Reverse Osmosis Separations for Some Alcohols and Phenols in Aqueous Solutions Using Aromatic Polyamide Membranes

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Synopsis

The performance of aromatic polyamide membranes for reverse osmosis separations of eight alcohol and four phenol solutes in dilute aqueous solutions has been studied. The Taft polar parameter σ^* for the solutes studied were in the range of -0.3 to 1.388. Positive solute separations were obtained for each one of the solutes. In the σ^* value range of -0.3 to 0, data on PR/PWP ratio scattered close to 1, and solute separation decreased with increase in σ^*. For the phenol solutes, PR/PWP ratio decreased and solute separation increased with increase in σ^*. The results are interpreted on the following basis. The aromatic polyamides are more nonpolar than cellulose acetates. In the σ^* range of -0.115 to -0.3, solute separation is governed primarily by polar interactions; in this range, solute transport parameter $D_{AM}/K\delta$ is well correlated by the expression $D_{AM}/K\delta = C^* \exp(\rho^*\sigma^*)$. The solute separation for ethyl and methyl alcohol solutes ($\sigma^* = -0.1$ and 0, respectively) is reduced by the nonpolar character of the membrane material. Positive solute separation for each of the phenolic solutes is due to preferential sorption of solute at the membrane–solution interface caused by both the nonpolar character of the membrane material and acidity of the solutes.

INTRODUCTION

Preferential sorption at membrane–solution interface, which is one of the factors governing solute separation in reverse osmosis, is a function of the polymer (membrane material)–solute–solvent interactions and experimental conditions. These interactions arise in general from the ionic, steric, polar, and/or nonpolar character of each one of the above three components in the system involved. The governing significance of these criteria with respect to solutes, in reverse osmosis separations involving aqueous solutions and cellulose acetate membranes, has been discussed in several papers.[1-6] The object of this paper is to initiate similar studies on aromatic polyamide membranes which constitute one of the newer classes of successful membranes presently being developed for reverse osmosis applications.[7-10] The chemical structure of polyamide membranes is significantly different from that of cellulose acetate membranes. While parameters for expressing quantitatively the steric, polar, and nonpolar character of solute molecules have been developed, such parameters for the polymeric

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membrane materials have not yet been developed.   However, from structural considerations of their chain repeat unit and of their model compounds, one may conclude that these polyamides are more nonpolar than cellulose acetates.   Excellent solute separation properties for polyamide membranes with respect to various organic solutes in aqueous solutions have been reported in reverse osmosis experiments.[11]   Consequently, the subject is also one of practical interest.

This work is concerned with the effect of the polar and nonpolar character of some alcohols and phenols in aqueous solutions on their reverse osmosis separations with some laboratory-made aromatic polyamide membranes.

EXPERIMENTAL

Polyamide membranes were made in this laboratory by a variation on the general Loeb-Sourirajan technique.   The material used for membranes was arbitrarily chosen for its relatively high solubility in N,N-dimethylacetamide (DMA) and its inability to develop appreciable long-range crystallographic order.   It was an essentially random copolymer consisting of the following repeat units:
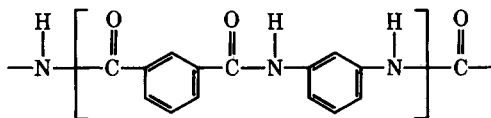
and
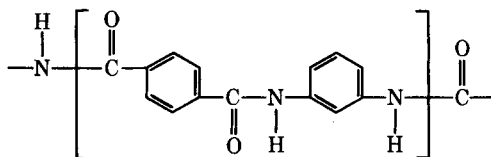
in a molar ratio of 7 to 3, respectively.   The synthesis and characterization of this material are described in detail elsewhere.[12]   The batch used for this work had an intrinsic viscosity of 0.8 dl/g (H_2SO_4) corresponding to an approximate number-average molecular weight ($\bar{M}_n$) of 16,000 (osmometry) and contained aromatic carboxylic acid end groups exclusively.   The composition by weight-% of the film-casting solution was: polymer, 12.5; DMA, 83.7; and anhydrous calcium chloride, 3.8.

The membranes were cast 21 mils thick on flame-cleaned Pyrex glass plates at 95°C in a convection oven and subjected to an evaporation period of 5 to 25 min depending on the pore size being aimed at.   The average pore size on the membrane surface could be reduced by choosing longer drying times.   The gelation medium was ice-cold water.   A final overnight immersion in distilled water at 25°C was given to membranes prior to mounting them in the reverse osmosis cells.   Membranes were initially subjected to a pure water pressure of 300 or 600 psig (as indicated) for 2 hr prior to reverse osmosis experiments.   The details of reverse osmosis experiments were the same as those described earlier.[1]   The permeation
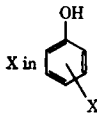
TABLE I
Performance of Polyamide Membranes Used with Aqueous Sodium Chloride Feed Solutions[a]

Film no.	1	2	3	4	5	6	7	8	9	10	11	12
Operating pressure, 250 psig												
Pure water permeability constant A, (g-mole H_2O/cm². sec. atm) $\times 10^6$	0.157	0.133	0.230	0.231	0.338	0.400	0.169	0.151	0.227	0.282	0.318	0.388
Solute transport parameter $(D_{AM}/K\delta)_{NaCl}$, (cm/sec) $\times 10^5$	0.114	0.357	1.10	1.72	4.17	7.63	—	—	—	—	—	—
Solute separation, %	96.9	89.7	86.9	78.1	69.0	57.9	97.3	90.7	87.2	82.2	70.7	62.2
Product rate, g/hr[b]	1.92	1.63	3.05	3.09	4.22	5.55	2.15	1.97	2.95	3.76	4.31	5.25

[a] Films 1–6 pressurized at 300 psig; films 7–12 pressurized at 600 psig. Feed concentration: 3500 ppm of NaCl; mass transfer coefficient k: 22 × 10⁻⁴ cm/sec.

[b] Area of film surface: 13.2 cm².

TABLE II
List of Alcohol and Phenol Solutes Used

	Solute				
No.	Name	Formula	Molecular weight	σ^*	E_s
		R in ROH			
1	t-Butyl alcohol	$t\text{-}C_4H_9$	74.1	−0.300	−1.54
2	s-Butyl alcohol	$s\text{-}C_4H_9$	74.1	−0.210	−1.13
3	Isopropyl alcohol	$i\text{-}C_3H_7$	60.1	−0.190	−0.70
4	n-Butyl alcohol	$n\text{-}C_4H_9$	74.1	−0.130	−0.39
5	Isobutyl alcohol	$i\text{-}C_4H_9$	74.1	−0.200	−0.93
6	n-Propyl alcohol	$n\text{-}C_3H_7$	60.1	−0.115	−0.36
7	Ethyl alcohol	C_2H_5	46.1	−0.100	−0.07
8	Methyl alcohol	CH_3	32.0	0	0

X in

9	p-Cresol	$p\text{-}CH_3$	108.1	0.413	—
10	Phenol	H	94.1	0.600	—
11	p-Chlorophenol	$p\text{-}Cl$	128.6	0.805	—
12	p-Nitrophenol	$p\text{-}NO_2$	139.1	1.388	—

rates obtained from the polyamide membranes used were small (compared to those obtained from the cellulose acetate membranes studied earlier[1]), but they were sufficient for chemical analysis to determine solute separations with which this work was particularly concerned. Some data on the performance of the polyamide membranes used with aqueous sodium chloride feed solutions are given in Table I.

Eight alcohols and four phenols, listed in Table II, were used in this work in single-solute aqueous solution systems in the concentration range of 0.001 to 0.015 g-mole/l. Since the feed concentrations used (89 to 512 ppm) were small, the osmotic pressure effects in reverse osmosis experiments were negligible. The experiments were conducted at ambient laboratory temperature (23° to 25°C), and the reported permeation rates are those corrected to 25°C using the relative viscosity and density data for pure water. The operating pressure was 250 or 500 psig as specified. In all experiments, the terms "product" and "product rates" refer to membrane-permeated solutions. In each experiment, solute separation f as defined by the relation

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

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 alcohols and phenols in the feed and product solutions. Analysis for sodium chloride in aqueous solutions was done using a conductivity bridge.

RESULTS AND DISCUSSION

Polar, Steric, and Nonpolar Parameters

It is desirable to assign numerical values for the polar, steric, and nonpolar character for each solute, so that the effect of each one of these parameters on solute separation in reverse osmosis may be considered.

Polar Parameters. The Taft number σ^*, representing the polar effect of the substituent group in the molecule, is available for all the eight alcohols (solutes 1 to 8) and the phenol (solute 10) from the Taft table.[13] The value of σ^* for water in the same scale is also available from the same table. The values of σ^* for p-cresol, p-chlorophenol, and p-nitrophenol (solutes 9, 11, and 12) in the same scale are, however, not available in the Taft table. They were hence estimated. The method of estimation was based on the general Taft equation and the linear correlation existing between σ^* and pK_a ($= -\log K_a$, where K_a is dissociation equilibrium constant) for the monocarboxylic acid corresponding to the substituent group in the alcohol or phenol. The general Taft equation is given by the relation[13]

$$\log \frac{K_a}{K_{a,0}} = \rho^* \sigma^* \tag{1}$$

where K_a and $K_{a,0}$ represent the equilibrium constants for a given reaction and a standard reaction, respectively; and ρ^* is a proportionality constant. The linear correlation between pK_a and σ^* for some of the substituent groups involved with respect to the solutes studied in this work is illustrated in Figure 1, and this correlation was assumed valid for the substituent groups involved in solutes 9, 11, and 12.
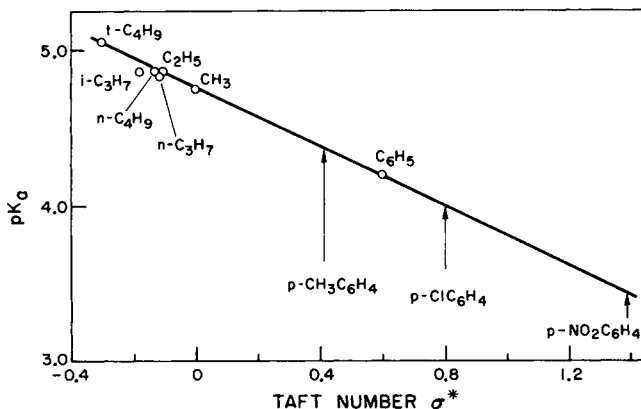

Fig. 1. Plot of σ^* vs. pK_a for monocarboxylic acid corresponding to the substituent group involved.

TABLE III
Nonpolar Parameter for Alcohols and Phenols

| | Solute | | | | | |
No.	Substituent group	Solubility in water, g-mole/l.[a]	Σs^*	$\Sigma s^*_{(sub)}$	Σs^*	$\Sigma s^*_{(H_2O, ref)}$
1	t-C$_4$H$_9$	∞		549	−15	459
2	s-C$_4$H$_9$	1.472	11	589	11	485
3	i-C$_3$H$_7$	∞		456	−108	366
4	n-C$_4$H$_9$	0.972	52	613	52	526
5	i-C$_4$H$_9$	1.159	35	589	35	509
6	n-C$_3$H$_7$	∞		480	−84	390
7	C$_2$H$_5$	∞		347	−217	257
8	CH$_3$	∞		214	−350	124
9	p-CH$_3$C$_6$H$_4$	0.183[b]	220		220	694
10	C$_6$H$_5$	0.670	90		90	564
11	p-ClC$_6$H$_4$	0.211	205		205	679
12	p-NO$_2$C$_6$H$_4$	0.115	266		266	740
Water	H			90	−474	0

[a] From ref. 14.
[b] From ref. 15.

From the known dissociation constants of p-toluic acid (pK_a = 4.36), p-chlorobenzoic acid (pK_a = 3.99), and p-nitrobenzoic acid (pK_a = 3.44), one can directly read the value of σ^* from Figure 1. Or, one can first calculate the value of ρ^* using eq. (1) and known values of σ^* for two substituent groups and the pK_a values of the corresponding monocarboxylic acids. The value of ρ^* so calculated (0.944 in this case) can then be used to calculate the required value of σ^* using eq. (1) and the data (σ^* and pK_a) for any reference substituent group and the corresponding monocarboxylic acid. The values of σ^* thus calculated for p-CH$_3$C$_6$H$_4$, p-ClC$_6$H$_4$, and p-NO$_2$C$_6$H$_4$ were 0.413, 0.805, and 1.388, respectively. These data, along with those taken directly from the Taft table for the other substituent groups involved, are included in Table II.

Steric Parameters. The steric parameters E_s for the substituent groups involved in the alcohol solutes 1 to 8 are available from the Taft table,[13] and they are also included in Table II. With respect to the other solutes studied, the values of E_s in the same scale for the substituent groups involved are not available in the literature.

Nonpolar Parameters. The modified Small's number Σs^* is a relative measure of the hydrophobicity or nonpolar character of the organic molecule.[4] Values of Σs^* for a compound can be obtained either from its molar solubility in water or its structural formula. Both these methods were used in this work. Further, a new scale was established to express the nonpolar character of the solute relative to that of pure water whose nonpolar parameter was fixed as zero. The technique used in this work for estimating Σs^* and expressing it relative to the nonpolar character of pure water is illustrated by the data given in Table III.

The linear relationship between Σs^* and log (molar solubility) was illustrated in the earlier paper.[4]   This relationship can be expressed by the equation

$$\Sigma s^* = -230.4 \log \text{(molar solubility)} + 49.6. \tag{2}$$

Finite data on molar solubility for solutes 2, 4, 5, and 9 to 12 are available in the literature,[14,15] and they are listed in column 3 of Table III.   Using eq. (2), the values of Σs^* were calculated for the above solutes, and these values are given in column 4 of Table III.   With respect to solutes 1, 3, 6, 7, and 8 each of whose solubility in water is ∞, eq. (2) is not applicable. However, the value of the modified Small's number for the substituent group alone, $\Sigma s^*_{(sub)}$, in each of these solutes can be calculated from chemical structure by simply adding the appropriate values of s^* given in Table III in reference 4 for the different structural units;   further, such $\Sigma s^*_{(sub)}$ values can be calculated for solutes 2, 4, and 5 also.   The values of $\Sigma s^*_{(sub)}$ so calculated are given in column 5 in Table III.

The values of $\Sigma s^* - \Sigma s^*_{(sub)}$ may now be considered as the s^* value for the structural unit —OH;   the data for solutes 2, 4, and 5 yield the values of -578, -561, and -554, respectively, for s^* for the structural unit —OH. Taking the average of the above three values, s^* for —OH is -564.   Using this value, Σs^* values for solutes 1, 3, 6, 7, and 8 were calculated from the relation

$$\Sigma s^* = \Sigma s^*_{(sub)} - 564. \tag{3}$$

The values of Σs^* so calculated are included in column 6 in Table III.   On the basis of eq. (3) and the s^* value of 90 for hydrogen,[4] the Σs^* value for pure water is calculated to be -474.   The nonpolar parameter for each solute relative to pure water, $\Sigma s^*_{(H_2O,ref)}$, can then be obtained from the relation

$$\Sigma s^*_{(H_2O,ref)} = \Sigma s^* + 474. \tag{4}$$

The values of $\Sigma s^*_{(H_2O,ref)}$ so calculated are given in the last column in Table III.

Correlations of Reverse Osmosis Data

Polar and Nonpolar Interactions.   Figure 2 gives the correlations of σ^* versus solute separation and PR/PWP ratio for three film samples.   The correlations are similar for all the three films.   Positive separations were obtained for each of the solutes studied in this work.   In σ^* value range of -0.3 to 0, the data on PR/PWP ratio scattered close to 1, and solute separation decreased with increase in σ^*.   For σ^* values higher than that of pure water (0.49), solute separation increased, and PR/PWP ratio decreased significantly with increase in σ^*.   These results are understandable on the following basis.   Positive solute separations for alcohols 1 to 8 are due to their lower Taft numbers (lower acidity or higher basicity) compared to the Taft number for water;   therefore, in each of the systems involving
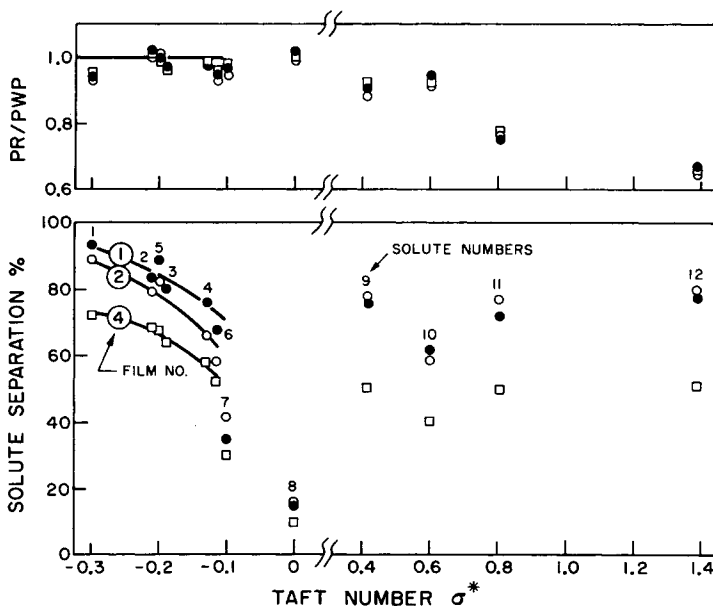
Fig. 2. Plot of σ^* vs. solute separation and PR/PWP ratio for feed solutions involving alcohol and phenol solutes. Operating pressure, 250 psig; solute numbers, same as in Table II.

the above alcohols, water is preferentially sorbed at the membrane–solution interface. Positive solute separations for the phenolic solutes 10, 11, and 12 are due to the preferential sorption of solute at the membrane–solution interface because of the higher Taft number (higher acidity) for the solute compared to that of pure water. These observations are in accordance with the principle enunciated earlier[16] for reverse osmosis separations of alcohols and phenols in aqueous solutions using porous cellulose acetate membranes, namely, that the component in the solution whose σ^* value is higher is preferentially sorbed at the membrane–solution interface.

On the basis of data on sodium chloride separations (Table I), the average pore size on the membrane surface increased in the order film 1 < film 2 < film 4. With respect to the alcohol solutes 1 to 6, solute separations decreased in the same order. This is what one would expect on the basis that polar effect governs solute separation with respect to the above solutes. On the other hand, with respect to ethyl alcohol and methyl alcohol (solutes 7 and 8), solute separations for film 2 were slightly higher than those obtained for film 1, indicating the existence of a maximum in solute separation with decrease in average pore size on the membrane surface. This effect is characteristic of the governing influence of nonpolar interactions at the membrane–solution interface.[4] Consequently, one may conclude that in the case of ethyl and methyl alcohol solutes ($\sigma^* = -0.1$ and 0, respectively), both polar and nonpolar effects govern solute separation for the type of membranes used.

Since σ^* for p-cresol (0.43) is only slightly less than that of water, solute separation for p-cresol in reverse osmosis should be expected to be negligibly
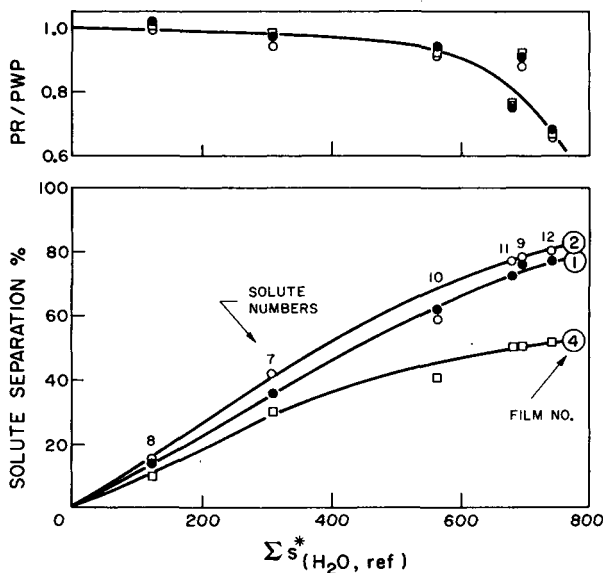
Fig. 3. Plot of $\Sigma s^*_{(H_2O,ref)}$ vs. solute separation and PR/PWP ratio for feed solutions involving ethyl alcohol, methyl alcohol, or phenol solutes. Operating pressure, 250 psig; solute numbers, same as in Table II.

small based on σ^* criterion only. However, experimental results showed high solute separations together with PR/PWP ratios of about 0.9 for all the three film samples. These results indicate that, under the conditions of the experiments, the σ^* effect was insignificant and nonpolar interactions were predominant, so that p-cresol was preferentially sorbed at the membrane–solution interface.

Since both higher acidity and higher hydrophobicity for solute relative to those of water result in preferential sorption for solute at the membrane–solution interface, it is possible that the positive separations obtained for phenol, p-chlorophenol, and p-nitrophenol (solutes 10, 11, and 12) resulted from their hydrophobic character just as well as their acidity. One would then expect a correlation between the nonpolar parameter $\Sigma s^*_{(H_2O,ref)}$ and solute separation for all solutes for which reverse osmosis separations are governed significantly by nonpolar interactions. Figure 3 confirms this expectation.

The correlations shown in Figure 3 are of interest from several points of view. They show that there exists a unique relationship between the nonpolar parameter $\Sigma s^*_{(H_2O,ref)}$ and solute separation in reverse osmosis with respect to solutes 7 to 12 which include ethyl alcohol, methyl alcohol, and p-cresol, whose σ^* values are less than 0.49, and phenol, p-chlorophenol, and p-nitrophenol, whose σ^* values are greater than 0.49. Further, solute separation increased with increase in $\Sigma s^*_{(H_2O,ref)}$ similar to the case of hydrocarbon solutes studied earlier.[4] These data show that reverse osmosis separation with respect to the above solutes was significantly governed by nonpolar interactions at the membrane–solution interface. A similar plot

of data for the other alcohols whose σ^* values were less than -0.1 did not show any correlation.

Consequently, one may conclude that with respect to polyamide membranes in contact with aqueous solutions of alcohols whose σ^* values are less than 0.49, nonpolar interactions at the membrane–solution interface are significant in the σ^* range of up to -0.1. The nonpolar effect is enhanced as the value of σ^* of the alcohol approaches that of water. The effect of the nonpolar interaction is to attract the solute toward the membrane surface. If the σ^* value of the solute is too close to that of water, this attraction may be strong enough to cause preferential sorption of solute at the membrane–solution interface, as in the case of p-cresol. If the σ^* value for the solute is much less than that of water but still in the region of nonpolar interactions, the effect of the latter is simply to reduce the preferential sorption of water at the membrane–solution interface. Consequently, decreased solute separation in reverse osmosis is observed, as in the case of ethyl and methyl alcohol solutes. If the σ^* value for the solute is sufficiently smaller than that of water to be outside the region of nonpolar interactions, as in the case of alcohols 1 to 6, whose σ^* values are less than -0.1, then the preferential sorption of water at the membrane–solution interface is practically unaffected by nonpolar interactions.

The steep decrease in PR/PWP ratio with increase in $\Sigma s^*_{(H_2O,ref)}$, shown in Figure 3, illustrate the increasing pore-blocking effect resulting from increasing preferential sorption of solute at the membrane–solution interface. Similar results have been reported earlier for the case of p-chlorophenol and hydrocarbon solutes in aqueous solutions using porous cellulose acetate membranes.[4]

Effects of Operating Pressure and Average Pore Size on Membrane Surface on Solute Separations. These effects were studied with respect to t-butyl alcohol, ethyl alcohol, and p-chlorophenol (solutes 1, 7, and 11, respectively) chosen for illustration. The operating pressures used were 250 and 500 psig. Six polyamide films whose sodium chloride separations at 250 psig were in the 62% to 97% range were used. The results obtained are shown in Figure 4.

With respect to t-butyl alcohol (solute 1), solute separation increased with increase in operating pressure and decrease in average pore size on the membrane surface. This tendency is characteristic of systems where water is preferentially sorbed at the membrane–solution interface and solute separation is not controlled by nonpolar effects.

With respect to ethyl alcohol (solute 7), solute separation increased with increase in operating pressure for each of the films used. Further, while solute separation passed through a maximum with decrease in pore size on the membrane surface at the operating pressure of 250 psig, the above maximum tended to disappear at 500 psig; at the latter pressure, solute separation simply tended to increase with decrease in average pore size.

The above data illustrate the case where solute separation is controlled both by the preferential sorption of water at the membrane–solution interface due to polar interactions and the simultaneous attraction of solute
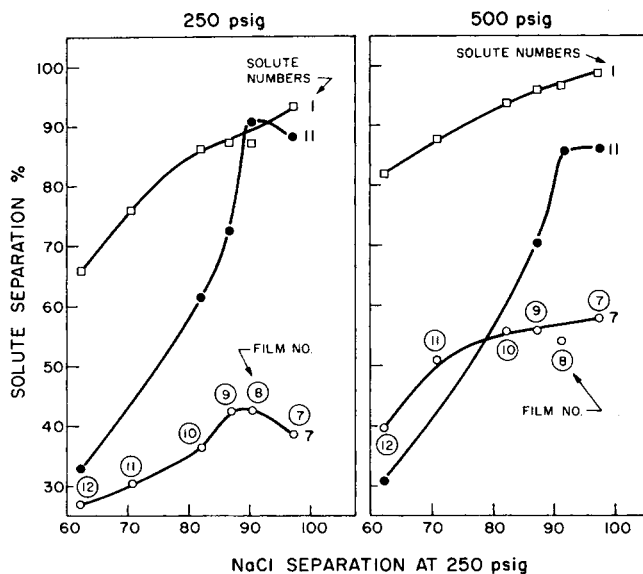
Fig. 4. Effect of operating pressure and average pore size on membrane surface on solute separation. Solute numbers, same as in Table II.

toward the membrane surface due to nonpolar interactions at the membrane–solution interface. The tendency for the maximum in solute separation to disappear at the higher operating pressure is understandable on the basis that the decrease in solute separation caused by nonpolar interactions is compensated by the increase in solute separation caused by the increase in mobility of the preferentially sorbed water at the higher operating pressure.

With respect to p-chlorophenol (solute 11), solute separation decreased with increase in operating pressure; and at each pressure, solute separation showed a tendency to pass through a maximum with decrease in average pore size on the membrane surface. These data are characteristic of preferential sorption of solute at the membrane–solution interface. With a membrane capable of giving 95% separation for sodium chloride, solute separation for p-chlorophenol at 250 psig was about 45% with cellulose acetate membrane[16] compared to ~90% with polyamide membrane. These latter data seem to give a measure of the increased nonpolar character of the polyamide membrane material and its contribution to the reduced mobility of the preferentially sorbed solute at the membrane–solution interface.

Solute Separation versus ΣE_s for Alcohols. Figure 5 gives the correlations of ΣE_s versus solute separation for alcohols 1 to 8 listed in Table II for three polyamide membranes. A decrease in the value of ΣE_s, just as a decrease in the value of σ^*, tends to increase solute separation. The correlations are particularly good for the alcohol solutes 1 to 6 whose σ^* values are less than -0.1 and whose separation data are primarily controlled by polar effects. When the polar effect is sufficiently high, as is generally the case with alcohols, solute separation data can be correlated entirely in
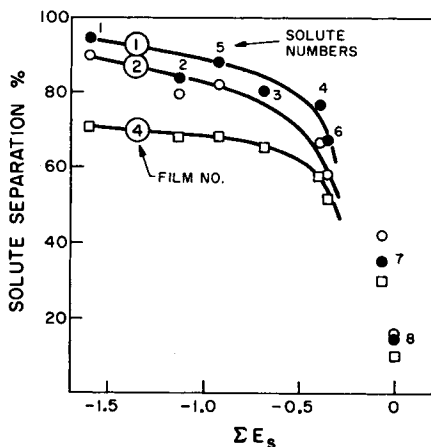
Fig. 5. Correlation of steric parameter with solute separation for alcohols. Operating pressure, 250 psig; solute numbers, same as in Table II.

terms of σ^*, and steric parameter has no independent effect on such correlation.[5] Consequently, one may consider that the correlations shown in Figure 5 simply reflect the σ^*-versus-solute separation correlations given in Figure 2.

Correlation of Solute Transport Parameter and Taft Number for Alcohols. From the reverse osmosis data obtained for the alcohol solutes 1 to 8 with film samples 1, 2, and 4, the values of solute transport parameter $D_{AM}/K\delta$ (in cm/sec) were calculated by the procedure described earlier.[2] The values of ln $(D_{AM}/K\delta)$ were plotted against σ^* values for the alcohols for each film. The results are shown in Figure 6. The $(D_{AM}/K\delta)$ values for alcohols 1 to 6 for each film were then subjected to least-squares analysis for linear correlation in accordance with the relationship

$$\ln (D_{AM}/K\delta) = \rho^*\sigma^* + \ln C^* \qquad (5)$$

where the quantities ρ^* and ln C^* represent, respectively, the slope and intercept for the least-squares straight line. Figure 6 also includes, for comparison, the straight-line correlations for films 3, 5, and 6 obtained from least-squares analysis of similar experimental data. The average value of the correlation coefficient R_{σ^*} obtained from least-squares analysis of all data was 0.97. On the basis of the results given in Figure 6, the following conclusions can be drawn.

The $D_{AM}/K\delta$ data for alcohols 1 to 6 are well represented by the correlation expressed by eq. (5), which has already been shown to be valid for cellulose acetate membranes also. The $D_{AM}/K\delta$ data for EtOH and MeOH fall outside the above correlation, and their actual values were higher than those given by the above correlation. This result is consistant with the conclusion stated earlier that the σ^* values of EtOH and MeOH lie in the region of nonpolar interactions at the membrane–solution interface.

The ρ^* values for the polyamide membranes used showed a tendency to increase with decrease in average pore size on the membrane surface. This
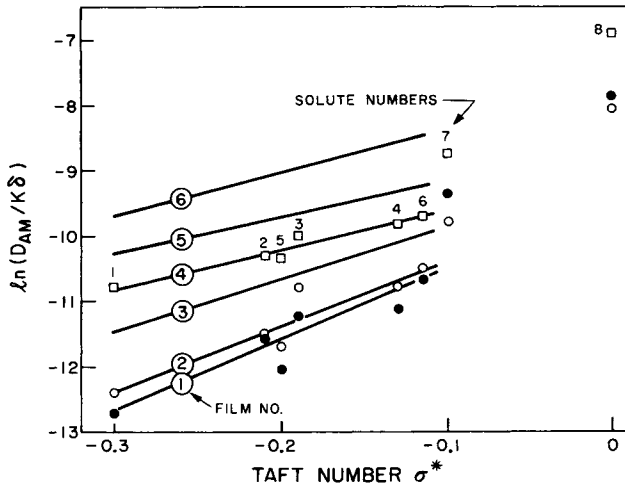
Fig. 6. Plot of σ^* vs. ln $(D_{AM}/K\delta)$ for alcohol solutes at 250 psig: ($\bullet$ $\bigcirc$ $\square$) experimental data; (———) least-squares straight line.
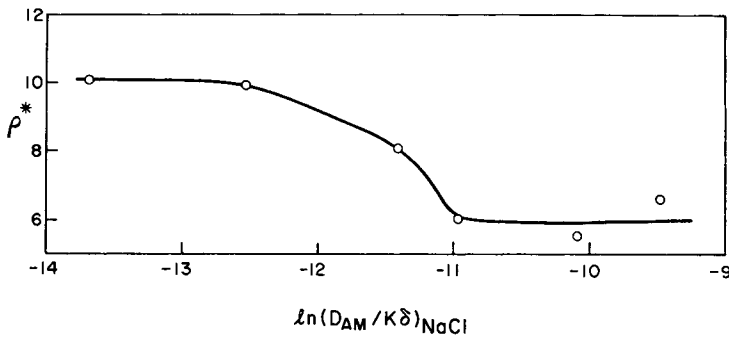

Fig. 7. Effect of average pore size on membrane surface on ρ^* for alcohol solutes in the σ^* range of -0.115 to -0.3. Operating pressure, 250 psig.

tendency is illustrated in Figure 7, which shows ρ^* as a function of the average pore size on membrane surface represented by ln $(D_{AM}/K\delta)$ values for sodium chloride obtained for the membrane studied. Figure 7 shows that when the average pore size is sufficiently big so that ln $(D_{AM}/K\delta)$ for sodium chloride is greater than ~ -11.0, ρ^* is essentially independent of pore size on membrane surface. When the average pore size is smaller, ρ^* tends to increase with decrease in pore size. This result is probably indicative of the influence of steric effect on solute transport when pore size is small. The actual values of ρ^* obtained with the polyamide membranes were in the range of 5.6 to 10.1. These values are considerably smaller than the corresponding value of 15.5 obtained for cellulose acetate membranes for the same range of σ^* values for the alcohol solutes.[5] A lower value of ρ^* for polyamide membranes indicates that solute transport through the latter membranes is less sensitive to changes in the polar character of the alcohols, compared to cellulose acetate membranes studied earlier.

CONCLUSIONS

The aromatic polyamides are relatively more nonpolar than cellulose acetates. The contribution of this property for the higher separation of preferentially sorbed phenolic solutes in aqueous solutions in reverse osmosis has been illustrated by the data on p-chlorophenol. With a membrane capable of giving $\sim$95% separation for sodium chloride, solute separation of t-butyl alcohol at 250 psig was about 80% with cellulose acetate membrane,[1] whereas it was over 90% with the polyamide membrane.

There are at least two possible reasons for this result: (i) increased mobility of the preferentially sorbed water at the membrane–solution interface due to higher hydrophobicity of the membrane material, and (ii) a higher basicity for the polar part of the membrane material. Both these possibilities appear reasonable. Consequently, where reverse osmosis separation is due to preferential sorption of water or solute at the membrane–solution interface, the chemical nature of the aromatic polyamide membrane material tends to enhance solute separation for alcohols and phenols by virtue of both its nonpolar (hydrophobic) and polar (basic) properties. This conclusion is of far-reaching significance. It calls for extensive investigations on all aspects of polyamide membranes for reverse osmosis, and it also offers guidelines for the choice of other membrane materials for different reverse osmosis applications.

References

1. T. Matsuura and S. Sourirajan, *J. Appl. Polym. Sci.*, **15**, 2905 (1971).
2. T. Matsuura and S. Sourirajan, *J. Appl. Polym. Sci.*, **17**, 1043 (1973).
3. T. Matsuura and S. Sourirajan, *J. Appl. Polym. Sci.*, **17**, 3661 (1973).
4. T. Matsuura and S. Sourirajan, *J. Appl. Polym. Sci.*, **17**, 3683 (1973).
5. T. Matsuura, M. E. Bednas, J. M. Dickson, and S. Sourirajan, *J. Appl. Polym. Sci.*, **18**, 2829 (1974).
6. T. Matsuura and S. Sourirajan, *J. Appl. Polym. Sci.*, **18**, 3593 (1974).
7. J. W. Richter and H. H. Hoehn, U.S. Pat. 3,567,632 (1971).
8. R. McKinney, Jr. and J. H. Rhodes, *Macromolecules*, **4**, 633 (1971).
9. R. McKinney, Jr., *Separation and Purification Methods*, **1**, 31 (1972).
10. R. McKinney, Jr., W. L. Hofferbert, and J. A. Carden, Research and Development Progress Report No. 886, Office of Saline Water, U.S. Department of the Interior, Washington, D.C., 1973.
11. E. S. K. Chian and H. H. P. Fang, Evaluation of New Reverse Osmosis Membranes for the Separation of Toxic Compounds from Water, paper presented at the 75th National Meeting of A.I.Ch.E., Detroit, Michigan, June 3–6, 1973.
12. P. Blais, D. J. Carlsson, L. H. Gan, T. Suprunchuk, and D. M. Wiles, *Macromolecules*, in press.
13. R. W. Taft, Jr., in *Steric Effects in Organic Chemistry*, M. S. Newman, Ed., Wiley, New York, 1956, pp. 556–675.
14. *Handbook of Chemistry and Physics*, C. H. Hodgman, R. C. Weast, and S. M. Selby, Ed., 43rd ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1961–62, pp. 764–1303.
15. H. Stephen and T. Stephen, Ed., *Solubility of Inorganic and Organic Compounds*, Vol. 1, Binary System, Part I, Pergamon Press, London, 1963, p. 479.
16. T. Matsuura and S. Sourirajan, *J. Appl. Polym. Sci.*, **16**, 2531 (1972).