the experimental conditions used are identical. While the latter requirement can be ensured, the former one cannot be so ensured because there is no direct way by which one can compare pore sizes on membrane surfaces at least with respect to the type of membranes used in this and the previous work.⁹ Therefore, one must look for some indirect method for ensuring that the average pore size on

TABLE IV
 ρ^* and δ^* Values for Cellulose Acetate and Polyamide Membranes

Polar functional group	$\Sigma\sigma^*$ range	ΣE_s range	Cellulose acetate		Polyamide		$\frac{(\rho^*)_{PA}}{(\rho^*)_{CA}}$
			ρ^*	δ^*	ρ^*	δ^*	
Alcohols	-0.30 to 0.0 ^a	-1.54 to 0.0 ^b	15.5	0	5.6	0.16 to 0.70	0.36
Aldehydes	-0.20 to 0.60	-0.93 to 0.0	1.7	0	0.65	1.28 to 2.48	0.38
Ketones	-0.40 to 0.60	-1.86 to 0.0	2.5	0.16 to 0.66	0.55	0.86 to 2.14	0.22
Ethers	-0.49 to 0.60	-2.24 to 0.0	0	1.06 to 2.02	0	0.98 to 2.16	—

^a Range for polyamide -0.30 to -0.115.

^b Range for polyamide -1.54 to -0.36.

the membrane surface is not widely different for the membranes chosen in this comparison. A basis for such a method seems available in the δ^* -versus-pore size correlation for ethers for which reverse osmosis separation is shown to be governed entirely by steric effects with respect to both polyamide and cellulose acetate membranes. If it can be assumed that the 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 one can consider that the polyamide film 3 shown in Figure 4 in this work, and the cellulose acetate film 7 shown in Figure 4 in reference 9, had average pore sizes comparable to each other.

Table V gives comparative data on solute separations for a number of ethers, ketones, aldehydes, and alcohols obtained with the above polyamide film 3 and cellulose acetate film 7 under identical experimental conditions. These data show that in all cases tested, solute separations were much higher with the polyamide membrane. If the assumption that the above two films had approximately the same average pore size on the membrane surface is correct, then a fundamental question arises as to why the organic solutes listed in Table II are better separated in reverse osmosis by the polyamide membrane compared to the cellulose acetate membrane. While a complete answer to this question has not yet emerged, it is reasonable to expect that the higher hydrophobicity of the polyamide membrane material with the consequent higher mobility of the preferentially sorbed water through the membrane pores is at least part of this answer.

Separations of Some Monocarboxylic Acids

Nine monocarboxylic acids listed in Table III in the concentration range of 0.0009 to 0.004 g-mole/l. were used in the feed solutions. The dissociation constants K_a for the acids used, expressed as $pK_a (= -\log K_a)$, were in the range of 5.05 to 2.17, and the acids were partially dissociated in the feed solution. There was practically no change in product rates with respect to each film under the conditions tested. Figure 8 gives the correlations of pK_a versus solute separation for three polyamide membranes. The results obtained were similar to those reported in the literature¹⁰ for cellulose acetate membranes, except that the levels of solute separations obtained with the polyamide membranes used in this work were generally much higher.

TABLE V
Comparison of Solute Separations by Polyamide and Cellulose Acetate
Membranes with Equivalent Pore Size Distribution

No.	Organic solute Name	Solute separation at 250 psig, %	
		Polyamide ^a	Cellulose acetate ^b
<i>Alcohols</i>			
1	<i>t</i> -Butyl alcohol	86.9	80.6
3	<i>s</i> -Butyl alcohol	77.8	48.1
4	Isopropyl alcohol	72.0	43.0
6	<i>n</i> -Butyl alcohol	66.3	20.6
7	Isobutyl alcohol	70.1	45.0
8	<i>n</i> -Propyl alcohol	57.3	19.1
9	Ethyl alcohol	16.7	15.3
10	Methyl alcohol	8.4	1.0
<i>Ethers</i>			
1	<i>t</i> -Butyl isopropyl ether	99.9	86.8
2	<i>t</i> -Butyl ethyl ether	99.0	80.2
3	Diisopropyl ether	99.9	72.1
4	Butyl ethyl ether	96.6	41.2
5	Di- <i>n</i> -propyl ether	98.3	39.1
6	Phenetole	78.6	34.5
7	Anisole	80.3	29.7
<i>Ketones</i>			
1	Diisopropyl ketone	97.1	38.9
2	Diisobutyl ketone	99.0	37.4
3	Cyclopentanone	82.6	25.7
4	Methyl isopropyl ketone	83.0	35.8
5	Methyl isobutyl ketone	88.5	33.1
6	Methyl ethyl ketone	76.6	7.7
7	Acetone	72.6	8.9
8	Benzyl methyl ketone	76.4	—
9	Acetophenone	65.0	—
10	Cyclohexanone	88.6	—
<i>Aldehydes</i>			
1	Isobutyraldehyde	91.4	39.1
2	Isovaleraldehyde	89.4	45.3
3	<i>n</i> -Butyraldehyde	71.9	33.6
4	Propionaldehyde	71.0	29.7
5	Acetaldehyde	46.9	30.8
6	Benzaldehyde	53.8	11.8
7	Hexanal	81.0	—

^a Film 3 specified in Table I of this paper.

^b Film 7 specified in Table II of ref. 9.

Figure 8 shows that solute separations passed through a minimum at pK_a value of ~ 4.8 . The same observation was made earlier¹⁰ with respect to cellulose acetate membranes, and the results were explained on the basis that the hydrogen bonding (basicity) effect was more dominant at pK_a values greater than 4.8, and the dissociation effect was more dominant at pK_a values less than 4.8. While this explanation is also applicable for the results obtained with the polyamide membranes, the latter results are also governed by both the nonpolar effect⁸ and the change in the polar character of the membrane material itself as indicated by the following considerations.

By changing the solute concentration in feed solution from 0.0009 to 0.004 g-mole/l., the degree of dissociation for *o*-chlorobenzoic acid (solute 8) changes

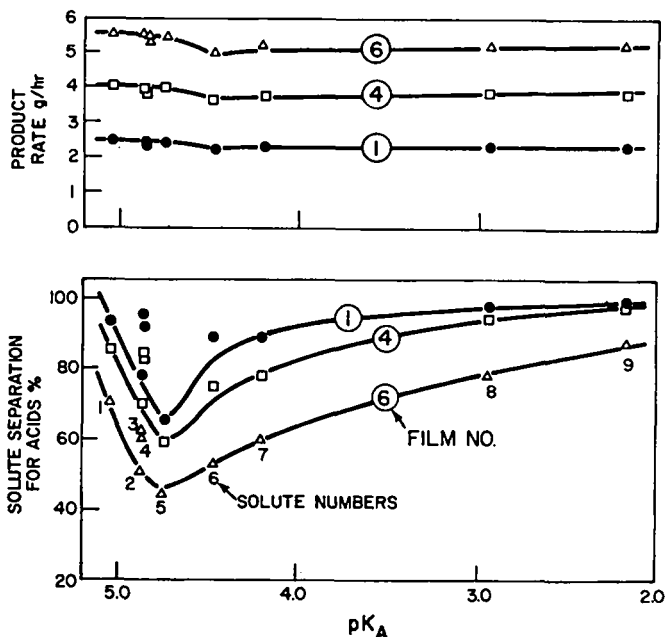


Fig. 8. Effect of pK_a on solute separation of monocarboxylic acids for films 1, 4, and 6. Film type, aromatic polyamide; operating pressure, 250 psig; feed concentration, 0.0009 ~ 0.004 g-mole/l.; flow rate, 400 cc/min; membrane area, 13.2 cm²; solute numbers, same as in Table III.

from 41.0% to 66.0%, and that for *o*-nitrobenzoic acid (solute 9) changes from 70.8% to 89.0%. For all the other acids used, the degree of dissociation is less than 16% in the above feed concentration range. This means that the dissociation effect is not the primary reason for minima in solute separations seen in Figure 8. Also, aromatic polyamides appear capable of undergoing binding interactions with certain cations, in particular H⁺ and Li⁺, and thus acquire some degree of polyelectrolyte character. This effect, well documented for aliphatic polyamides¹⁷ and for some polyamino acids (polypeptides),¹⁸ would *a priori* be expected to confer a net localized positive charge on the membrane surface whose ion-repelling effectiveness would then depend on the pH, ionic strength, and the chemical nature of the solution. Further experimental work and quantitative analysis of data are needed to establish the technique for predicting solute separations when the latter are governed simultaneously by polar, nonpolar, dissociation, and other effects.

Separations of Some Inorganic Salts

A new parameter, called the free-energy parameter, governing reverse osmosis separation of solutes was established earlier with particular reference to ionic solutes.¹¹ This parameter was represented by the symbol $(-\Delta\Delta G/RT)_i$, which has a specific numerical value for each ion depending only on the chemical nature of the solvent and membrane material and independent of the average pore size on the membrane surface. For aqueous solutions and cellulose acetate membranes, the applicable numerical values of $(-\Delta\Delta G/RT)_i$ for several inorganic ions were calculated by using the experimental data on solute transport

parameter for different inorganic salts, and a modified form of the Born expression for the free energy of ion-solvent interaction applied to both the bulk solution phase and the membrane-solution interface where water is preferentially sorbed. The utility of the parameter $(-\Delta\Delta G/RT)_i$ for predicting solute separations in reverse osmosis was illustrated with particular reference to cellulose acetate membranes.¹¹

The object of this part of the work was to obtain similar data on $(-\Delta\Delta G/RT)_i$ for different ions in aqueous solutions with respect to polyamide membranes and to compare such data with the corresponding data applicable for cellulose acetate membranes reported earlier. Nine inorganic solutes were chosen for this purpose; these solutes included the chlorides of Li, Na, K, Rb, and Cs, the other halides of Na, and NaIO₃. Values of $(-\Delta\Delta G/RT)_i$ for Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺ and those for F⁻, Cl⁻, Br⁻, and I⁻ were calculated as before¹¹ using the following relation:

$$\left(-\frac{\Delta\Delta G}{RT}\right)_i = \frac{1}{RT} \left\{ \left(\frac{E_I}{r_i + \Delta_i}\right) - \left(\frac{E_B}{r_i + \Delta_B}\right) \right\} \quad (5)$$

where the subscript i refers to the particular ion under consideration, the subscripts B and I represent the bulk solution phase and interface, respectively, and

$$\Delta\Delta G = (\Delta G_I - \Delta G_B), \text{ kcal/mole}$$

$$\Delta G = -\frac{E}{r_i + \Delta}$$

$$E = \frac{1}{2}N(Z_i e_0)^2 \left(1 - \frac{1}{\epsilon_s}\right)$$

r = ionic radius, Å

Δ = an adjustment to r_i , Å

R = gas constant

T = absolute temperature (298°K)

N = Avogadro number

Z_i = valency of the ion

e_0 = electronic charge

and

ϵ_s = dielectric constant of solvent.

Analysis of data showed that the values of E_B , E_I , Δ_B , and Δ_I were respectively 182.0, 176.8, 0.89, and 0.86 for monatomic monovalent cations, and 120.5, 123.3, -0.20, and -0.18 for monatomic monovalent anions. Equation (5) was used to calculate the values of $(-\Delta\Delta G/RT)_i$ for Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺, and F⁻, Cl⁻, Br⁻, and I⁻ ions. The free-energy parameter for IO₃⁻ was obtained from reverse osmosis data and the relation

$$\ln(D_{AM}/K\delta) = \ln C^* + \Sigma(-\Delta\Delta G/RT)_i \quad (6)$$

along with the data on $(-\Delta\Delta G/RT)_i$ for Na⁺ and Cl⁻.

The value of the constant $\ln C^*$ in eq. (6) can be obtained from a single set of experimental data for any reference solution system such as NaCl-H₂O. The results of the foregoing analysis are given in Table VI.

Figure 9 gives the experimental solute separation data as a function of ionic radius, obtained with two polyamide membranes. For comparison, the figure

TABLE VI
Free-Energy Parameters for Some Monovalent Ions at 25°C

Ions	Ionic radius, Å	ΔG_B	ΔG_I	$\Delta\Delta G$	$-\Delta\Delta G/RT$
<i>Cation</i>					
Li ⁺	0.60	-122.15	-121.10	1.05	-1.77
Na ⁺	0.95	-98.91	-97.68	1.23	-2.08
K ⁺	1.33	-81.98	-80.73	1.25	-2.11
Rb ⁺	1.48	-76.79	-75.56	1.23	-2.08
Cs ⁺	1.69	-70.54	-69.33	1.21	-2.04
<i>Anion</i>					
F ⁻	1.36	-103.88	-104.49	-0.61	+1.03
Cl ⁻	1.81	-74.84	-75.64	-0.80	+1.35
Br ⁻	1.95	-68.86	-69.66	-0.80	+1.35
I ⁻	2.16	-61.48	-62.27	-0.79	+1.33
IO ₃ ⁻	—	—	—	—	+0.66

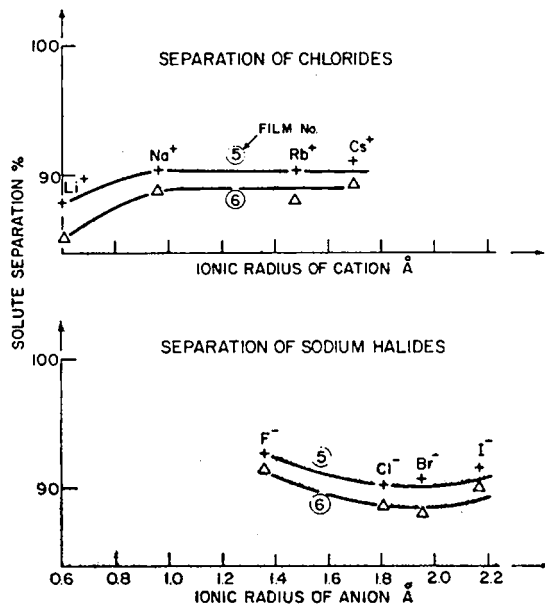


Fig. 9. Effect of ionic radius on solute separation of alkali metal chlorides and sodium halides for films 5 and 6. Film type, aromatic polyamide; operating pressure, 250 psig; feed concentration, 0.0018 ~ 0.0076 g-equivalent/l.; flow rate, 400 cc/min; membrane area, 13.2 cm².

also gives the corresponding solute separation data (solid lines) predicted by the application of eq. (6) using only the experimental data for the system NaCl-H₂O for each film and the numerical values of $(-\Delta\Delta G/RT)_t$ given in Table VI. The excellent agreement between the experimental and predicted data on solute separations confirm the validity of the numerical values of $(-\Delta\Delta G/RT)_t$ given in Table VI for different ions.

It is interesting to compare the values of $(-\Delta\Delta G/RT)_t$ given in Table VI with the corresponding values given earlier¹¹ for cellulose acetate membranes. The results show that the above values for cations are negative and those for anions

are positive for polyamide membranes, whereas the corresponding values have a reverse sign for cellulose acetate membranes. These results mean that the cations are repelled and the anions are attracted at the membrane-solution interface, which in turn suggests that the polyamide membrane surface behaves as if it is positively charged and hence an acid (proton donor). Furthermore, the magnitude of $(-\Delta\Delta G/RT)_i$ for different ions for polyamide membranes is only 20% to 40% of the corresponding value for cellulose acetate membranes, which means that the polar character of polyamide membranes is only 20% to 40% of that of cellulose acetate membranes. This conclusion is consistent with the relatively lower values of ρ^* obtained for polyamide membranes as shown in Table IV.

It is particularly interesting to compare the chemical nature of polyamide and cellulose acetate membrane materials on the basis of the $\Sigma(-\Delta\Delta G/RT)_i$ values for the different inorganic salts in aqueous solutions involving the ions listed in Table VI. Such comparison shows that for any given solute, the value of $\Sigma(-\Delta\Delta G/RT)_i$ for the polyamide membrane material is significantly smaller than the corresponding value for the cellulose acetate membrane material. This result is of enormous significance. Since a lower value for $\Sigma(-\Delta\Delta G/RT)_i$ results in a lower value for $\ln(D_{AM}/K\delta)$ for a given membrane, the above result means that better solute separations can be obtained with polyamide membranes than with cellulose acetate membranes for a given average pore size on the membrane surface. The above result also offers a basis for the choice of membrane materials for different reverse osmosis applications. These aspects of the subject need detailed explorations.

Relative Polar Character of Polyamide and Cellulose Acetate Membranes

On the basis of the sign of the parameter $(-\Delta\Delta G/RT)_i$ for different ions given in Table VI for polyamide membranes and the corresponding data given earlier for cellulose acetate membranes,¹¹ the polar character of the polyamide membrane material may be described as acid (proton donor), and that of cellulose acetate membrane material may be described as base (proton acceptor). It may be recalled^{8,12} that with respect to the separation of alcohols whose σ^* values are far less than σ^* for water, decrease in σ^* (i.e., increase in basicity) for the solute molecule results in an increase in solute separation in the case of both cellulose acetate and polyamide membranes, i.e., ρ^* is positive for both types of membranes. That this result is consistent with the polar (basic) character of the cellulose acetate membrane material is obvious. That the above result is also consistent with the polar (acidic) character of the polyamide membrane material can be seen from the following considerations.

With particular reference to the separation of the alcohol solutes mentioned above, consider the relation expressed by eq. (1). The value of ρ^* may be considered to be the sum of two parts, one part due to the polar character of water (ρ_w^*) and another part due to the polar character of the membrane material (ρ_m^*), so that

$$\rho^* = \rho_w^* + \rho_m^* \quad (7)$$

In view of the highly polar character of water compared to that of either membrane material under consideration, it is reasonable to consider that

$$\rho_w^* \gg \rho_m^* \quad (8)$$

The relatively more basic alcohol solute has a natural tendency to be attracted by the relatively more acidic water in the bulk solution phase. This tendency is enhanced by the basic character of the cellulose acetate membrane, while the same tendency is diminished by the acid character of the polyamide membrane; consequently, ρ_m^* is positive for cellulose acetate and negative for polyamide. Therefore,

$$\frac{(\rho^*)_{PA}}{(\rho^*)_{CA}} = \frac{(\rho_w^* + \rho_m^*)_{PA}}{(\rho_w^* + \rho_m^*)_{CA}} < 1 \quad (9)$$

where the subscripts PA and CA represent the polyamide and cellulose acetate materials, respectively. The above relationship explains why $(\rho^*)_{PA}$ is less than $(\rho^*)_{CA}$ while both $(\rho^*)_{PA}$ and $(\rho^*)_{CA}$ are still positive.

In view of the relatively low electronegativity value for iodine,¹⁹ the IO_3^- ion may be considered to be basic. One may extend the foregoing considerations on the relative polar character of the cellulose acetate and polyamide membrane materials with particular reference to the basicity of the iodate ion. Let the free energy parameter for the ion consist of two parts, one due to the valency of the ion and the other due to its basicity, so that

$$(-\Delta\Delta G/RT)_{\text{IO}_3^-} = (-\Delta\Delta G/RT)_{\text{valence}} + \rho^*(\text{basicity of IO}_3^-).$$

Therefore,

$$\begin{aligned} \frac{\{(-\Delta\Delta G/RT)_{\text{IO}_3^-} - (-\Delta\Delta G/RT)_{\text{valence}}\}_{PA}}{\{(-\Delta\Delta G/RT)_{\text{IO}_3^-} - (-\Delta\Delta G/RT)_{\text{valence}}\}_{CA}} \\ = \frac{(\rho^*)_{PA}(\text{basicity of IO}_3^-)}{(\rho^*)_{CA}(\text{basicity of IO}_3^-)} = \frac{(\rho^*)_{PA}}{(\rho^*)_{CA}}. \end{aligned} \quad (10)$$

No precise value is available for $(\Delta\Delta G/RT)$ for IO_3^- ion due to its valency only; however, as a first approximation, assuming that

$$(-\Delta\Delta G/RT)_{\text{valence}} = (-\Delta\Delta G/RT)_{\text{I}^-} \quad (11)$$

eq. (9) becomes

$$\begin{aligned} \frac{(\rho^*)_{PA}}{(\rho^*)_{CA}} &= \frac{\{(-\Delta\Delta G/RT)_{\text{IO}_3^-} - (-\Delta\Delta G/RT)_{\text{I}^-}\}_{PA}}{\{(-\Delta\Delta G/RT)_{\text{IO}_3^-} - (-\Delta\Delta G/RT)_{\text{I}^-}\}_{CA}} \\ &= \frac{(0.66) - (1.33)}{(-5.69) - (-3.98)} = 0.39 \end{aligned} \quad (12)$$

which shows that the polyamide membrane material is only about 39% as polar as cellulose acetate membrane material. This result is in agreement with the $(\rho^*)_{PA}/(\rho^*)_{CA}$ ratios given in Table IV for alcohol and aldehyde solutes as discussed earlier.

CONCLUSIONS

For the aromatic polyamide membranes used in this work, reverse osmosis separation is essentially a function of the steric parameter for ethers and of both polar and steric parameters for ketones, aldehydes, and alcohols. The polyamide membrane material is much less polar than cellulose acetate, and the polar char-

acter of the polyamide material appears acidic. These characteristics of polyamide membrane materials contribute to their potential for enhanced solute separation in reverse osmosis with respect to both organic and inorganic solutes in aqueous solutions.

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