

Reverse Osmosis Separation of Organic Acids in Aqueous Solutions Using Porous Cellulose Acetate Membranes

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Synopsis

Reverse osmosis data obtained using porous cellulose acetate membranes and aqueous feed solutions involving one of 22 monocarboxylic acids, seven dicarboxylic acids, and four hydroxycarboxylic acids have been analyzed. The operating pressure used was 250 psig in all cases, and the solute concentration used was ~ 100 ppm in most cases. The results yield the following physicochemical criteria for preferential sorption at the membrane-solution interface with respect to the un-ionized acid. At $pK_a = 4.2$ (for monocarboxylic acids), or Taft number (σ^*) = 0.6 or Hammett number (σ) = 0, neither the un-ionized acid nor water is preferentially sorbed at the membrane-solution interface; at $pK_a < 4.2$ (for monocarboxylic acids) or $\sigma^* > 0.6$ or $\sigma > 0$, the un-ionized acid is preferentially sorbed at the membrane-solution interface. For practical purposes, preferential sorption of water at the membrane-solution interface may be considered negligible in the σ^* region of 0 to 0.6. The results also show that the criterion of acidity of the molecule governing the extent of its repulsion or attraction at the membrane-solution interface is valid for both ionized and un-ionized acid. Further, when the acid molecule contains three or more straight-chain carbon atoms *not* associated with a $-\text{COOH}$ group, the nonpolar character of the molecule also affects its separation in reverse osmosis.

INTRODUCTION

Data on reverse osmosis separation of several monocarboxylic acids in aqueous solutions using Loeb-Sourirajan-type porous cellulose acetate membranes have been reported and discussed.¹ The correlation of such data with the dissociation constant K_a of the acid showed that both solute separation and membrane permeated product rate passed through a minimum in the $pK_a (= -\log K_a)$ range of 4.2 to 4.8. Similar results were obtained by the correlation of reverse osmosis data with Taft number (σ^*) and Hammett number (σ) representing the contribution of the substituent group to the total polar effect of the acid molecule. It was also shown that, with respect to each acid, solute separation always increased with increase in its degree of dissociation. These results were explained on the basis that preferential sorption of water at the membrane-solution interface, and hence solute separation in reverse osmosis, were governed by the hydrogen bonding ability of the organic solute molecule when it was essentially un-

dissociated, and by the electrostatic repulsion of ions when the molecule was partially or completely dissociated. This paper is a continuation of the above work.

Acid ions are always repelled by the membrane material; consequently, with respect to the ionic species, water is preferentially sorbed at the membrane-solution interface. On the other hand, depending on its hydrogen bonding ability, the undissociated acid may be repelled or attracted by the membrane material resulting in preferential sorption of either water, acid, or neither at the membrane-solution interface under the reverse osmosis operating conditions. This paper is particularly concerned with the physicochemical criteria for preferential sorption at the membrane-solution interface with respect to the un-ionized acid molecule.

In this work, reverse osmosis separations of sodium salts of a few monocarboxylic acids have been studied; the results obtained indicate the effect of acidity of the molecule on the extent of repulsion of the carboxylate ion at the membrane-solution interface. Using these results, the data on the reverse osmosis separation of monocarboxylic acids reported earlier have been further analyzed, and the fluxes of the ionized and un-ionized species have been estimated. This work also includes reverse osmosis data on the separation of some dicarboxylic and hydroxycarboxylic acids in aqueous solutions. All these results confirm the basic physicochemical criteria for preferential sorption stated earlier and lead to new correlations of scientific and practical interest.

EXPERIMENTAL

This work is concerned with the analysis of reverse osmosis data for aqueous feed solutions involving one of 22 monocarboxylic acids, seven dicarboxylic acids, and four hydroxycarboxylic acids listed in Table I, which also includes data on some physicochemical parameters for each of the above acids pertinent to this work. The apparatus, films, and the operating conditions employed to obtain the reverse osmosis data were identical to those described earlier. The solute concentrations used were in the range of 0.00007 to 0.0545 g-mole/l.; in most cases, the solute concentration was ~100 ppm. The operating pressure used was 250 psig in all cases. Since the feed concentrations used were small, the osmotic pressure and other effects^{2,3} were effectively eliminated. All experiments were of the short-run type, each lasting for about 2 hr. 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. In each experiment, the per cent solute separation, defined as

$$\left[\frac{\text{solute ppm in feed} - \text{solute ppm in product}}{\text{solute ppm in feed}} \right] \times 100,$$

the product rate [PR], and the pure water permeation rate [PWP] in grams per hour per given area of film surface (7.6 cm^2) were determined at the specified operating conditions. All reverse osmosis data are for single-solute systems. The solute numbers in all figures in this paper are the same as those listed in Table I.

The specifications⁴ of the films used in this work were as follows: pure-water permeability constant A (in $\text{g mole H}_2\text{O}/\text{cm}^2 \text{ sec atm}$) = 2.48×10^{-6} , 5.35×10^{-6} , and 9.73×10^{-6} for films 1, 3, and 5, respectively; and solute transport parameter ($D_{AM}/K\delta$) for sodium chloride (in cm/sec) = 3.22×10^{-5} , 16.89×10^{-5} , and 144.4×10^{-5} for films 1, 3, and 5, respectively. At the feed flow rate used in this work, the value of the mass transfer coefficient k on the high-pressure side of the membrane was $57 \times 10^{-4} \text{ cm}/\text{sec}$ for 1500 ppm $\text{NaCl-H}_2\text{O}$ feed solution.

Analysis

A Beckman total carbon analyzer (Model 915) was used to measure the concentration of the organic solutes. The analytical procedure was the same as that used before.¹ An automatic sample injection syringe was used to obtain a sample size of 20 microliters for each analysis; the use of the automatic syringe resulted in very reproducible peak heights. The accuracy of the analysis was ± 1 ppm in terms of carbon content.

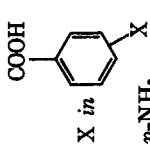
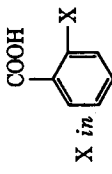
The analysis for sodium chloride in aqueous solutions was done using a conductivity bridge.

RESULTS AND DISCUSSION

Separation of Monocarboxylic Acids in Aqueous Solutions

Separation of Ionized Species in Solutions. The reverse osmosis data for the separation of sodium salts of pivalic acid (33), valeric acid (36), propionic acid (38), phenyl acetic acid (42), benzoic acid (43), anisic acid (46), *p*-chlorobenzoic acid (50), *m*-nitrobenzoic acid (51), *p*-nitrobenzoic acid (52), *o*-chlorobenzoic acid (53), and *o*-nitrobenzoic acid (54) were studied. The numbers given in parentheses refer to solute numbers in Table I. The acid concentration used in each case was 0.0007 g-mole/l.; solutions of the sodium salts were prepared by adding an equivalent amount of sodium hydroxide to the acid solution. The pH values of the resulting solutions were between 6 and 7. The dissociation constants for the above acids are in the range of $10^{-5.05}$ to $10^{-2.17}$ (Table I). Even with respect to the acid whose dissociation constant is lowest, the degree of dissociation of the sodium salt in solution may be easily calculated to be 99.9%.^{5b} Consequently, all the above salts were practically completely dissociated in the aqueous solutions used; and for any given membrane, data on solute separations gave a relative measure of the repulsion experienced by the different carboxylate ions in the vicinity of the membrane surface.^{3,6}

TABLE I
 Acidity Parameters and Other Data for Acids

No.	Solute		Mol. wt.	pK_a^a	σ^* or σ	V_1 , cm ³ / g-mole	$D_{4B} \times 10^6$, cm ² /sec	$k \times 10^4$, cm/ sec
	Name and formula	R in $RCOOH$						
<i>Monocarboxylic Acids</i>								
33	Pivalic acid	$t-C_4H_9$	102.1	5.05	-0.300	130.4	0.822	29
34	Isobutyric acid	$i-C_3H_7$	88.1	4.86	-0.190	108.2	0.919	33
35	Cyclohexanecarboxylic acid	cyclo- C_6H_{11}	128.2	4.91	-0.150	152.4	0.748	26
36	Valeric acid	$n-C_4H_9$	102.1	4.86	-0.130	130.4	0.822	29
37	<i>n</i> -Butyric acid	$n-C_3H_7$	88.1	4.83	-0.115	108.2	0.919	33
38	Propionic acid	$n-C_2H_5$	74.1	4.87	-0.100	86.2	1.055	37
39	Acetic acid	CH_3	60.1	4.75	0	63.8	1.262	45
40	4-Phenylbutyric acid	$C_6H_5(CH_2)_3$	164.2	4.73	0.020	196.8	0.642	23
41	β -Phenylpropionic acid	$C_6H_5(CH_2)_2$	150.2	4.66	0.080	174.6	0.690	24
42	Phenylacetic acid	$C_6H_5(CH_2)$	136.1	4.31	0.215	152.4	0.748	26
43	Benzoic acid	C_6H_5	122.1	4.20	0.600	130.2	0.823	29
44	Caprylic acid	$n-C_7H_{15}$	144.2	4.90	-0.134	197.0	0.642	23
 X in								
45	<i>p</i> -Aminobenzoic acid	$p-NH_2$	137.1	4.82	-0.660	144.4	0.773	27
46	Anisic acid	$p-OCH_3$	152.1	4.47	-0.268	162.3	0.721	26
47	<i>m</i> -Aminobenzoic acid	$m-NH_2$	137.1	4.60	-0.161	144.4	0.773	27
48	<i>m</i> -Toluic acid	$m-CH_3$	136.1	4.24	-0.069	152.4	0.748	26
49	<i>m</i> -Hydroxybenzoic acid	$m-OH$	138.1	4.08	-0.002	142.2	0.780	28
43	Benzoic acid	—	122.1	4.20	0	130.2	0.823	29
50	<i>p</i> -Chlorobenzoic acid	$p-Cl$	156.6	3.99	0.277	148.1	0.761	27
51	<i>m</i> -Nitrobenzoic acid	$m-NO_2$	167.1	3.45	0.710	158.7	0.730	26
52	<i>p</i> -Nitrobenzoic acid	$p-NO_2$	167.1	3.44	0.778	158.7	0.730	26
 X in								
σ^*								

43	Benzoic acid	H	122.1	4.20	0	130.2	0.823	29
53	<i>o</i> -Chlorobenzoic acid	Cl	156.6	2.94	0.20	148.1	0.761	27
54	<i>o</i> -Nitrobenzoic acid	NO ₂	167.1	2.17	0.80	158.7	0.730	26
<i>Dicarboxylic Acids</i>								
<i>R in R(COOH)_n</i>								
55	Oxalic acid	—	90.0	{ 1.23 4.19 }	σ* 0.98	75.8	1.138	40
56	Malonic acid	—CH ₂ —	104.1	{ 2.83 5.69 }	0	98.0	0.975	35
57	Succinic acid	—(CH ₂) ₂ —	118.1	{ 4.16 5.61 }	-0.200	120.0	0.951	34
58	Adipic acid	—(CH ₂) ₄ —	146.1	{ 4.43 4.41 }	-0.260	164.6	0.715	25
59	Pimelic acid	—(CH ₂) ₅ —	160.2	{ 4.48 5.31 }	-0.266	186.8	0.662	23
60	Suberic acid	—(CH ₂) ₆ —	174.2	{ 4.52 5.50 }	-0.268	209.0	0.619	22
61	Azelaic acid	—(CH ₂) ₇ —	188.2	{ 4.55 5.50 }	-0.268	231.2	0.583	21
<i>Hydroxycarboxylic Acids</i>								
62	Lactic acid	CH ₃ CHOHCOOH	90.1	3.08	σ* { -0.1(OH) -0.1 (COOH) }	98.0	0.975	35
63	<i>D,L</i> -Malic acid	HOOCCH(OH)CH ₂ COOH	134.1	{ 3.40 5.11 }	{ -0.1(OH) -0.2 (COOH) }	132.2	0.815	29
64	Tartaric acid	HOOCCH(OH)CH(OH)COOH	168.1	{ 2.94 4.34 }	{ -0.2(OH) -0.2 (COOH) }	144.2	0.774	27
65	Citric acid	HOOCCH ₂ C(OH)(COOH)CH ₂ COOH	192.1	{ 3.14 5.95 6.39 }	{ -0.19(OH) -0.42 (COOH) }	188.6	0.659	23

* pK_i values were obtained from references 15 and 16.

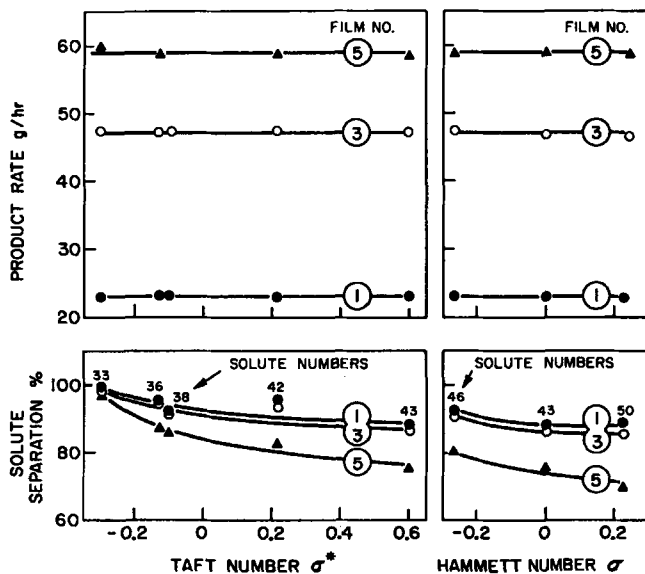


Fig. 1. Correlation of Taft or Hammett number and data on reverse osmosis separation of sodium salts of monocarboxylic acids. Operating pressure, 250 psig; feed concentration, 0.0007 g-mole/l., membrane area, 7.6 cm². Solute numbers refer to acids listed in Table I.

The solute separation and product rate data obtained with films 1, 3, and 5 for the sodium salts of the first seven acids mentioned above are plotted in Figure 1 as a function of Taft (σ^*) or Hammett (σ) number (Table I) for the substituent group in the acid molecule. The relevance of σ^* or σ to reverse osmosis separation of acids has already been discussed.¹ A higher value of σ^* or σ represents a relatively higher acidity (proton-donating or electron-withdrawing power) for the carboxylate ion concerned. The reverse osmosis data in Figure 1 cover a σ^* range of -0.300 to $+0.600$, and a σ range of -0.268 to $+0.227$. The data show that high positive solute separations were obtained with all the films tested in the entire range of σ^* or σ involved. With respect to each solute, solute separation was higher for the membrane whose average surface pore size was smaller; and, with respect to each membrane, solute separation tended to decrease with increase in the value of σ^* or σ . Further, with respect to each membrane, the product rate remained constant for all the solution systems studied.

The product rate data show that the pore structure on the membrane surface was unaffected by the acidity of the carboxylate ions studied. The separation data show that water was preferentially sorbed at the membrane-solution interface in all the above cases, and the extent of preferential sorption of water showed a tendency to decrease with increase in the value of σ^* or σ . Therefore, one may conclude that increase in the acidity of the carboxylate ion tends to lessen the extent of repulsion for the ion at the membrane-solution interface and hence bring the ion closer to the mem-

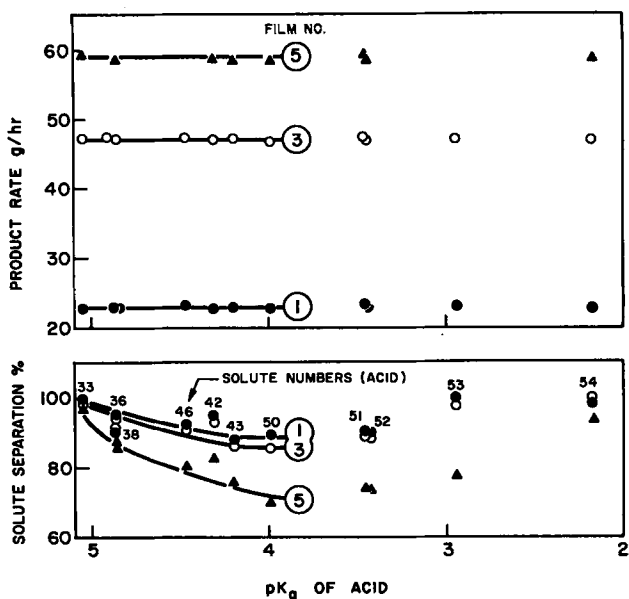


Fig. 2. Correlation of pK_a of acid and data on reverse osmosis separation of sodium salts of monocarboxylic acids. Operating pressure, 250 psig; feed concentration, 0.0007 g-mole/l., membrane area, 7.6 cm². Solute numbers refer to acids listed in Table I.

brane surface. Consequently, with increase in σ^* or σ , the thickness of the preferentially sorbed interfacial pure water layer decreases resulting in lower solute separation in reverse osmosis. A similar conclusion was arrived at earlier¹ with respect to the reverse osmosis separation of alcohols in aqueous solution. These results confirm that (a) ions in aqueous solution are repelled at the membrane-solution interface, (b) the cellulose acetate membrane material used behaves as a proton acceptor, and (c) the basic criterion of acidity of the molecule governing the extent of its repulsion at the membrane-solution interface is valid for both ionized and un-ionized solutes.

The existence of unique linear relationships between the acidity parameters σ^* or σ and pK_a of acids has been established.^{1,7} Hence, the correlation of pK_a with solute separation and product rate is of interest. This correlation is illustrated in Figure 2, in which the reverse osmosis data for all the 11 solution systems studied are plotted as a function of pK_a of acid. A decrease in pK_a represents an increase in the acidity for the carboxylate ion. With respect to each membrane, the product rate remained constant for all the solution systems studied, indicating that the porous structure on the membrane surface was unaffected by the acidity of the ions in solution. In the pK_a range of 5.05 to 3.99, solute separation decreased with increase in acidity; in this range, the correlation is similar to that in Figure 1. The solute separation, however, showed a tendency to increase for the sodium

salts of *m*-nitrobenzoic acid, *p*-nitrobenzoic acid, *o*-chlorobenzoic acid, and *o*-nitrobenzoic acid (solute numbers 51, 52, 53, and 54 in Table I) whose pK_a values are lower than 3.99. The above tendency is contrary to that observed for the separation of the carboxylate ions of the other seven acids the data for which are plotted in Figures 1 and 2. The separation data for the carboxylate ions of the four acids mentioned above seem to indicate simply that acidity is not the only criterion governing the extent of repulsion of carboxylate ions at the membrane-solution interface.

Separation of Un-ionized Species in Solution. Reverse osmosis data on the separation of monocarboxylic acids in aqueous solutions reported earlier¹ involved solution systems in each of which the acid was partially ionized. In order to extract from the above data valid information on the reverse osmosis separation of the un-ionized species alone, an acceptable technique is required for the analysis of the overall solute separation and product rate data with respect to the flux of the un-ionized species only. Such a technique, used in this work, is described below.

The technique is based on the following assumptions: (i) the un-ionized and ionized species behave independently with respect to reverse osmosis transport; (ii) at a given feed flow rate, the mass transfer coefficient on the high-pressure side of the membrane is the same for both the un-ionized and the ionized species; and (iii) the un-ionized species is mobile. Assumption (i) is justified because of the proven applicability of the simple additivity principle for predicting reverse osmosis data for mixed solute aqueous solution systems illustrated in the literature.^{8,9} Assumption (ii) is justified because the contribution of hydrogen to the total molal volume of solute at normal boiling point is small,¹⁰ and hence the diffusivities of both the ionized and un-ionized acids, as calculated from the empirical equation of Wilke and Chang,¹¹ may be considered to be essentially the same. Assumption (iii) is valid when water is preferentially sorbed at the membrane-solution interface; when the un-ionized acid is preferentially sorbed at the interface, the preferentially sorbed layer may consist of both mobile and immobile molecules which possibility must be kept in view in interpreting reverse osmosis data.

The basic equations expressing the flux of ionized and un-ionized acid (solute) in reverse osmosis transport can be written as follows:

$$N_t = N_i + N_u \quad (1)$$

$$N_i = \left[\frac{D_{AM}}{K\delta} \right]_i c(X_{i2} - X_{i3}) \quad (2)$$

$$N_u = \left[\frac{D_{AM}}{K\delta} \right]_u c(X_{u2} - X_{u3}) \quad (3)$$

$$X_{i2} = X_{i3} + (X_{i1} - X_{i3}) \exp \{ [PR]/3600 SM_B kc \} \quad (4)$$

$$X_{u2} = X_{u3} + (X_{u1} - X_{u3}) \exp \{ [PR]/3600 SM_B kc \} \quad (5)$$

where N_i = total solute flux, g-mole/cm²sec; N = flux of ionized or un-ionized species, g-mole/cm²sec; $\left[\frac{D_{AM}}{K\delta}\right]$ = solute transport parameter, cm/sec; c = molar density of solution assumed constant and equal to that of pure water, g-mole/cm³; X = mole fraction of solute; $[PR]$ = product rate, g/hr; S = membrane area, cm²; M_B = molecular weight of water; k = mass transfer coefficient on the high-pressure side of the membrane; subscripts i and u refer to ionized and un-ionized solute respectively, and subscripts 1, 2, and 3 refer to bulk feed solution and boundary solution on the high-pressure side of the membrane and the product solution on the low-pressure side of the membrane, respectively. Equation (1) is based on the independence of ionized and un-ionized species in reverse osmosis transport. The form of eqs. (2) and (3) is based on Kimura-Sourirajan analysis of reverse osmosis transport.⁴ The form of eqs. (4) and (5) has been derived in an earlier paper¹² for dilute solutions.

For the purpose of present analysis, a dimensionless quantity V_u , defined as the ratio of the permeation velocity of the un-ionized solute (v_u) to that of solvent water (v_B) through the membrane, is used. When N_B represents the flux of solvent water through the membrane (in g-mole/cm²sec), and X_B represents the mole fraction of water in the product solution,

$$V_u = \frac{v_u}{v_B} = \frac{N_u/cX_{u2}}{N_B/cX_B} \approx \frac{N_u/X_{u2}}{N_B} \quad (6)$$

since $X_B \approx 1$ under the experimental conditions used.

The meaning of the quantity V_u must be clear. It is concerned only with un-ionized solute molecules. With respect to such molecules, when solute flux is zero, $V_u = 0$ and solute separation is 100%. When $V_u = 1$, the permeation velocity of solute and that of solvent water through the porous membrane are the same, so that solute separation is zero. This situation may be expected when neither solute nor water is preferentially sorbed at the membrane-solution interface. The quantity V_u is also a measure of solute concentration in the product solution relative to that in the boundary solution on the high-pressure side of the membrane; consequently, V_u is a measure of solute separation based on boundary concentration. A value of $V_u > 1$ means negative solute separation in reverse osmosis, i.e., solute enrichment in the product solution; and a value of $V_u < 1$ means positive solute separation in reverse osmosis. While a value of $V_u > 1$ means that the solute is preferentially sorbed on the membrane-solution interface, a value of $V_u < 1$ does not necessarily mean that solute is not preferentially sorbed on the membrane-solution interface in view of the mobility effect of the preferentially sorbed layer on solute separation discussed earlier.¹³

The object of the present analysis is to calculate V_u from the overall solute separation and product rate data and establish correlations of V_u with the acidity parameters discussed above. Under steady-state operating conditions of reverse osmosis experiment, the total concentrations of acid (x_i , in g-mole/l.) in the feed and product solutions, and hence the

overall solute separation, and the product rate $[PR]$ (in g/hr) per given area (S) of film surface are known. From these data, the calculation of V_u involves the following steps.

Step 1. From the experimental product rate data, calculate N_B using the relation

$$N_B = \frac{[PR]}{3600 \times S \times M_B} \quad (7)$$

Step 2. From the experimental solute separation and product rate data, calculate total solute flux N_t using the relation¹²

$$N_t = \frac{[PR](\text{ppm})_{\text{feed}}(1-f)}{3600 \times S \times M_A \times 10^6} \quad (8)$$

where $(\text{ppm})_{\text{feed}}$ represents total solute (acid) concentration in ppm in the feed solution, f represents fraction solute separation, and M_A represents the molecular weight of solute.

Step 3. From the experimental data on total acid concentrations (x_t) in the feed and product solutions; and data on dissociation constant K_a of the acid, calculate the concentrations of the ionized acid (x_i in g-mole/l.) in the respective solutions using the following relation¹:

$$x_i = x_t \left[\left\{ \frac{1}{4} \left(\frac{K_a}{x_t} \right)^2 + \left(\frac{K_a}{x_t} \right) \right\}^{1/2} - \frac{1}{2} \left(\frac{K_a}{x_t} \right) \right] \quad (9)$$

The concentrations of the un-ionized acid in the feed and product solutions are then obtained from the respective differences ($x_t - x_i$).

Step 4. From the data obtained in step 3 above, calculate the mole fractions X_{a1} , X_{a3} , X_{u1} , and X_{u3} .

Step 5. Calculate the mass transfer coefficient k applicable for the experiment from the relation¹²

$$k = \left(\frac{k}{D_{AB}} \right)_{\text{ref}} \cdot D_{AB} \quad (10)$$

where D_{AB} refers to the diffusivity of solute in water, and the quantity $(k/D_{AB})_{\text{ref}}$ involves the values of k and D_{AB} for the reference feed solution system 1500 ppm NaCl-H₂O. The diffusivity data for the acids are obtained from the following empirical equation of Wilke and Chang¹¹:

$$D_{AB} = 7.4 \times 10^{-8} \frac{(\chi M_B)^{1/2} T}{\mu V_1^{0.6}} \quad (11)$$

where χ = association parameter of solvent (=2.6 for water); M_B = molecular weight of water; T = temperature, °K (=298); μ = viscosity of solution, centipoise (=0.8937 for water); and V_1 = molal volume of solute at normal boiling point, cm³/g-mole. The values of V_1 , obtained by summation of atomic volume data listed in the literature,¹⁰ and the calculated values of k applicable for the systems studied in this work are given in Table I.

Step 6. Using the values of X_{i1} , X_{i3} , X_{u1} , and X_{u3} obtained from step 4 and the values of k obtained from step 5 above, calculate X_{i2} and X_{u2} from eqs. (4) and (5).

Step 7. Estimate the applicable value of $(D_{AM}/K\delta)_i$ as follows. Find solute separation f and product rate $[PR]$ by interpolation of data from Figure 2 corresponding to pK_a of acid under consideration. From the above data, calculate the solute transport parameter for the ionized species with sodium as the cation, designated as $(D_{AM}/K\delta)_{i,Na}$, from the relation¹²

$$\left(\frac{D_{AM}}{K\delta}\right)_{i,Na} = \frac{[PR]}{3600 Sd} \frac{(1-f)}{f} \left\{ \frac{1}{\exp \left[\frac{[PR]}{3600 Skd} \right]} \right\} \quad (12)$$

where d is the density of solution (g/cm^3). It was found experimentally that the value of $(D_{AM}/K\delta)_i$ for the ionized acid was higher than $(D_{AM}/K\delta)_{i,Na}$, and the average value of the ratio of $(D_{AM}/K\delta)_i/(D_{AM}/K\delta)_{i,Na}$ was 2.23 with the films used in this work. Therefore, the value of $(D_{AM}/K\delta)_i$ is estimated as 2.23 times the value of $(D_{AM}/K\delta)_{i,Na}$ calculated above.

Step 8. Calculate N_i from eq. (2) using the values of X_{i3} , X_{i2} , and $(D_{AM}/K\delta)_i$ obtained from steps 4, 6, and 7, respectively.

Step 9. Calculate N_u from eq. (1) using the value of N_i and N_t obtained from steps 2 and 8, respectively.

Step 10. Finally, calculate V_u from eq. (6) using the values of N_B , X_{u2} , and N_u obtained from steps 1, 6, and 9, respectively.

Regarding step 7 above, some additional comments are called for. It is difficult to determine precisely the value of $(D_{AM}/K\delta)_i$ for an acid which is only partially ionized. For the purpose of determining the ratio of $(D_{AM}/K\delta)_i/(D_{AM}/K\delta)_{i,Na}$, experimental data on 99% dissociated *o*-nitrobenzoic acid (whose K_a value was the highest in the series of acids studied) and the sodium salt of the above acid were used. This ratio was assumed constant for the ionic species of all the other acids studied. Admittedly, there is some uncertainty regarding the estimated values of $(D_{AM}/K\delta)_i$. But this uncertainty is not critical for the purpose of calculating V_u . This is illustrated by the following results. Considering the reverse osmosis data for aqueous solutions of *p*-aminobenzoic acid as example, for film 1, the value of $(D_{AM}/K\delta)_i$ calculated by the technique used was 5.858×10^{-5} cm/sec, from which the value of V_u may be calculated to be 0.9628. For the same film, if the value of $(D_{AM}/K\delta)_i$ is assumed to be twice that given above, the value of V_u would then be 0.9622. Thus, a 100% change in the value of $(D_{AM}/K\delta)_i$ changes the value of V_u insignificantly for film 1. Secondly, Figure 3, which is based on the values of V_u calculated by the above technique, shows that V_u is independent of feed concentration. This result is what one would expect on the basis that boundary and product concentrations are uniquely related for a given film—a fact already established in the literature for both ionic and nonionic solutes.⁴ Therefore, Figure 3 supports the essential validity of the procedure used for estimating the values of

N_u and hence V_u . Further, even if one assumes a constant value for $(D_{AM}/K\delta)_i$ for all acids, the essential conclusion from the correlations of V_u with the acidity parameters may be shown to remain unchanged. Therefore, one may conclude that the precision obtained for the values of $(D_{AM}/K\delta)_i$ by the method of estimation given in step 7 above is adequate for the present purpose.

Correlations of V_u with Acidity Parameters. Figure 4 gives the correlations of V_u and pK_a of acid for films 1 and 5. These correlations illustrate three important results. First, for both films, V_u was less than 1 at high pK_a values (>4.8), and V_u was greater than 1 at low pK_a values (<4). These results show that when the acidity of the acid is sufficiently low, water is preferentially sorbed, and when the acidity of the acid is sufficiently high, the un-ionized acid is preferentially sorbed at the membrane-solution interface. These results confirm the acidity criteria for preferential sorption stated earlier with respect to the separation of alcohols.¹ Secondly, in

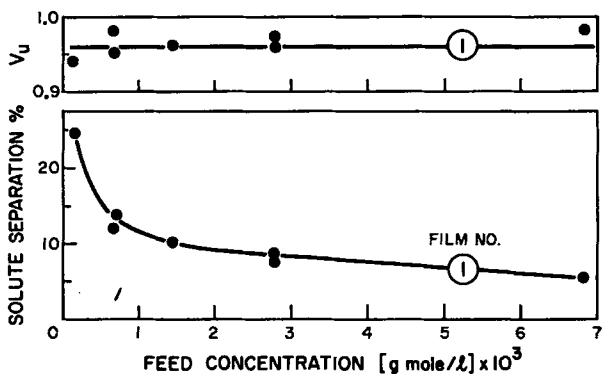


Fig. 3. Effect of feed concentration on reverse osmosis separation of *p*-aminobenzoic acid. Operating pressure, 250 psig; membrane area, 7.6 cm².

the region of pK_a values where water is preferentially sorbed, the value of V_u is lower for film 1 than for film 5; and, in the region of pK_a values where the un-ionized acid is preferentially sorbed, the value of V_u is higher for film 1 than for film 5. These results are understandable on the basis that a membrane whose average surface pore size is smaller (film 1 in the present case) yields a product which is more enriched in the preferentially sorbed constituent of the feed solution. Thirdly, the correlations indicate that the change of preferential sorption of water to that of un-ionized acid at the membrane-solution interface occurs at a pK_a value of 4.2 above which water is preferentially sorbed, below which the un-ionized acid is preferentially sorbed and at which neither is preferentially sorbed. The pK_a value of 4.2 corresponds to benzoic acid (solute 43) in the series of acids studied. On either side of $pK_a = 4.2$, there is a region of pK_a values (~ 3.9 to 4.7) at which very little preferential sorption occurs, which partly accounts for the scatter in V_u values shown in Figure 4.

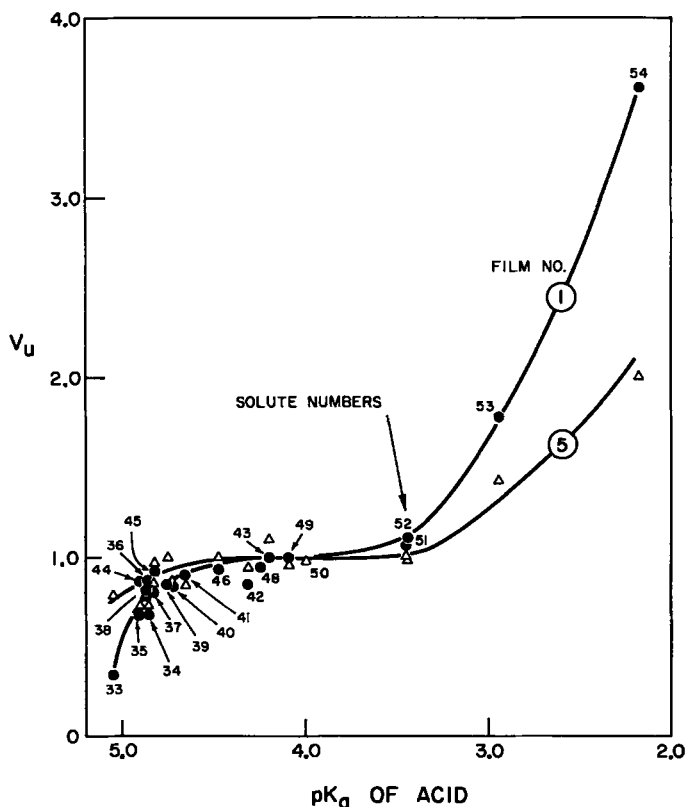


Fig. 4. Effect of pK_a of acid on reverse osmosis separation of unionized monocarboxylic acids. Operating pressure, 250 psig; solute numbers same as given in Table I.

Similar conclusions can be drawn from the correlations of V_u with Taft (σ^*) and Hammett (σ) numbers for the substituent groups in the acid molecules, illustrated in Figure 5. On the basis of the correlations given in Figures 4 and 5, one can conclude that when pK_a of the acid is less than 4.2, or the Taft number for the substituent group in the acid molecule is more than 0.6, or the corresponding Hammett number is greater than zero, the un-ionized acid may be expected to be preferentially sorbed at the cellulose acetate membrane-aqueous solution interface. As pointed out already, there is a considerable region on either side of the above physicochemical reference points where preferential sorption for either water or the un-ionized acid at the interface is negligibly small; in this region, significant solute separation by reverse osmosis using cellulose acetate membranes is possible only by dissociating the acid molecule.

Correlation of pK_a , Degree of Dissociation, and Solute Separation.

For any given acid, solute separation increases with increase in the degree of dissociation of the acid in the feed solution. This was illustrated before¹ with the data on the separation of *p*-aminobenzoic acid in aqueous solution

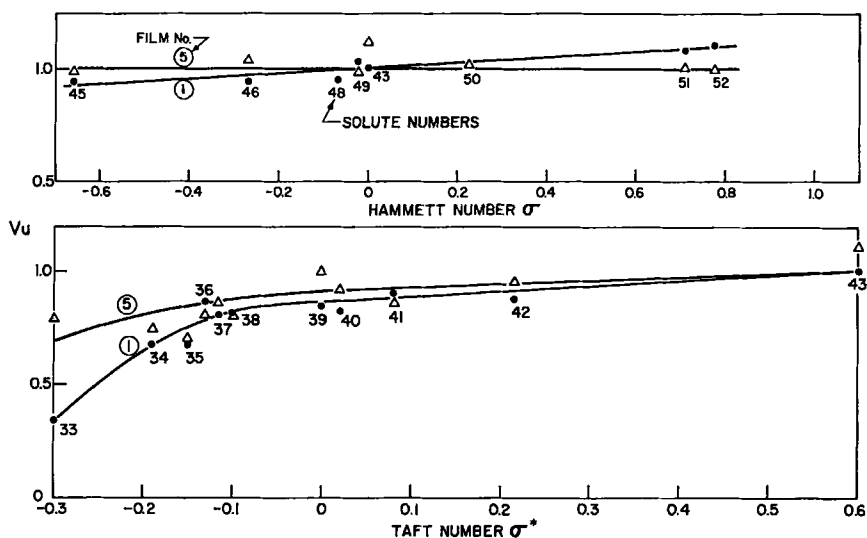


Fig. 5. Effect of Taft or Hammett number on reverse osmosis separation of unionized monocarboxylic acids. Operating pressure, 250 psig. Solute numbers same as given in Table I.

whose degree of dissociation in the feed solution was changed by changing its concentration. Figure 6 refers to data for all the monocarboxylic acids studied and illustrates the correlation of the acidity parameter pK_a of acid with its degree of dissociation in the feed solution and overall solute separation in reverse osmosis, when the concentration of acid in the feed solution was held approximately constant. Consequently, the change in the degree of dissociation was essentially due to the change in pK_a of acid. The experimental data in Figure 6 correspond to a feed concentration of 0.0006 to 0.0008 g-mole acid per liter of solution.

The shape of the curve for film 1, representing the correlation of degree of dissociation and solute separation, is particularly illustrative of the preferential sorption characteristics of the ionized and un-ionized solute at the membrane-solution interface. Referring to solute separation data for film 1, the shape of the above curve may be discussed in four parts, each part corresponding to a different pK_a region.

In the pK_a region of 5.05 to 4.7, solute separation decreased from 66% to 16%; in this region, degree of dissociation of acid was only 10% to 15%. Consequently, solute separation in the above region was essentially due to preferential sorption of water caused by the relative repulsion of the un-ionized solute at the membrane-solution interface. Since the magnitude of such repulsion steeply decreases with increase in the acidity of the solute molecule,¹ the decrease in solute separation with decrease in pK_a is readily understood.

In the pK_a region 4.7 to 3.9, solute separation increased from 16% to 40%; in this region, degree of dissociation also increased from 15% to 42%.

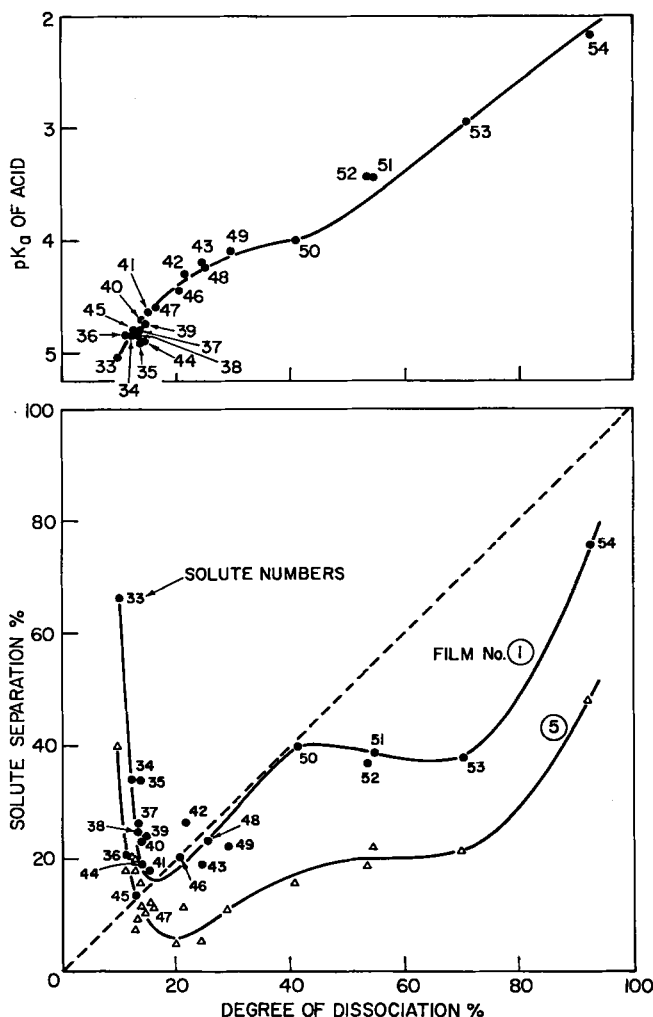


Fig. 6. Correlation of pK_a , degree of dissociation, and solute separation in reverse osmosis separation of monocarboxylic acids. Operating pressure, 250 psig; feed concentration, 0.0006 to 0.0008 g-mole/l. Solute numbers same as given in Table I.

This result is understandable on the basis that, in the above pK_a region, V_u is close to 1, as shown in Figure 4, and solute separation is entirely due to the repulsion of the ionized species at the membrane-solution interface. The proximity of the solute separation data with those of degree of dissociation of acid indicates that the average pore size on the surface of the membrane used was close to the critical pore size with respect to the ionized acid.

In the pK_a region of 3.9 to 2.9, solute separation changed very little and showed a tendency to pass through a slight minimum even though the degree of dissociation of the acid in the feed solution increased from 42% to 70%. These results indicate the existence of opposing effects on solute

separation. Figure 4 shows that in the above pK_a region, V_u is greater than 1, which means that the un-ionized solute permeates through the membrane preferentially. Consequently, the overall solute separation shown in Figure 6 is the net result of positive solute separation caused by the repulsion of ions and the negative solute separation caused by the preferential sorption of the unionized acid at the membrane-solution interface.

In the pK_a region of 2.9 to 2.17, solute separation showed a steep increase; in this region, degree of dissociation of acid increased from 70% to 92%. The steep increase in solute separation in the above region is understandable on the basis that in this region of pK_a values, the dissociation effect is progressively more predominant.

The shape of the degree of dissociation-solute separation curve for film 5 is essentially similar to the corresponding curve for film 1. Since the average pore size on the membrane surface was bigger for film 5, more of the bulk solution including the dissociated acid permeated through the latter membrane, thus causing correspondingly lower solute separations.

Separation of Dicarboxylic Acids in Aqueous Solutions

Reverse osmosis separations of seven dicarboxylic acids of the general formula $\text{HOOC}(\text{CH}_2)_n\text{COOH}$, with $n = 0, 1, 2, 4, 5, 6,$ or 7 (solutes 55 to 61 in Table I), were studied, using an acid concentration of 0.0016 g-mole/l. in the feed solutions. The experimental data were correlated with the degree of dissociation of the acid in the feed solution and the Taft number for the substituent group in the acid. The methods of calculation of degree of dissociation and estimation of Taft number together with the results of correlation of experimental data are discussed below.

Calculation of Degree of Dissociation of a Dibasic Acid. The dissociation of a dibasic acid, H_2A , may be represented as follows:



from which two dissociation constants, K_1 and K_2 , for the acid are obtained as

$$K_1 = \frac{x_{\text{H}^+} \cdot x_{\text{HA}^-}}{x_{\text{H}_2\text{A}}} \quad (15)$$

and

$$K_2 = \frac{x_{\text{H}^+} \cdot x_{\text{A}^{2-}}}{x_{\text{HA}^-}} \quad (16)$$

where x_{H^+} , x_{HA^-} , $x_{\text{H}_2\text{A}}$, and $x_{\text{A}^{2-}}$ denote the concentration of each species at equilibrium. Let x_0 represent the total initial concentration of H_2A in feed solution. From material balance and electroneutrality considerations,

$$x_{\text{H}_2\text{A}} = x_0 - x_{\text{HA}^-} - x_{\text{A}^{2-}} \quad (17)$$

$$x_{\text{H}^+} = x_{\text{HA}^-} + 2x_{\text{A}^{2-}} \quad (18)$$

Equations (15) to (18) may be combined to give^{5a}

$$x_{H^+}^3 + x_{H^+}^2 K_1 - x_{H^+}(K_1 x_0 - K_1 K_2) - 2K_1 K_2 x_0 = 0. \quad (19)$$

Dividing eq. (19) by x_0^3 ,

$$\left(\frac{x_{H^+}}{x_0}\right)^3 + \left(\frac{x_{H^+}}{x_0}\right)^2 \left(\frac{K_1}{x_0}\right) - \left(\frac{x_{H^+}}{x_0}\right) \left\{ \left(\frac{K_1}{x_0}\right) - \left(\frac{K_1}{x_0}\right) \left(\frac{K_2}{x_0}\right) \right\} - 2 \left(\frac{K_1}{x_0}\right) \left(\frac{K_2}{x_0}\right) = 0. \quad (20)$$

Equation (20) can be written as

$$p^3 + ap^2 + bp + c = 0 \quad (21)$$

where

$$p = \left(\frac{x_{H^+}}{x_0}\right) \quad (22)$$

$$a = \left(\frac{K_1}{x_0}\right) \quad (23)$$

$$b = - \left\{ \left(\frac{K_1}{x_0}\right) - \left(\frac{K_1}{x_0}\right) \left(\frac{K_2}{x_0}\right) \right\} \quad (24)$$

and

$$c = -2 \left(\frac{K_1}{x_0}\right) \left(\frac{K_2}{x_0}\right). \quad (25)$$

It is obvious that $p = 0$ when the degree of dissociation is zero, and $p = 2$ when the acid is completely dissociated. Equation (21) may be solved numerically for p using the Newton algorithm of successive approximations.¹⁴ Once the value of p is known, the degree of dissociation (d.d.) is calculated from the relation:

$$\text{d.d.} = 1 - \frac{x_{H_2A}}{x_0} = \frac{\frac{a}{p} + p}{\frac{a}{p} + 2} \quad (26)$$

which can be derived from eqs. (15), (17), and (18).

Estimation of Taft Numbers for Dicarboxylic Acids. The procedure used for estimating Taft numbers for dicarboxylic acids is the same as that used earlier¹² with respect to polyhydric alcohols. Thus, the Taft number for the dicarboxylic acid is simply twice the Taft number for the substituent group in the molecule obtained by replacing one of the $-\text{COOH}$ groups by a hydrogen atom. As before,¹² σ^* for the substituent group $n\text{-C}_6\text{H}_{11}$ was taken to be -0.133 , and that for $n\text{-C}_n\text{H}_{2n+1}$, where $n = 6$ or more, was taken to be -0.134 ; the σ^* values for the other substituent groups were taken from Taft.⁷

Correlation of Taft Number ($\Sigma\sigma^*$), Degree of Dissociation, and Data on Membrane Performance. Figure 7 illustrates the correlation of the acidity parameter $\Sigma\sigma^*$ for the acid with its degree of dissociation in the feed solution and overall solute separation and product rate in reverse osmosis.

As in Figure 6, the shape of the curve for film 1, representing the correlation of degree of dissociation and solute separation, is particularly illustrative of the preferential sorption characteristics of the ionized and un-ionized solute at the membrane-solution interface. The shape of the corresponding curve for film 5 is similar. Referring to solute separation data for film 1, the shape of the above curve may be discussed in three parts each part corresponding to a different $\Sigma\sigma^*$ region.

In the $\Sigma\sigma^*$ region of 0.98 to 0, solute separation decreased from 94% to 56% and the degree of dissociation also decreased from 98% to 61%. The proximity of the solute separation data with those of degree of dissociation indicates that in the above acidity region, V_u is close to 1, and solute separation is predominantly due to the repulsion of the ionized species at the membrane-solution interface.

In the $\Sigma\sigma^*$ region 0 to -0.260 , solute separation decreased from 56% to 40% and the degree of dissociation decreased from 61% to 15%. The extent of decrease in solute separation was considerably small relative to the extent of decrease in degree of dissociation, and at $\Sigma\sigma^* = -0.260$, solute separation was 40% while degree of dissociation was only 15%. These results indicate that in the above region of acidity, the preferential sorption characteristics of both ionized and un-ionized molecule effect overall solute separation in reverse osmosis. The results are understandable on the basis that the observed overall solute separation is the combined result of decrease in degree of dissociation which tends to decrease solute separation and decrease in $\Sigma\sigma^*$ which tends to increase solute separation.

In the $\Sigma\sigma^*$ region of -0.260 to -0.268 , degree of dissociation decreased only slightly (from $\sim 15\%$ to 11%), whereas solute separation decreased steeply (from 40% to 16%). Since the degree of dissociation involved was $< 15\%$ in all the three cases tested, solute separation may be expected to be governed predominantly by the preferential sorption characteristics of the undissociated acid. In any case, a decrease in the degree of dissociation tends to decrease solute separation whereas a decrease in $\Sigma\sigma^*$ tends to increase solute separation. In view of these opposing tendencies, one would expect very little change in solute separation in the above region of acidity. But the experimental data were otherwise, indicating the possible existence of factors other than polar effect which simultaneously govern solute separation in reverse osmosis.

On the basis of similar data reported earlier for the separation of C_4 - C_7 alcohols, it has already been pointed out that solute separation should also be expected to be governed by the nonpolar character of the solute molecule.¹² Since each of the acids studied in the above acidity range (solutes 59, 60, and 61) involves three or more straight-chain carbon atoms *not* associated with a $-\text{COOH}$ group, each acid may be expected to exhibit

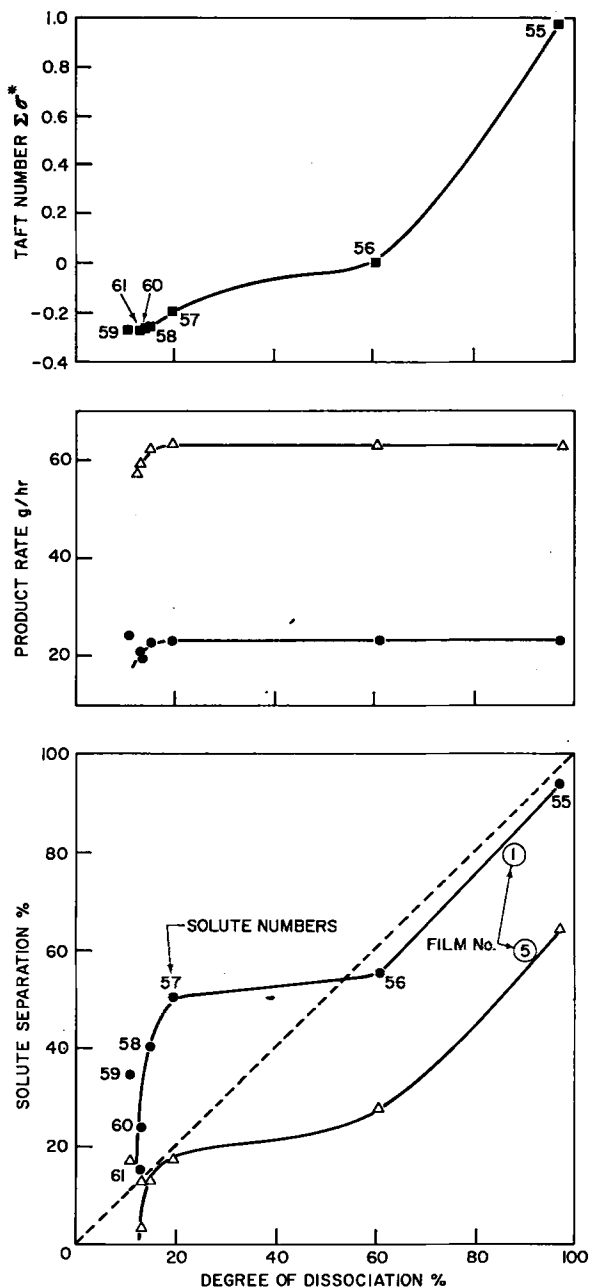


Fig. 7. Correlation of Taft number, degree of dissociation, solute separation and product rate in reverse osmosis separation of dicarboxylic acids. Operating pressure, 250 psig; feed concentration, 0.0016 g-mole/l. Solute numbers same as given in Table I.

significant nonpolar effect which tends to attract the molecule toward the membrane surface. The result of this attraction is either to reduce the preferential sorption of water or to promote the preferential sorption of solute at the membrane-solution interface. Thus, the steep decrease in solute separation in the $\Sigma\sigma^*$ range of -0.260 to -0.268 is understandable on the basis of the nonpolar effect of the solute molecule concerned. This basis is further supported by the tendency of the corresponding product rate data to decrease, indicating partial blocking of pores by solute molecules attracted to the membrane surface.

Separation of Hydroxycarboxylic Acids in Aqueous Solutions

The reverse osmosis separations of lactic acid, *d,l*-malic acid, tartaric acid, and citric acid were studied in the concentration range of 0.00045 to 0.0545 g-mole/l. (49 to 4900 ppm of acid). The degree of dissociation of acid in the feed solution was calculated in each case by the method described earlier for monocarboxylic and dicarboxylic acids. In the case of citric acid which contains three $-\text{COOH}$ groups, the lowest two $\text{p}K_a$ values were used for calculating the degree of dissociation.

Figure 8 shows the degree of dissociation versus solute separation correlations for films 1 and 3. Some results obtained with monocarboxylic acids are also given in Figure 8 for comparison. The corresponding product rate data (not included in Fig. 8) showed no significant change. Solute separation was generally in the order monohydroxytricarboxylic acid (citric) > dihydroxydicarboxylic acid (tartaric) > monohydroxydicarboxylic acid (malic) > monohydroxymonocarboxylic acid (lactic) > monocarboxylic acids (acetic, propionic, butyric, valeric, and benzoic). The above order indicates that an increase in the number of polar functional groups in the solute molecule results in higher preferential sorption for

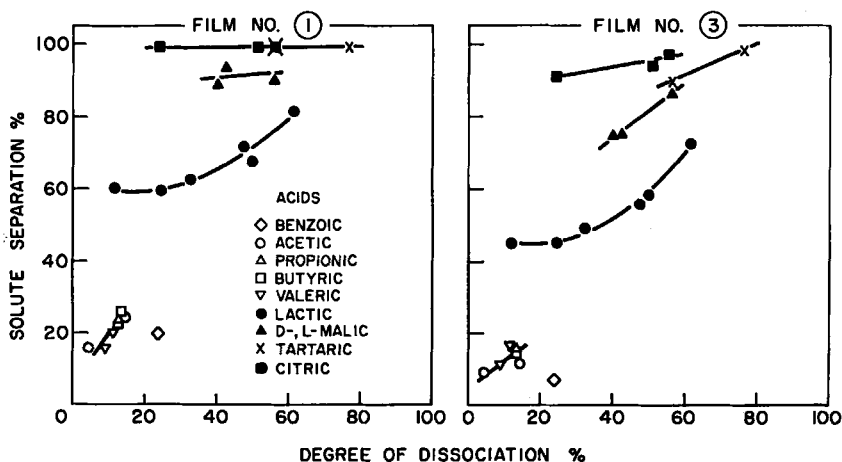


Fig. 8. Effect of degree of dissociation on reverse osmosis separation of acids. Operating pressure, 250 psig.

TABLE II
Relative Values of V_u for Hydroxycarboxylic Acids

Solute no.	Acid	$\Sigma\sigma^*$	V_u	
			Film 1	Film 5
62	Lactic acid	-0.2	0.44	0.74
63	D,L-Malic acid	-0.3	0.13	0.41
64	Tartaric acid	-0.4	~0	0.20
65	Citric acid	-0.61	~0	0.10

water and hence higher solute separation in reverse osmosis. Further, solute separation increased with increase in degree of dissociation of the acid in all cases.

The Taft numbers for hydroxycarboxylic acids were estimated by the same technique reported earlier for polyhydric alcohols.¹² While each monocarboxylic acid has naturally a single Taft number, each hydroxycarboxylic acid has two Taft numbers, one for each functional group, as given in Table I. The Taft number ($\Sigma\sigma^*$) for each hydroxycarboxylic acid is arbitrarily expressed as the sum of its Taft numbers for each functional group ($\sigma^*_{\text{COOH}} + \sigma^*_{\text{OH}}$) in Table II which also gives values of V_u for each acid calculated by the technique described earlier using an average constant value of $(D_{AM}/K\delta)_i$ obtained for monocarboxylic acids. In spite of the approximations involved in the estimations of $\Sigma\sigma^*$ and $(D_{AM}/K\delta)_i$ values, the general trend in the correlation of $\Sigma\sigma^*$ with V_u is significant. The results show that as $\Sigma\sigma^*$ decreases, V_u approaches zero. This means that as the magnitude of $\Sigma\sigma^*$ for the acid molecule becomes more negative, the undissociated acid is repelled to a greater extent resulting in an increase in the extent of preferential sorption for water at the membrane-solution interface with consequent increase in solute separation in reverse osmosis. Referring to data for film 1, Table II shows that the undissociated citric acid ($\Sigma\sigma^* = -0.61$) and the undissociated tartaric acid ($\Sigma\sigma^* = -0.40$) were almost completely separated under the specified reverse osmosis operating conditions.

CONCLUSIONS

The basic criterion of acidity of the molecule governing the extent of its repulsion or attraction at the membrane-solution interface is valid for both ionized and un-ionized acid. With respect to un-ionized acid, at $\text{p}K_a = 4.2$ (for monocarboxylic acids), or σ^* (or $\Sigma\sigma^*$) = 0.6, or $\sigma = 0$, neither acid nor water is preferentially sorbed at the membrane-solution interface. At $\text{p}K_a < 4.2$ (for monocarboxylic acids) or σ^* (or $\Sigma\sigma^*$) > 0.6 or $\sigma > 0$, the un-ionized acid is preferentially sorbed at the membrane-solution interface. For practical purposes, preferential sorption of water at the membrane-solution interface may be considered negligible in the σ^* (or $\Sigma\sigma^*$) region of 0 to 0.6. The foregoing physicochemical criteria for preferential sorption

are applicable for monocarboxylic, dicarboxylic, and hydroxycarboxylic acids in aqueous feed solutions used in conjunction with porous cellulose acetate membranes in reverse osmosis at the pressure and temperature conditions studied in this work.

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