Polar and Steric Effects in Reverse Osmosis

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Synopsis

The effects of polar parameter $\Sigma\sigma^*$ and steric parameter ΣE_s on reverse osmosis separations of alcohols, aldehydes, ketones, and ethers (noncyclic) in aqueous solutions involving single solute systems and porous cellulose acetate membranes are discussed. The least-squares and multiple-regression analyses of solute transport parameter data show that the separation of aldehydes, just as that of alcohols, is predominantly a function of $\Sigma\sigma^*$, and that of ethers is predominantly a function of ΣE_s, whereas that of ketones is best represented as a function of both $\Sigma\sigma^*$ and ΣE_s. The results also indicate that even where water is preferentially sorbed at the membrane solution interface, solute separation in reverse osmosis is affected by the nonpolar character of the solute molecule. A general expression for solute transport parameter in reverse osmosis is presented for further study.

INTRODUCTION

The effect of the polar parameter σ^* (Taft number) on reverse osmosis separations of alcohols, aldehydes, ketones, and noncyclic ethers in single solute aqueous solution systems using Loeb-Sourirajan-type porous cellulose acetate membranes has been discussed.[1-4] This paper is concerned with both polar and steric effects on such separations. For the purpose of this paper, the steric parameter E_s given by Taft[5] is used.

The definition, significance, and limitations of the polar (σ^*) and steric (E_s) parameters are reviewed extensively in the literature.[5,6] It may be recalled that Taft defined

$$\sigma^* = \frac{1}{2.48}\left[\log\left(\frac{k}{k_0}\right)_B - \log\left(\frac{k}{k_0}\right)_A\right] \tag{1}$$

and

$$E_s = \log\left(\frac{k}{k_0}\right)_A \tag{2}$$

where σ^* and E_s are polar and steric substituent constants, respectively; k and k_0 are rate constants for the hydrolysis of RCOOR' and CH_3COOR' respectively; and the subscripts B and A refer, respectively, to alkaline and acid hydrolysis carried out for the same R' under identical experi-

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mental conditions. These definitions are based on the following assumptions: (i) the mechanisms for acidic and alkaline hydrolysis are similar and hence resonance and steric effects essentially cancel out, and (ii) the susceptibility of acidic hydrolysis to polar effects is virtually zero. Even though these assumptions are not always valid,[6] it is useful to consider that the Taft parameters σ^* and E_s represent predominantly the polar and steric effects, respectively, of the substituent group in the molecule.

Consequently, following the form of the Hammett equation discussed earlier, the analogous Taft equation can be written in one of the following forms as shown by Taft[5]:

$$\log (k/k_0) = \rho^* \sigma^* \tag{3}$$

$$\log (k/k_0) = \delta^* E_s \tag{4}$$

or

$$\log (k/k_0) = \rho^* \sigma^* + \delta^* E_s \tag{5}$$

where k and k_0 represent the rate or equilibrium constants for a given reaction and a standard reaction, respectively; σ^* and E_s are polar and steric substituent constants independent of the nature of the reaction; and ρ^* and δ^* are corresponding proportionality constants depending on the nature of the reaction and reaction conditions. Equation (3) may be expected to be applicable where steric effect is small or negligible; and eq. (4), where polar effect is small or negligible; and eq. (5), where both polar and steric effects are not either small or negligible. Further, the additivity principle may be assumed applicable for both polar and steric parameters for purposes of correlation of experimental data.[5-9]

The relevance of $\Sigma\sigma^*$ for reverse osmosis transport has been discussed.[1-4] It has been shown that in small ranges of $\Sigma\sigma^*$ (0 to −0.3, for example), the solute transport parameter $(D_{AM}/K\delta)$ for alcohol and the corresponding $\Sigma\sigma^*$ are related by the expression[4]

$$(D_{AM}/K\delta) = C^* \exp (\rho^*\Sigma\sigma^*). \tag{6}$$

On the basis of eq. (3), one may expect that eq. (6) is applicable where steric effects are small or negligible. Following the form of eqs. 4, 5, and 6, solute transport parameter in reverse osmosis can also be expressed as follows:

$$(D_{AM}/K\delta) = C^* \exp (\delta^*\Sigma E_s) \tag{7}$$

or

$$(D_{AM}/K\delta) = C^* \exp (\rho^*\Sigma\sigma^* + \delta^*\Sigma E_s). \tag{8}$$

Equation (7) may be expected to apply where polar effects are small or negligible, and eq. 8, where both polar and steric effects are not either small or negligible. The object of this paper is to investigate the applicability of eqs. (6), (7), and (8) for reverse osmosis transport of solutes which are less polar than alcohols.

TABLE I
Physicochemical Data on Solutes Studied

No.	Name	Formula	Mol. wt.	Solubility in water $\times 10^3$, g-mole/l.	$D_{AB} \times 10^5$, cm²/sec	$k \times 10^4$, cm/sec	σ^* or $\Sigma\sigma^*$	E_s or ΣE_s	Equivalent $\Sigma\sigma_s^*$
Ethers		R_1, R_2 in R_1-O-R_2							
1	t-Butyl i-propyl ether	t-C$_4$H$_9$, i-C$_3$H$_7$	116.2	2.26[a]	0.765	13.23	−0.490	−2.24	659
2	t-Butyl ethyl ether	t-C$_4$H$_9$, C$_2$H$_5$	102.2	27.5[a]	0.831	13.98	−0.400	−1.61	409
3	Diisopropyl ether	i-C$_3$H$_7$, i-C$_3$H$_7$	102.2	19.6	0.831	13.98	−0.380	−1.40	443
4	Butyl ethyl ether	n-C$_4$H$_9$, C$_2$H$_5$	102.2	13.1[a]	0.831	13.98	−0.230	−0.46	483
5	Dipropyl ether	n-C$_3$H$_7$, n-C$_3$H$_7$	102.2	24.5	0.831	13.98	−0.230	−0.72	421
6	Phenetole	C$_2$H$_5$, C$_6$H$_5$	122.2	2.68[a]	0.832	13.99	+0.500	−0.13	644
7	Anisole	CH$_3$, C$_6$H$_5$	108.1	7.97[a]	0.919	14.96	+0.600	−0.06	535
Aldehydes		R in RCHO							
1	i-Butyraldehyde	i-C$_3$H$_7$	72.1	1526	1.091	16.78	−0.190	−0.70	7
2	i-Valeraldehyde	i-C$_4$H$_9$	86.1	53.7[a]	0.964	15.44	−0.200	−0.93	342
3	n-Butyraldehyde	n-C$_3$H$_7$	72.1	513	1.091	16.78	−0.115	−0.36	116
4	Propionaldehyde	C$_2$H$_5$	58.1	3442	1.277	18.65	−0.100	−0.07	−74
5	Acetaldehyde	CH$_3$	44.1	∞	1.582	21.53	0	0	−∞
6	Benzaldehyde	C$_6$H$_5$	106.1	31.1	0.965	15.45	+0.60	−0.06	397
Ketones		R_1, R_2 in $R_1-\overset{\displaystyle O}{\overset{\|}{C}}-R_2$							
1	Diisopropyl ketone	i-C$_3$H$_7$, i-C$_3$H$_7$	114.2	17.38[a]	0.796	13.59	−0.380	−1.40	455
2	Diisobutyl ketone	i-C$_4$H$_9$, i-C$_4$H$_9$	142.2	7.31[a]	0.689	12.33	−0.400	−1.86	542
3	Cyclopentanone	cyclo-C$_4$H$_8$	84.1	—	0.984	15.66	−0.250	−0.51	—
4	Methyl isopropyl ketone	CH$_3$, i-C$_3$H$_7$	86.1	197[a]	0.964	15.44	−0.190	−0.70	212
5	Methyl isobutyl ketone	CH$_3$, i-C$_4$H$_9$	100.2	190	0.869	14.41	−0.200	−0.93	216
6	Methyl ethyl ketone	CH$_3$, C$_2$H$_5$	72.1	4896	1.091	16.78	−0.100	−0.07	−109
7	Acetone	CH$_3$, CH$_3$	58.1	∞	1.277	18.65	0	0	−∞
8	Benzyl methyl ketone	C$_6$H$_5$(CH$_2$), CH$_3$	134.2	29.2[a]	0.756	13.12	+0.215	−0.38	403
9	Acetophenone	C$_6$H$_5$, CH$_3$	120.1	24.8[a]	0.818	13.84	+0.600	−0.06	420

[a] Measured in this work; others are from ref. 18.

EXPERIMENTAL

Reverse Osmosis Experiments

Seven noncyclic ethers, six aldehydes, and nine ketones listed in Table I (along with some of their physicochemical data pertinent to this work) were used in this work in single solute systems. The apparatus and experimental procedure used were the same as those reported earlier.[1-4,10a] Batch 316(10/30)-type cellulose acetate membranes[11] were used at the operating pressure of 500 psig. The specifications[10b] of membranes used are given in Table II in terms of pure water permeability constant A (in g-mole H_2O/cm²-sec-atm) and solute transport parameter $(D_{AM}/K\delta)$ for sodium chloride (in cm/sec) at 500 psig. Table II also includes solute separation and product rate data for the membranes used at the operating pressure of 500 psig with 1500 ppm NaCl–H_2O feed solutions at feed flow rates corresponding to a mass transfer coefficient of 22×10^{-4} cm/sec on the high-pressure side of the membrane.

The feed concentrations for the organic solutes used were in the range 0.0006 to 0.0098 g-mole/l. In most cases, the solute concentration in the feed was ~200 ppm. The osmotic pressure of the feed solution was practically negligible in all cases.

All experiments were of the short run type, and they were carried out at the laboratory temperature (23–25°C). The reported product 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. The fraction solute separation in each case was obtained from the relation

$$ f = \left[\frac{\text{solute ppm in feed} - \text{solute ppm in product}}{\text{solute ppm in feed}} \right]. $$

In each experiment, the pure water premeation rate (PWP) and product rate (PR) in grams per hour per given area of film surface (13.2 cm² in all cases in this work) and solute separation were determined at the operating

TABLE II
Film Specifications[a]

	Film 7	Film 8	Film 9	Film 11	Film 12
Pure water permeability constant A, $\dfrac{\text{g-mole } H_2O}{\text{cm}^2\text{-sec-atm}} \times 10^6$	1.58	2.04	2.58	3.25	5.87
Solute transport parameter $(D_{AM}/K\delta)_{\text{NaCl}}$, (cm/sec) $\times 10^5$	3.76	6.31	8.27	25.06	124.4
Solute separation, %	96.0	93.9	92.3	79.3	48.5
Product rate, g/hr	44.4	56.9	71.5	89.5	162.4

[a] Operating pressure, 500 psig; area of film surface 13.2 cm²; feed solution, 1500 ppm NaCl–H_2O.

conditions. The solute numbers given in all figures in this paper are the same as those given in Table I with respect to each group of compounds.

Analysis

The concentrations of organic solutes were determined by gas-chromatographic analysis. A 100-ft-long, 0.020-in.-i.d. support-coated open tubular (S.C.O.T.) column containing Carbowax 1540 was employed. It was used in a Perkin-Elmer Model 154 gas chromatograph at temperatures of 50°, 75°, or 85°C. Helium carrier gas pressure was 10 psig, and flow rate was 10 ml/min at 50°C. Sample sizes were between 1 and 2 microliters, and a split ratio of 3.5 was used. The entire effluent from the column passed into a hydrogen flame ionization detector.

A broad water peak interfered in analysis in a few cases. In such cases, a 4-in.-long, $1/_4$-in.-o.d. forecolumn containing 10% diglycerol on 60–80 mesh Neutraport was employed. The inlet and forecolumn, maintained at 130°C, were attached to the gas sampling valve and used for only 20 to 30 sec after injection and then bypassed. During this time, the components of interest passed through the forecolumn and onto the analyzing column while water was retained at least 40 sec to over 2 min. The forecolumn was then back-flushed by an auxiliary carrier gas line during the completion of the chromatogram.

Methyl ethyl ketone or acetone was used as the internal standard. Between 10 and 40 microliters of a stock solution (7.5% in water) was added to the sample in a 10-ml volumetric flask and made up to volume with the sample. The resultant concentration of internal standard was 75 to 300 ppm.

Peak areas were measured with a voltage-to-frequency converter (Dymec, Model 2210) connected to a scaler (Phillips, Model PW4231) and printer (Victor). Standard solutions were made up and the internal standard added in the same manner as for the samples. These were run on the same day as the samples and the calibration factors for the components calculated.

The standard deviations were between 1% and 3%; the latter figure was usually associated with the less soluble components.

Solubility Measurements

For the organic solutes studied for which solubility data are not readily available in the literature, such data were determined experimentally as follows. About 5 ml of the solute was added to 100 ml water, and the mixture was stirred vigorously in an Erlenmeyer flask for 1 hr. Then, the mixture was transferred to a separating funnel and left therein until the two phases separated completely, which took 1 to 24 hr. After separation of the aqueous phase from the organic phase, several 20-microliter samples of the aqueous phase were analyzed by a Beckman Total Carbon Analyzer Model 915 for total carbon content, from which the solubility of the organic compound was calculated.

The experimentally determined solubility data and those available in the literature were used to determine the magnitude of the nonpolar parameter for the solute using the molar solubility-versus-modified Small's number (Σs^*) correlation established earlier for hydrocarbons.[12] The nonpolar parameter so determined for the ethers, aldehydes, and ketones studied in this work are designated as "equivalent Σs^*," and they are listed in Table 1.

RESULTS AND DISCUSSION

Estimation of E_s Values

The E_s values for a number of substituent groups (acyl component R) are given by Taft.[5] These values can be used directly wherever applicable. With respect to substituent groups for which E_s values are not listed, a method of estimating the values is called for. One such method, based on an interpolation technique, is illustrated in Figure 1.

Figure 1a is a correlation of E_s of R versus E_s of $(R)_2CH$ as given in the Taft table. For the purpose of this correlation, the substituent groups CH_3, C_2H_5, $n-C_3H_7$, $i-C_4H_9$, and $t-C_4H_9CH_2$ were chosen to represent R. This correlation can be used to obtain E_s value for $(R)_2CH$ if the corresponding value for R is known, or vice versa. For example, the E_s values for $n-C_4H_9$ and $t-C_4H_9$ are -0.39 and -1.54, respectively, from the Taft table. From Figure 1a, the E_s values for $(n-C_4H_9)_2CH$ and $(t-C_4H_9)_2CH$ can be estimated to be -2.13 and -3.00, respectively.

Figure 1b is a correlation of ΣE_s ($= E_s$ for $R_1 + E_s$ for R_2) versus E_s of $\begin{matrix} R_1 \\ R_2 \end{matrix} CH$. For the purpose of this correlation, R_1 and R_2 were represented, respectively, by the pair of groups (CH_3 and CH_3), (C_2H_5, C_2H_5), ($n-C_3H_7$, $n-C_3H_7$), ($i-C_4H_9$, $i-C_4H_9$), ($t-C_4H_9CH_2$, $t-C_4H_9CH_2$), (CH_3, C_2H_5), (CH_3, $t-C_4H_9CH_2$), ($n-C_4H_9$, $n-C_4H_9$), and ($t-C_4H_9$, $t-C_4H_9$). The E_s values for the latter two sets of R_1 and R_2 were obtained from Figure 1a, and those for all the other sets were taken from the Taft table. Figure 1b enables one to estimate ΣE_s from the E_s value of R_1R_2CH, and vice versa. For example, using E_s values of -1.19 for $(CH_3)(C_6H_5)CH$, -1.50 for $(C_2H_5)(C_6H_5)CH$, and -1.76 for $(C_6H_5)_2CH$ given in the Taft table, Figure 1b gives ΣE_s values of -0.07 for (CH_3, C_6H_5), -0.11 for (C_2H_5, C_6H_5), and -0.15 for $(C_6H_5)_2$. Since E_s values for CH_3 ($= 0$) and C_2H_5 ($= -0.07$) are known from the Taft table, the above ΣE_s values yield E_s values of -0.07, -0.04, and -0.075 for C_6H_5; taking an average of the latter values, E_s for C_6H_5 is estimated as -0.06, which is about the same as that for C_2H_5.

Figure 1 is not applicable for cyclo compounds. In this work, E_s for for cyclo-C_4H_9 is approximated as -0.51, which is the value given in the Taft table for cyclo-C_5H_9.

Relative Polar Character of Alcohols, Aldehydes, Ketones, and Ethers

On the basis of experimental heats of varporization data and Flory-Huggins polymer interaction parameter as measured by swelling equilib-
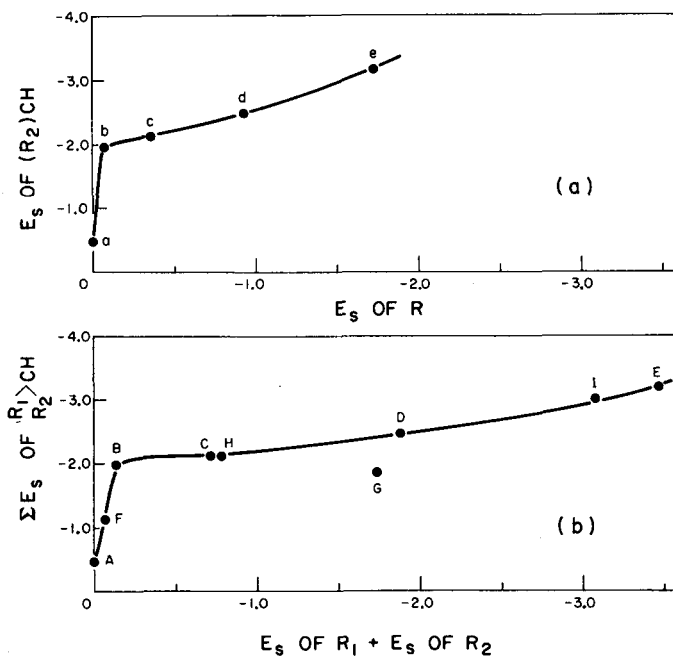
Fig. 1. Estimation of E_s values for different acyl groups. Acyl groups:

	R
a	CH_3
b	C_2H_5
c	$n\text{-}C_3H_7$
d	$i\text{-}C_4H_9$
e	$t\text{-}C_4H_9CH_2$

	R_1	R_2
A	CH_3	CH_3
B	C_2H_5	C_2H_5
C	$n\text{-}C_3H_7$	$n\text{-}C_3H_7$
D	$i\text{-}C_4H_9$	$i\text{-}C_4H_9$
E	$t\text{-}C_4H_9CH_2$	$t\text{-}C_4H_9CH_2$
F	CH_3	C_2H_5
G	CH_3	$t\text{-}C_4H_9CH_2$
H	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$
1	$t\text{-}C_4H_9$	$t\text{-}C_4H_9$

rium, Pinsky[13] gave the following order for the polarity of functional groups: —COOH > —OH > C=O > C—O—C. This order is confirmed by the numerical data given by Diamond and Wright[14] (Table III) on the effect of the polar group on the change in partial molar free energy of solution in water ($\Delta\Delta F_w$). Consequently, one may conclude that, with respect to the polar groups under study in this work, the alcohol group is the most polar and the ether group is the least polar. Therefore, the ap-

TABLE III
Effect of Polar Group on the Change in Partial Molar Free Energy of Solution in Water[a]

Polar group	Partial molar free energy $\Delta\Delta F_w$, cal/mole
$\overset{\overset{\text{O}}{\|}}{-\text{C}}-\text{OH}$	-8600
$-\text{OH}$	-7000
$-\text{NH}_2$	-6600
$-\overset{\overset{\text{H}}{\|}}{\text{C}}=\text{O}$	—
$>\text{C}=\text{O}$	-6100
$-\text{C}\equiv\text{N}$	-5800
$-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{O}-\text{R}$	-5400
$-\text{O}-$	-4000

[a] From ref. 14.

plicability of eqs. (6), (7), and (8) for the reverse osmosis separations of ethers, aldehydes, and ketones was investigated, and the results are discussed below.

Separation of Noncyclic Ethers

Figure 2 illustrates the correlations of ΣE_s and data on solute separation and product rate for two film samples with respect to seven ethers in the ΣE_s range of -0.06 to -2.24. Several aspects of these correlations are significant.

The data cover a wide range of solute separations, and the correlations are similar for both film samples. Hence, the form of correlations has general significance. The ΣE_s-versus-solute separation correlation for ethers (which are the least polar of compounds under study in this work) is similar to the $\Sigma\sigma^*$-versus-solute separation correlation for alcohols (which are the most polar of the compounds under comparison). A decrease in the value of ΣE_s, just as a decrease in the value of $\Sigma\sigma^*$, tends to increase solute separation of ethers. This means that the result of steric effect of solute in reverse osmosis is the same as solute repulsion at the membrane–solution interface. Consequently, an increase in steric effect (i.e., more negative ΣE_s) tends to increase solute separation in reverse osmosis. These results also indicate that eq. (7) is probably applicable for the reverse osmosis separation of ethers, just as eq. (6) is applicable for similar separation of alcohols.

Figure 2 shows that solute separation data for diisopropyl ether for both films do not fall on the correlation lines applicable for the other solutes considered. This observation indicates the need for reassignment of E_s value for i-C$_3$H$_7$ (analogous to the reassignment of σ^* value for i-C$_4$H$_9$ discussed earlier[4]). The value of E_s for i-C$_3$H$_7$ given by Taft is -0.47. Figure 2 shows that a E_s value of -0.70 fits the correlation better with respect to the separations of both diisopropyl ether and t-butyl isopropyl ether.
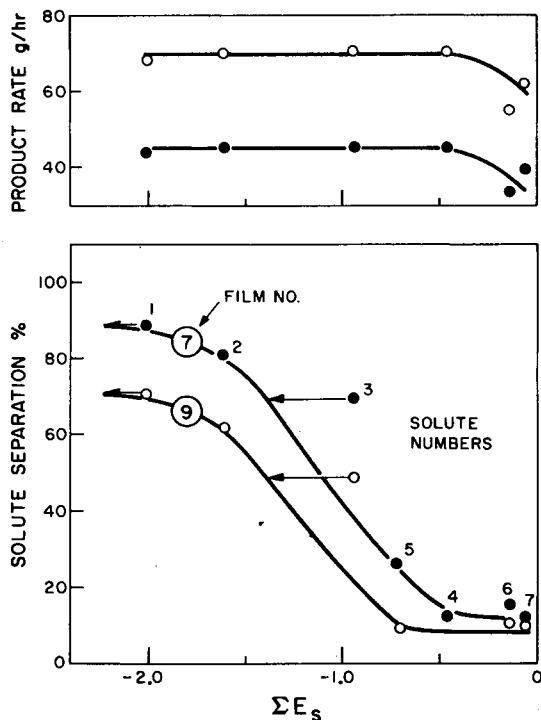
Fig. 2. Effect of ΣE_s on solute separation and product rate for ether–water systems: film type, cellulose acetate (Batch 316); operating pressure, 500 psig; feed concentration, 0.0013 ∼ 0.0075 g-mole/l.; membrane area, 13.2 cm²; solute numbers and calculated k values, same as in Table I for ethers.

Consequently, for purposes of correlation of reverse osmosis data, an E_s value of −0.70 for i-C_3H_7 is used throughout this work. On this basis, the ΣE_s values for diisopropyl ether and t-butyl isopropyl ether are −1.40 and −2.24, respectively.

Except for the systems involving solutions of phenetole and anisole, for all the other solution systems studied the product rates were essentially constant with respect to each film sample. These data showed that in each of the latter cases, water was preferentially sorbed at the membrane–solution interface, and the porous structure of the film samples was unaffected during the experiment.

The solute separation and product rate data for the solution systems involving phenetole and anisole are particularly interesting. In both cases, product rates were significantly lower than those obtained with the other solution systems studied, indicating probable pore-blocking effect during the experiments. The solute separations were low but positive. Comparing the data for phenetole and anisole systems, solute separation was relatively lower and product rate was relatively higher for the latter system. These observations, combined with the facts that ΣE_s values for phenetole
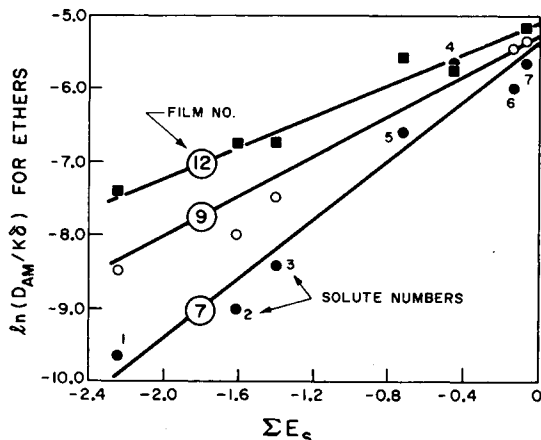
Fig. 3. Plot of ΣE_s vs. ln $(D_{AM}/K\delta)$ for ethers based on experimental data in Fig. 2:
(———) linear correlation by method of least squares; (●) (○) (■) experimental data.

and anisole are very low (−0.13 and −0.06, respectively), $\Sigma\sigma^*$ values are high and positive (0.5 and 0.6, respectively), and equivalent Σs^* values are also high (644 and 535, respectively),[12] indicate that positive separations for the above solutes were due to preferential sorption of solute at the membrane–solution interface and the relatively lower mobility of the preferentially sorbed solute compared to that of water under the experimental conditions used.   Further experimental work is needed to confirm the above conclusion.

In order to investigate the applicability of eqs. (7) and (8) for reverse osmosis transport of ethers, the values for the solute transport parameter $(D_{AM}/K\delta)$ for each ether was then calculated for five different film samples (films 7, 8, 9, 11, and 12) from the experimental solute separation (f) and product rate (PR) data.   The procedure used for this calculation was the same as that used before for alcohols.[4]   For each experiment, the mass transfer coefficient k on the high-pressure side of the membrane was calculated from the relation

$$ k = k_{ref} \left[\frac{D_{AB}}{(D_{AB})_{ref}} \right]^{2/3} \tag{9} $$

where k_{ref} = mass transfer coefficient on the high-pressure side of the membrane for the reference solution system sodium chloride–water, and $(D_{AB})_{ref}$ and D_{AB} refer to diffusivity of sodium chloride and ether, respectively, in water,.   The value of D_{AB} was calculated as before from the empirical equation of Wilke and Chang.[15,16]   The above values of D_{AB} and k for the solutes discussed in this work are included in Table I.   Using the applicable values of k and the experimental f and PR data, the value of $(D_{AM}/K\delta)$ was calculated from the relation

$$ (D_{AM}/K\delta) = \frac{(PR)}{3600\,S\,d} \frac{(1-f)}{f} \left[\exp\left\{ \frac{(PR)}{3600\,S\,k\,d} \right\} \right]^{-1} \tag{10} $$

TABLE IV
Results of Least-Squares and Multiple-Regression Analysis of Reverse Osmosis Data

Class of solutes	Film no.	Number of data considered	Correlation coefficient from least-squares analysis R		Coefficient of determination from regression analysis $R^2_{\Sigma\sigma*}$	Coefficient of determination from regression analysis $R^2_{\Sigma E_s}$
Ethers			$R_{\Sigma E_s}$			
	7	7	0.972		<0.01	
	8	7	0.967		<0.01	
	9	5	0.991			
	11	5	0.964			
	12	6	0.979		0.016	0.943
Aldehydes			$R_{\Sigma\sigma*}$			
	8	9	0.943		0.834	0.064
	9	9	0.941		0.914	0.040
	11	7	0.970		0.898	0.049
Ketones			$R_{\Sigma\sigma*}$	$R_{\Sigma E_s}$		
	7	7	0.951	0.947	0.493	0.441
	8	7	0.919	0.911	0.486	0.383
	9	7	0.941	0.897	0.744	0.147
	11	7	0.897	0.906	0.367	0.476

Class of solutes	Coefficient of determination from least-squares analysis $R^2_{\Sigma\sigma*}$	Coefficient of determination from least-squares analysis $R^2_{\Sigma E_s}$	Multiple coefficient of determination from regression analysis $R^2_{\Sigma\sigma*} + R^2_{\Sigma E_s}$
Ketones	0.904	0.897	0.933
	0.844	0.830	0.868
	0.885	0.805	0.890
	0.804	0.821	0.843

where S = effective membrane area (in cm²) and d = solution density (in g/cm³).

The $(D_{AM}/K\delta)$ data obtained for different ethers with five different film samples were subjected to least-squares analysis for correlation in terms of eq. (7) which involves only the steric parameter ΣE_s with respect to solutes. Figure 3 is a plot of ΣE_s versus ln $(D_{AM}/K\delta)$ for a few representative films; the plot includes both experimental data and the corresponding straight line for a least-squares fit of such data. The values for the correlation coefficient $R_{\Sigma E_s}$ obtained from the least-squares analysis are given in Table IV. The $(D_{AM}/K\delta)$ data obtained for films 7, 8, and 12 were also subjected to multiple-regression analysis[17] for correlation in terms of eq. (8) which involves both polar $(\Sigma\sigma*)$ and steric (ΣE_s) parameters with respect to solutes. The values for the coefficients of determination $R^2_{\Sigma\sigma*}$ and $R^2_{\Sigma E_s}$ obtained from the multiple-regression analysis are also given in Table IV. It may be pointed out that each of the values of $R^2_{\Sigma\sigma*}$ and
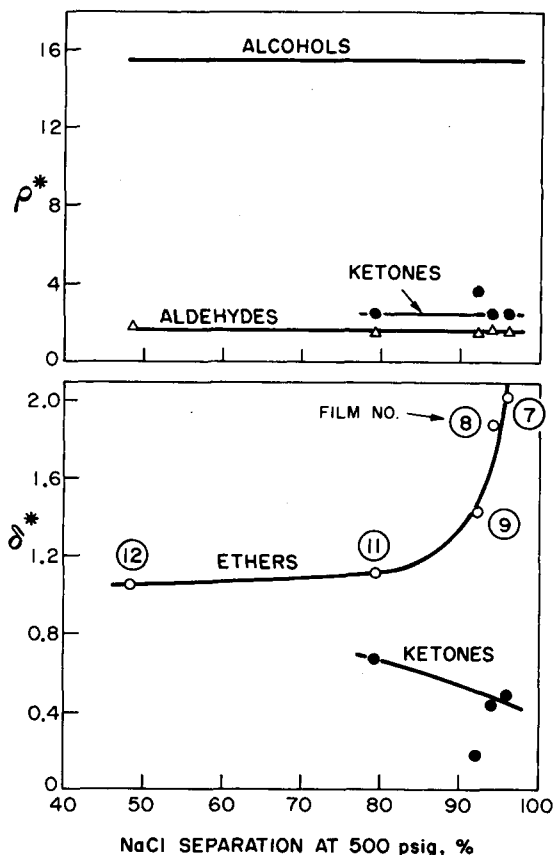
Fig. 4. Effect of pore size on membrane surface on ρ^* and δ^* for
alcohols, aldehydes, ketones, and ethers listed in Table I.

$R^2_{\Sigma E_s}$ represents the fraction of total variance of the dependent variable
ln $(D_{AM}/K\delta)$ which is related, respectively, to the particular factor $\Sigma\sigma^*$
or ΣE_s considered.

Referring to data presented in Table IV, values of $R^2_{\Sigma\sigma^*}$ for films 7 and
8 were less than 0.01, and hence the $\Sigma\sigma^*$ parameter was dropped from re-
gression analysis of the corresponding $(D_{AM}/K\delta)$ data. The values of
$R^2_{\Sigma\sigma^*}$ and $R^2_{\Sigma E_s}$ for film 12 were 0.016 and 0.943, respectively. Since
$R^2_{\Sigma\sigma^*}$ values were very small, the values of $R_{\Sigma E_s}$ only were determined for
all the films tested by least-squares analysis. The results show high values
of $R_{\Sigma E_s}$ (from 0.964 to 0.991), which means essentially that the values of
$(D_{AM}/K\delta)$ for the ethers considered are practically well represented by the
linear correlation expressed by eq. (7) involving only the steric parameter
with respect to solutes.

The slopes, δ^* in eq. (7), of the least-squares correlation lines in Figure 3
are not the same for all the films tested. The values of δ^* depend on the
porous structure of the membrane surface; more particularly, δ^* increases

with decrease in average pore size on the membrane surface. This latter correlation is explicitly represented in Figure 4 in which the average pore size on the membrane surface is represented arbitrarily in terms of sodium chloride separations obtained with 1500 ppm $NaCl-H_2O$ feed solution at 500 psig at feed flow rates corresponding to a value of 22×10^{-4} cm/sec. The sodium chloride separations varied in the range of 48.5% to 96.0% in the films tested. Figure 4 shows that δ^* increases steeply with decrease in average pore size on the membrane surface. On the basis of this result, one may conclude that when solute separation is predominantly a function of ΣE_s, steric repulsion at the membrane–solution interface increases with decrease in average pore size.

The data presented in Figures 3 and 4 and Table IV are significant. They show that the experimental δ^*-versus-average pore size correlation (Fig. 4) and eq. (7) together offer a practical means of predicting solute separation for noncyclic ethers in the ΣE_s range of -0.06 to -2.24.

Separation of Aldehydes

The $(D_{AM}/K\delta)$ values obtained for six different aldehydes with three different film samples (films 8, 9, and 11) were calculated by the same procedure as that used for similar calculations with respect to ethers. The results were then subjected to least-squares analysis for correlation in terms of eq. (6) involving the polar parameter $\Sigma\sigma^*$ and multiple-regression analysis for correlation in terms of eq. (8) involving both polar $(\Sigma\sigma^*)$ and steric (ΣE_s) parameters. The values for the correlation coefficient $R_{\Sigma\sigma^*}$ obtained from the least-squares analysis and the coefficients of determination $R^2_{\Sigma\sigma^*}$ and $R^2_{\Sigma E_s}$ obtained from the multiple-regression analysis are given in Table IV. The results show that the least-squares analysis gave values in the range of 0.94 to 0.97 for $R_{\Sigma\sigma^*}$, whereas the multiple regression analysis gave values in the range 0.834 to 0.914 for $R_{\Sigma\sigma^*}^2$ and 0.04 to 0.064 for $R^2_{\Sigma E_s}$. On the basis of these results, one may conclude that even though steric effect is not negligible in terms of eq. (7), it is sufficiently small so that the $(D_{AM}/K\delta)$ data for the aldehydes considered are practically well represented by the linear correlation expressed by eq. (6) involving only the polar parameter with respect to the solutes.

Figure 5 gives plots of $\Sigma\sigma^*$ versus ln $(D_{AM}/K\delta)$ obtained with three different film samples for the aldehydes studied. The plots include both the experimental data and the corresponding straight line for the least-squares fit of such data. The results show that the least-squares straight lines for all the films tested are essentially parallel so that their slopes, ρ^* in eq. (6), are essentially independent of the average pore size on the film surface as shown in Figure 4. These results (Figs. 4 and 5 with respect to aldehydes) are similar to those obtained for alcohols.[4] On the basis of these results, one may conclude that aldehydes, even though they are less polar than alcohols, behave similar to alcohols in reverse osmosis transport, and eq. (6) offers a practical means of predicting solute separation for aldehydes in the $\Sigma\sigma^*$ range of 0.6 to -0.19.
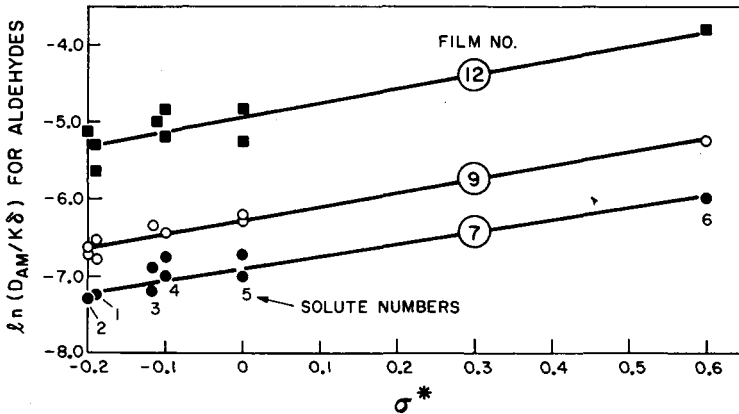
Fig. 5. Plot of $\Sigma\sigma^*$ vs. ln $(D_{AM}/K\delta)$ for aldehydes: film type, cellulose acetate (Batch 316); operating pressure, 500 psig; feed concentration, 0.0019 $\sim$ 0.0091 g-mole/l.; solute numbers and calculated k values, same as in Table I for aldehydes; (——) linear correlation by method of least squares; (●) (○) (■) experimental data.

Separation of Ketones

The $(D_{AM}/K\delta)$ values obtained for seven different ketones with four different film samples (films 7, 8, 9, and 11) were calculated by the same procedure as that used for similar calculations with respect to ethers and aldehydes. The results were then subjected to least-squares analysis for correlations in terms of eq. (6) involving only the polar parameter ($\Sigma\sigma^*$) and eq. (7) involving only the steric parameter (ΣE_s) with respect to the solutes. The $(D_{AM}/K\delta)$ data were also subjected to multiple-regression analysis for correlation in terms of eq. (8) involving both polar ($\Sigma\sigma^*$) and steric (ΣE_s) parameters. The values for the correlation coefficients $R_{\Sigma\sigma^*}$ and $R_{E\Sigma_s}$ obtained from the least-squares analysis and the coefficients of determination $R_{\Sigma\sigma^*}^2$ and $R_{\Sigma E_s}^2$ obtained from the multiple regression analysis are given in Table IV. The results show that the least-squares analysis gave values in the range 0.897 to 0.951 for $R_{\Sigma\sigma^*}$ and 0.897 to 0.947 for $R_{\Sigma E_s}$, whereas the multiple-regression analysis gave values in the range of 0.367 to 0.744 for $R_{\Sigma\sigma^*}^2$ and in the range 0.147 to 0.476 for $R_{\Sigma E_s}^2$. Further, a comparison of the values of $R_{\Sigma\sigma^*}^2$ and $R_{\Sigma E_s}^2$ obtained by least-squares analysis with the values of $(R_{\Sigma\sigma^*}^2 + R_{\Sigma E_s}^2)$ obtained from multiple-regression analysis shows that all the three quantities are nearly comparable in magnitude and that the latter values are in each case slightly higher than either of the former values.

The foregoing results point out that even though the $(D_{AM}/K\delta)$ data for ketones are just as well correlated in terms of either polar or steric parameter alone, eq. (6) or (7), both parameters have in fact comparable effect on reverse osmosis transport of ketones. Consequently, the $(D_{AM}/K\delta)$ data for ketones are better and more appropriately correlated by eq. 8 involving both polar and steric parameters. This conclusion is only logical in view
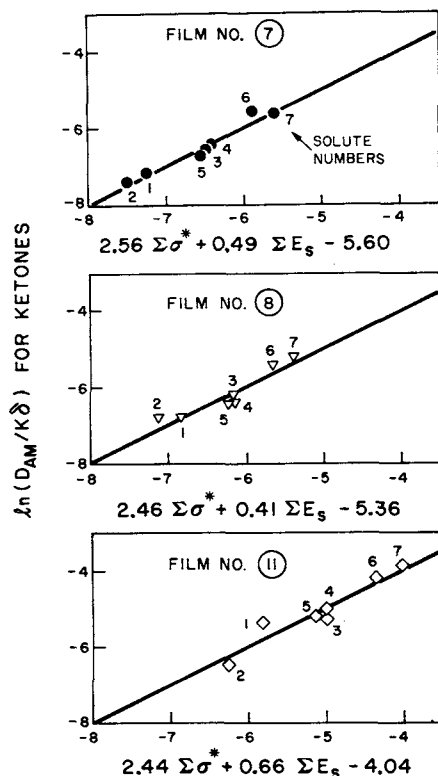
Fig. 6. Plot of $(\rho^*\Sigma\sigma^* + \delta^*\Sigma E_s + \ln C^*)$ vs. $\ln (D_{AM}/K\delta)$ for ketones: film type, cellulose acetate (Batch 316); operating pressure, 500 psig; feed concentration, $0.0019 \sim 0.0035$ g-mole/l.; solute numbers and calculated k values, same as in Table I for ketones; (———) linear correlation by multiple regression analysis; ($\bullet$) (∇) ($\Diamond$) experimental data.

of the following facts: (i) the $(D_{AM}/K\delta)$ data for alcohols are well correlated in terms of their polar ($\Sigma\sigma^*$) parameter only, eq. (6); (ii) the $(D_{AM}/K\delta)$ data for ethers are well correlated in terms of their steric (ΣE_s) parameter only; and (iii) the polar character of ketones is intermediate between that of alcohols and ethers.

Figure 6 gives correlations of $\ln (D_{AM}/K\delta)$ versus $(\rho^*\Sigma\sigma^* + \delta^*\Sigma E_s + \ln C^*)$ obtained from multiple regression analysis of data on solute transport parameter for ketones for films 7, 8, and 11. The figure includes both experimental data and the straight lines representing them in terms of eq. (8). The results of analysis show that ρ^* values are essentially independent of the average pore size on the membrane surface and δ^* values show a tendency to decrease with decrease in average pore size on the membrane surface (Fig. 4). The former result is similar to that observed for alcohols and aldehydes and is understandable on the same basis. The latter result is opposite to that observed for the case of ethers discussed above; this result probably indicates that solute separation with respect to ketones is not only

a function of polar and steric repulsions but also a function of the attraction of the solute molecule at the membrane–solution interface due to the nonpolar character of the solute and that of the membrane material. The attraction of the solute molecule toward the membrane surface (nonpolar effect) may be expected to increase with decrease in average pore size on the membrane surface and the consequent ,closer proximity of the solute molecule to the membrane material. This conclusion is strengthened by the fact that four out of seven ketones studied have equivalent Σs^* values larger than 400 (Table I) on the basis of their solubility data. It has been shown before[12] that hydrocarbons with such Σs^* values are preferentially sorbed at the membrane–solution interface.

Therefore, it is reasonable to expect solute repulsion due to polar and steric effects to be reduced by solute attraction due to nonpolar effect, so that solute sepeation is a function of polar, steric, and nonpolar effects. Consequently, the values of ρ^* and δ^* obtained by analysis of solute separation data in terms of eq. (8) may be expected to be affected to varying extents by the governing influence of the nonpolar effect, which factor is not included in eq. (8). The effect of nonpolar parameter of solute on the preferential sorption of water in reverse osmosis needs detailed quantitative study. On the basis of Figures 4 and 6, one can, however, conclude that the experimental δ^*-versus-average pore size on membrane surface correlation and eq. (8), involving both polar and steric parameters, together offer a practical means of predicting solute separation for ketones in the $\Sigma \sigma^*$ range of 0.6 to -0.4 and ΣE_s range of 0 to -1.86.

CONCLUSIONS

The foregoing results and discussion bring out the relative importance of polar and steric factors with respect to the separation of alcohols, aldehydes, ketones, and noncyclic ethers in aqueous solutions in reverse osmosis using porous cellulose acetate membranes. The solute transport parameter for alcohols and aldehydes can be represented by eq. (6), which involves only the polar parameter; that for noncyclic ethers, by eq. (7), which involves only the steric parameter; and that for ketones, by eq. (8), which involves both polar and steric parameters, in the range of $\Sigma \sigma^*$ and ΣE_s values given in Table V which also gives the applicable values of ρ^* and δ^* in eqs. (6), (7), and (8) for the set of polar solutes discussed.

TABLE V
Applicable Values of ρ^* and δ^* for Use in Eqs. (6), (7), and (8)

Polar functional group	$\Sigma \sigma^*$ range	ΣE_s range	ρ^*	δ^*
Alcohols	-0.30 to 0.0	-1.54 to 0.0	15.5	0
Aldehydes	-0.20 to 0.60	-0.93 to 0.0	1.7	0
Ketones	-0.40 to 0.60	-1.86 to 0.0	2.5	$0.16 \sim 0.66$
Ethers (noncyclic)	-0.49 to 0.60	-2.24 to -0.06	0	$1.06 \sim 2.02$

It can be seen from Table V that the values of ρ^* decrease in the order alcohol $>$ aldehyde $\approx$ ketone $>$ ether $(= 0)$, whereas the values of δ^* increase in the order alcohol $(= 0)$ $\approx$ aldehydes $<$ ketone $<$ ether. The above order corresponds to decreasing polarity as shown by data on $\Delta\Delta F_w$ given in Table III. Thus, for highly polar solutes, solute transport parameter is predominantly a function of $\Sigma\sigma^*$. As the polar character of the solute decreases, it tends to be in closer proximity to the membrane material at the membrane–solution interface; under these conditions, preferential sorption of water decreases and steric repulsion tends to control solute separation. Further, ρ^* values of alcohols, aldehydes, and ketones have positive values with all film samples tested; this result confirms the earlier conclusion[1-4] that solute separation tends to increase with increase in basicity (i.e., decrease in $\Sigma\sigma^*$) of the solute molecule.

This work also indicates that solute separation in reverse osmosis is governed not only by the polar and steric factors but also by the nonpolar character of the solute even where water is preferentially sorbed. Even though the nonpolar effect has been explicitly noted in the case of the ketones studied in this work, such effect may be expected in the case of alcohols, aldehydes, and ethers also to different extents. Consequently, following the form of eqs. (6), (7), and (8), the most general expression for solute transport parameter for systems involving preferential sorption of water at the membrane–solution interface can be given as

$$(D_{AM}/K\delta) = C^* \exp (\delta^*\Sigma\sigma^* + \delta^*\Sigma E_s + \omega^*\Sigma s^*) \qquad (11)$$

where Σs^* is the equivalent nonpolar parameter based on solubility data for solutes and ω^* is the corresponding proportionality constant. While ρ^* may be expected to be independent of the average size of pores on the membrane surface, both δ^* and ω^* should be expected to be dependent on the average size of pores on the membrane surface. Even through the foregoing discussion is explicitly concerned with reverse osmosis data obtained with cellulose acetate membranes, similar analysis may be expected to be applicable for membranes other than cellulose acetate also. Consequently, investigations on the applicability of eq. (11) for a wide variety of solution-membrane systems in reverse osmosis are called for.

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