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Physicochemical Criteria for Reverse Osmosis Separation of Alcohols, Phenols, and Monocarboxylic Acids in Aqueous Solutions Using Porous Cellulose Acetate Membranes

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Synopsis

Reverse osmosis data of 32 different alcohols and phenols and 22 different monocarboxylic acids in aqueous solutions in the concentration range 0.0001 to 0.007M ($\backsim$100 ppm in most cases) have been studied using porous cellulose acetate membranes at 250 psig. Solute separation data for alcohols and phenols are correlated with $\Delta\nu_s$ (shift in the OH band maximum in the IR spectra), and those for the monocarboxylic acids are correlated with K_a (dissociation constant) and the degree of dissociation of the molecule. Solute separation decreases with increase in $\Delta\nu_s$ for alcohols and phenols. The solute separation-versus-K_a correlation for acids passes through a minimum, and solute separation always increases with increase in the degree of dissociation. The separation data are also correlated with Taft and Hammett numbers which represent the effect of the substituent group on the polar effect of the molecule. The product rate data show a general tendency to decrease with decrease in solute separation in all cases. These results show that, with respect to the systems considered, solute separation in reverse osmosis is governed by the hydrogen bonding ability of the organic molecule when it is essentially undissociated and by electrostatic repulsion of ions when the molecule is partially or completely dissociated. Thus, data on $\Delta\nu_s$ for alcohols and phenols, and those on K_a and degree of dissociation for monocarboxylic acids, constitute precise physicochemical criteria for reverse osmosis separation of the above solutes in aqueous solutions using porous cellulose acetate membranes.

INTRODUCTION

Reverse osmosis separations of organic solutes in aqueous solutions using asymmetric porous cellulose acetate membranes are of interest from the point of view of both the mechanism of the process as well as its application for waste water treatment and water pollution control.[1–5] Kesting and Eberlin[3] studied such separations with respect to a number of C_3 and C_4 compounds with different functional groups, including alcohol and monocarboxylic acid. They used a feed concentration of 1% by weight of solute in water and an operating pressure of 102 atm in each case. They tried to correlate solute transport through the membrane with the hydrogen bonding index of the solute; the latter was defined as the wavelength of maximum absorption of the third water band (in millimicrons) when 1%

by weight of water was dissolved in the permeant species. This index was taken as a measure of the capacity of the solute for hydrogen bonding with water. Even though a plot of their data on hydrogen bonding index versus solute separation does not yield any consistent correlation for all the solutes studied, most of their data do indicate the existence of a general correlation showing an increase in solute permeation with increase in hydrogen bonding index.

Duvel, Helfgott, and Genetelli[5] studied the separation of several organic solutes, including alcohols and acids, using cellulose acetate membranes and feed concentrations in the range 0.001 to 0.01M at an operating pressure of 600 psig and a temperature of 40°C. With respect to alcohols, their results are briefly as follows: Primary alcohols with no side chain pass through the membrane readily; primary alcohols with single methyl side group, or unbranched secondary alcohols where the hydroxyl off to the side acts as a single branch, are separated better; and tertiary alcohols or doubly branched primary and secondary alcohols are separated still better. According to the above authors, all alcohols are expected to have the same chemical affinity for the membrane, and differences in separation are primarily due to differences in diffusion rates of the solutes across the membrane. They correlated the separation of alcohols with the cross-sectional area of the molecule. Duval et al.[5] also studied the separation of a series of C_4 compounds of similar size and shape but different chemical characteristics and established the following order of solute separation: butyric acid < 1-butylamine, butyramide, 1-butanol < diethyl sulfone, butyraldehyde, 2-butanone < methyl propionate, ethyl acetate. These results were explained mainly on the basis of the differences in the solubility of the solute in the membrane depending on the degree of hydrogen bonding between the solute and the membrane. They, however, used no physicochemical parameter as a measure of hydrogen bonding and developed no quantitative correlation between solute separation and the chemical nature of the solute molecule.

The object of this program of work is to establish useful correlations between physicochemical parameters of organic molecules and their separations from aqueous solutions by reverse osmosis, using asymmetric porous cellulose acetate membranes. This paper is concerned with the separation of alcohols, phenols, and monocarboxylic acids. This work follows a different approach to the subject.

In this approach, solute separation in reverse osmosis is thought of as a function of the extent of preferential sorption of water by the membrane material and the porous structure of the membrane surface. Consequently, the separation data obtained with a given membrane–solution-operating system do not represent the limiting values for the process. With reference to a given membrane material, preferential sorption of water is a function of the chemical nature of the organic solute. Both the functional group (—OH, —COOH, etc.) and the substituent group in the organic molecule affect preferential sorption of water, and hence solute

separation. Therefore, the chemical nature of the solute is treated first in terms of the different functional groups, and then, within each functional group, the substituent group is explicitly differentiated in quantitative terms. One of the physicochemical criteria governing reverse osmosis separation of organic solutes in aqueous solution is the polar effect of the solute molecule, which includes the effects of both the functional group and the substituent. For the separation of alcohols, phenols, and monocarboxylic acids, acidity (or the proton-donating characteristic of the molecule) is considered to be the relevant expression of the polar effect of the molecule. A measure of acidity is given by the ease of hydrogen bond formation and/or the degree of dissociation of the molecule in solution. The relative hydrogen-bonding ability of the solute, representing the relative acidity of the molecule, is quantitatively expressed by the shift in the OH band maximum in the IR spectra ($\Delta\nu_s$).[6] The degree of dissociation is quantitatively expressed by the dissociation constant (K_a) for the molecule[7] and its concentration in solution. Thus, quantitative data on $\Delta\nu_s$ and K_a represent acidity parameters as relevant expressions of the polar effect of the molecules; these parameters are naturally related to Taft and Hammett numbers[8] which give a quantitative measure of the effect of the substituent on the polar effect of the molecules. Consequently, in this work, separation data for alcohols and phenols are correlated with $\Delta\nu_s$, and those for the monocarboxylic acids are correlated with K_a and the degree of dissociation; all the data are also correlated with Taft and Hammett numbers. These correlations give a consistent picture of the experimental separation data for alcohols, phenols, and monocarboxylic acids, and hence make a significant contribution to the development of precise physicochemical criteria of preferential sorption in reverse osmosis.

EXPERIMENTAL

Reverse Osmosis Experiments

Organic solute substances in the concentration range 0.0001 to 0.007 g-mole/l. and laboratory-made Batch 316-type porous cellulose acetate membranes were used. The apparatus and film details have been reported.[9,10] The film casting conditions used were as follows: casting solution composition—cellulose acetate (acetyl content 39.8%), 17.0 wt-%; acetone, 69.2 wt-%; magnesium perchlorate, 1.45 wt-%; and water, 12.35 wt-%; temperature of casting solution, 0°C; temperature of casting atmosphere, 24°C; casting atmosphere—ambient air in contact with aqueous solution of 30 wt-% acetone; solvent evaporation time, 6 min; gelation period in ice-cold water, >1 hr; and nominal film thickness, ~0.005 in. Membranes shrunk at different temperatures were used to give different levels of solute separation at a given set of operating conditions. The effective area of film used was 7.6 cm^2 in all cases. All mem-

branes were subjected to an initial pure water pressure of 300 psig for about 2 hr, prior to subsequent use in reverse osmosis experiments, all of which were carried out at 250 psig at the laboratory temperature (23–25°C) using a feed flow rate of 400 cc/min. Since the feed concentrations were very small (~100 ppm in most cases), the osmotic pressure and other effects[11,12] on solute separation were essentially eliminated. The 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 of pressure, feed concentration, and feed flow rate. 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 Tables II and III.

Data on solute separation and membrane flux have firm significance only when the membranes and feed flow conditions used are specified.[13] Table I gives data on specifications of the membranes used, in terms of the pure water permeability constant A and the solute transport parameter $D_{AM}/K\delta$ for sodium chloride; these data were obtained from the experimental [PWP], [PR], and solute separation data for the reference solution system sodium chloride–water. 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 57×10^{-4} cm/sec for the reference solution system containing 1500 ppm of salt. Table I also gives some performance data for the

TABLE I
Specifications of Membranes and Some Performance Data[a]

Film no.	1	2	3
Film shrinkage temperature, °C	81	78	75
Pure water permeability constant A, $\left(\frac{\text{g-mole}}{\text{cm}^2\cdot\text{sec}\cdot\text{atm}}\right) \times 10^6$	2.48	3.53	5.35
Solute transport parameter $(D_{AM}/K\delta)_{NaCl}$, (cm/sec) $\times 10^5$	3.22	9.50	16.89
Performance data:			
Feed concentration, ppm NaCl	1500	1500	1500
Mass transfer coefficient k, (cm/sec) $\times 10^4$	57	57	57
Solute separation, %	94.7	90.4	87.0
Product rate, gal/day·ft^2	14.83	21.31	32.02

[a] Film type: Batch 316; operating pressure: 250 psig; solution system: sodium chloride–water.

latter system to illustrate the productivity of the particular membranes used in this work.

Analysis

The Beckman total carbon analyzer, Model 915, was used to measure the concentrations of alcohols and aliphatic carboxylic acids. In this apparatus, the solution sample was injected and swept by an air stream into a high-temperature (~950°C) catalytic combustion tube where the total carbon in the sample was oxidized to CO_2 which was analyzed by a Beckman Model IR-215A nondispersive infrared analyzer. A blank experiment with distilled water used for dissolving the organic solute was also carried out. After subtracting the carbon content in the blank sample (usually less than 4 ppm) from that in the solution sample, the concentration of the alcohol or the acid in the sample was calculated. A sample size of 20 microliters and an air flow rate of 150 cc/min were used for the analysis. Several injections (usually five or more) were made to confirm the peak heights obtained for each sample. The total carbon content in the solution sample was obtained from predetermined calibration curves. The accuracy of the analysis was ±1 ppm in terms of carbon content.

The concentrations of phenols and aromatic carboxylic acids were measured by determining the ultraviolet absorption maxima in the wavelength region 223 to 315 millimicrons.[14-16] A Beckman Model D-1 double-beam-recording ultraviolet spectrophotometer was used. Absorption spectra were scanned downward from 350 millimicrons to find the exact wavelength for maximum absorption. All spectral measurements were made in a 1-cm quartz cell. Lambert-Beer's law was followed excellently by each substance in a certain concentration range which was determined and used for analysis. Calibration curves were prepared separately for each substance and for each pH change when the latter changed absorption maximum and extinction coefficient. The accuracy of analysis was ±1% in all cases.

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

IR Spectra

A grating infrared spectrophotometer (Perkin Elmer Model 621) was used to obtain accurate readings of frequencies corresponding to the OH band maximum for a number of alcohols and phenols in carbon tetrachloride and ether solutions; the shift in the frequency of the OH band maximum ($\Delta\nu_s$, cm^{-1}) was measured in each case following the method of Barrow.[17] The resolving power of the instrument was 0.3 cm^{-1} at 1000 cm^{-1}, and the spectral slit widths were 2.63 and 3.10 cm^{-1} at frequencies of 3000 and 3500 cm^{-1}, respectively. A cell length of 1 mm was used. Reagent-grade carbon tetrachloride and absolute ether were used as

solvents. The solute concentration used for IR spectra was 0.025 g-mole/l. except in case of some phenols which were not soluble in carbon tetrachloride to that extent; in the latter case, saturated solutions were used. All measurements were made at room temperature (23–25°C). The frequency measurements had an accuracy of ± 1 cm^{-1} in carbon tetrachloride solutions and ± 2 cm^{-1} in ether solutions.

RESULTS AND DISCUSSION

Acidity Parameters

The work of Barrow[17] is the basis for correlating data on $\Delta\nu_s$, as measured in this work, with the relative hydrogen-bonding ability of alcohols and phenols in aqueous solution under the reverse osmosis operating conditions. According to Barrow, $\Delta\nu_s$ is a measure of the stretching of the OH bond corresponding to the incipient ionization of the alcohol or phenol molecule in ether solution, with the hydrogen atom becoming more positively charged. Consequently an increase in the value of $\Delta\nu_s$ means that the molecule is approaching more the limiting case of the ion pair consisting of alkoxide ion and protonated ether. Thus $\Delta\nu_s$ constitutes an effective quantitative measure of the relative acidity, or the proton donating characteristic, of the molecule for the practically nonionic alcohols and phenols.

On the other hand, the monocarboxylic acids are significantly ionizable; for them, the dissociation constant K_a (or $pK_a = -\log K_a$) gives a quantitative measure of the acidity of the molecule. The dissociation of a monocarboxylic acid (RCOOH) can be expressed as

$$K_a[\mathrm{RCOOH}] = [\mathrm{RCOO^-}][\mathrm{H^+}] \tag{1}$$

or

$$K_a(x_0 - x) = x^2 \tag{2}$$

where x_0 and x represent, respectively, the initial concentration of acid (g-mole/l.) and the concentration of each of the ionic species in solution. Equation (2) yields

$$\frac{x}{x_0} = \sqrt{{}^1/_4\left(\frac{K_a}{x_0}\right)^2 + \left(\frac{K_a}{x_0}\right)} - {}^1/_2\left(\frac{K_a}{x_0}\right). \tag{3}$$

Thus from data on K_a and x_0, the degree of dissociation, x/x_0, can be calculated from eq. (3).

Table II gives the experimental data on $\Delta\nu_s$ obtained for all the alcohols and phenols studied in this work. The corresponding data available from the literature[17,18] are also included in the table for comparison; though there are some differences in the actual data, they all follow the same order. The data obtained in this work are used in the correlations discussed below.

TABLE II
Acidity Parameters for Alcohols and Phenols

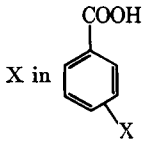
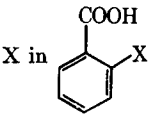
Solute No.	Solute			$\Delta\nu_s$, cm^{-1}			σ^* or σ
	Name	Formula	Molecular Weight	This Work	Ref. 17 (Barrow)	Ref. 18 (Kuhn)	(Ref. 8)
		R in ROH					σ^*
1	t-Butyl alcohol	t-C_4H_9	74.1	123	116	128	-0.300
2	3-Pentanol	3-C_5H_{11}	88.2	136	-	-	-0.225
3	s-Butyl alcohol	s-C_4H_9	74.1	137	123	135	-0.210
4	i-Propyl alcohol	i-C_3H_7	60.1	135	122	-	-0.190
5	Cyclohexanol	cyclo-C_6H_{11}	102.2	129	-	-	-0.150
6	n-Butyl alcohol	n-C_4H_9	74.1	145	135	150	-0.130
7	i-Butyl alcohol	i-C_4H_9	74.1	140	-	-	-0.129
8	n-Propyl alcohol	n-C_3H_7	60.1	141	-	-	-0.115
9	Ethyl alcohol	C_2H_5	46.1	143	133	-	-0.100
10	Methyl alcohol	CH_3	32.0	149	136	151	0
11	Phenethyl alcohol	$C_6H_5(CH_2)_2$	122.2	163	-	-	+0.08
12	Benzyl alcohol	$C_6H_5(CH_2)$	108.1	156	-	-	+0.215
13	Phenol	C_6H_5	94.1	288	276	278	+0.600
14	n-Amyl alcohol	n-C_5H_{11}	88.2	142	-	-	-
15	n-Hexyl alcohol	n-C_6H_{13}	102.2	144	-	-	-
16	n-Heptyl alcohol	n-C_7H_{15}	116.2	145	-	-	-
17	n-Octyl alcohol	n-C_8H_{17}	130.2	142	-	-	-
		X in 					σ
18	p-Aminophenol	p-NH_2	109.1	-	-	-	-0.660
19	Hydroquinone	p-OH	110.1	-			-0.357
20	p-Methoxyphenol	p-OCH_3	124.1	283			-0.268
21	p-Cresol	p-CH_3	108.1	286			-0.170
22	m-Aminophenol	m-NH_2	109.1	-	-	-	-0.161
23	m-Cresol	m-CH_3	108.1	283			-0.069
24	Resorcinol	m-OH	110.1	284			-0.002
13	Phenol	-	94.1	288	276	278	0.000
25	p-Chlorophenol	p-Cl	128.6	313	-	-	+0.227
26	m-Chlorophenol	m-Cl	128.6	315	-	-	+0.373
27	m-Nitrophenol	m-NO_2	139.1	407	-	-	+0.710
28	p-Nitrophenol	p-NO_2	139.1	-	-	-	+0.778
		X in 					σ^*
29	o-Cresol	CH_3	108.1	282			-0.17
13	Phenol	H	94.1	288	276	278	0
30	o-Chlorophenol	Cl	128.6	-			+0.20
31	o-Nitrophenol	NO_2	139.1	-			+0.80
32	Pyrocatechol	OH	110.1	291			-

Table III gives data on pK_a obtained from the literature[7] for all the monocarboxylic acids studied in this work.

The Hammett and Taft Numbers

Within reaction series of the *m*- and *p*-substituted derivatives of benzene, the effect of structure on rates or equilibria is nearly always determined by the polar effect of the substituent. This is expressed by the Hammett equation:

TABLE III
Acidity Parameters for Monocarboxylic Acids

Solute no.	Solute: Name	Solute: Formula	Molecular weight	pK_a (ref. 7)	σ^* or σ (ref. 8)
		R in RCOOH			σ^*
33	Pivalic acid	t-C_4H_9	102.1	5.05	−0.300
34	i-Butyric acid	i-C_3H_7	88.1	4.86	−0.190
35	Cyclohexanecarboxylic acid	cyclo-C_6H_{11}	128.2	4.91	−0.150
36	Valeric acid	n-C_4H_9	102.1	4.86	−0.130
37	n-Butyric acid	n-C_3H_7	88.1	4.83	−0.115
38	Propionic acid	n-C_2H_5	74.1	4.87	−0.100
39	Acetic acid	CH_3	60.1	4.75	0
40	4-Phenylbutyric acid	$C_6H_5(CH_2)_3$	164.2	4.73	+0.020
41	β-Phenylpropionic acid	$C_6H_5(CH_2)_2$	150.2	4.66	+0.080
42	Phenylacetic acid	$C_6H_5(CH_2)$	136.1	4.31	+0.215
43	Benzoic acid	C_6H_5	122.1	4.20	+0.600
44	Caprylic acid	n-C_7H_{15}	144.2	4.90	—
					σ
45	p-Aminobenzoic acid	p-NH_2	137.1	4.82	−0.660
46	Anicic acid	p-OCH_3	152.1	4.47	−0.268
47	m-Aminobenzoic acid	m-NH_2	137.1	4.60	−0.161
48	m-Toluic acid	m-CH_3	136.1	4.24	−0.069
49	m-Hydroxybenzoic acid	m-OH	138.1	4.08	−0.002
43	Benzoic acid	—	122.1	4.20	0
50	p-Chlorobenzoic acid	p-Cl	156.6	3.99	+0.227
51	m-Nitrobenzoic acid	m-NO_2	167.1	3.45	+0.710
52	p-Nitrobenzoic acid	p-NO_2	167.1	3.44	+0.778
					σ^*
43	Benzoic acid	H	122.1	4.20	0
53	o-Chlorobenzoic acid	Cl	156.6	2.94	+0.20
54	o-Nitrobenzoic acid	NO_2	167.1	2.17	+0.80

$$\log\left(\frac{k}{k_0}\right) = \sigma\rho \tag{4}$$

where k and k_0 represent the rate or equilibrium constants for a given reaction and a standard reaction, respectively; σ is a substituent constant (called Hammett number) independent of the nature of the reaction; and ρ is a proportionality constant dependent on the nature of the reaction and reaction conditions. For obtaining the values of σ, Hammett selected as the standard reaction the ionization of substituted benzoic acids in

water at 25°C, i.e., $\sigma \equiv \log (k/k_0)$ for the above reaction, where the subscript zero refers to the unsubstituted benzene derivative. Thus, the Hammett number σ is a quantitative measure of the polar effect of a given *m*- or *p*-substituent relative to a hydrogen atom in any reaction.

The Hammett equation is limited to polar effects on reactions of aromatic *m*- and *p*-substituents which are remote enough within the molecule not to involve interference from primary steric effects.

In reactions involving aromatic ortho compounds and aliphatic compounds, the substituent group is close to the reaction center. For such reactions Taft's equation is applicable. Taft defined

$$\sigma^* = \frac{1}{2.48}\left[\log\left(\frac{k}{k_0}\right)_B - \log\left(\frac{k}{k_0}\right)_A\right] \tag{5}$$

where σ^* is a polar substituent constant called Taft number; k and k_0 are the rate constants for the hydrolyses of RCOOR′ and CH_3COOR', respectively; and the subscripts B and A refer respectively to alkaline and acid hydrolyses carried out for the same R′ under identical experimental conditions; the arbitrary constant 2.48 adjusts σ^* to the same scale as that of σ. The assumption here is that the mechanisms for acidic and alkaline hydrolyses are similar, and hence resonance and steric effects essentially cancel out; consequently, the quantity $\log (k_B/k_A)$ and hence σ^* give a measure entirely of the polar effect of the substituent. The same approach was applied to ortho-substituted benzenes using the hydrolysis of ortho-$CH_3C_6H_4COOR'$ as the standard reaction. Taft proposed that the changes induced by substituents in log k in reactions other than those of ester hydrolysis (for which substituent constants σ^* can be determined) would be proportional to the σ^* values of the substituents as given by ester hydrolysis. Consequently, the Taft equation, analogous to the Hammett equation, is

$$\log\left(\frac{k}{k_0}\right) = \sigma^*\rho^*. \tag{6}$$

The Taft number σ^* is entirely analogous to the Hammett number σ, but of different origin.

The significance of Taft (σ^*) and Hammett (σ) numbers is discussed extensively in the literature.[8,19–21] The object of the foregoing review is simply to point out that (i) both σ and σ^* quantitatively express the effect of the substituent group on the polar effect of the organic molecule; (ii) the data on σ are applicable to *m*- and *p*-substituted aromatic compounds, and those on σ^* are applicable to aliphatic compounds, phenol, and ortho-substituted aromatic compounds; (iii) both σ and σ^* are independent of the nature of the reaction considered and hence have wide general applicability; and (iv) with reference to a given functional group, a lower value of σ or σ^* indicates lower acidity for the molecule. These inherent characteristics of σ and σ^* offer a basis for the application of these parameters in reverse osmosis to explicitly differentiate each substit-

uent group, within each functional group, in the organic molecule. Extensive data on σ and σ^* are available in the literature,[8] and those relating to the substituents studied in this work are included in Tables II and III.

Separation of Alcohols and Phenols

$\Delta\nu_s$ and Solute Separations. Figure 1 illustrates correlations of $\Delta\nu_s$ of solute versus solute separation and product rate for a number of alcohols and phenols in aqueous solution. Five membranes of different surface porosities were tested, and the data obtained with two of them only are given in Figure 1 for illustration. The performance data obtained with the other films are similar. In all, 32 different alcohols and phenols, listed in Table II, were tested in the concentration range 0.001 to 0.006 g-mole/l. (corresponding to a solute concentration in each case of ~100 ppm).

The data show that there is no necessary correlation between solute separation and molecular weight of solute but that there exists a definite correlation between solute separation and $\Delta\nu_s$ of solute. Solute separation

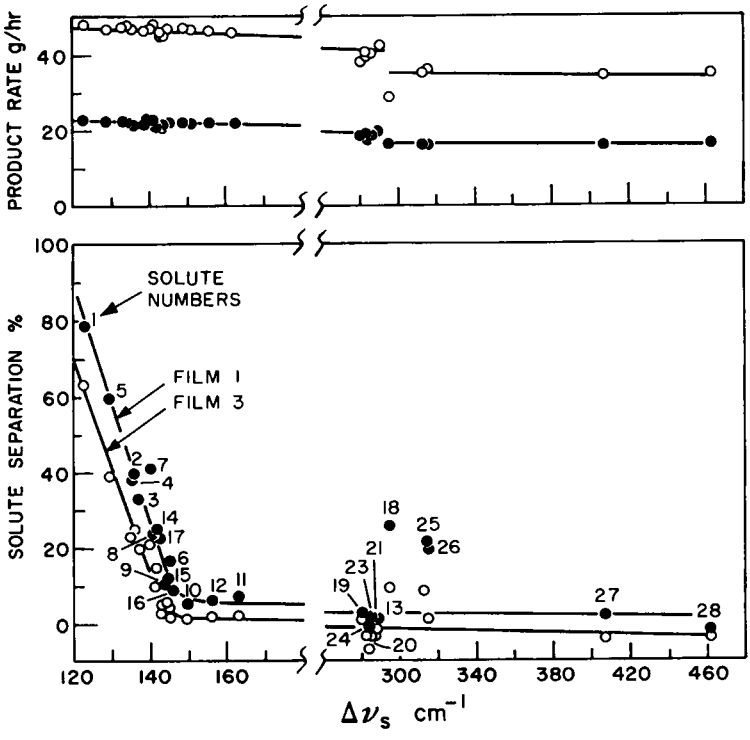


Fig. 1. Effect of $\Delta\nu_s$ of solute on reverse osmosis separation of alcohols and phenols in aqueous solution using porous cellulose acetate membranes. Film type, Batch 316; operating pressure, 250 psig; feed concentration, 0.001 to 0.006 g-mole/l.; feed flow rate, 400 cc/min; membrane area, 7.6 cm^2; (●) film 1; (○) film 3.

decreases with increase in $\Delta\nu_s$, i.e., with increase in the acidity, and hence with the hydrogen bonding ability of the solute molecule. The dissociation constants for alcohols and phenols are extremely small (pK_a for phenol $\sim$10); consequently the solutes exist essentially as molecules in solution. For such solutions, it is only reasonable to expect that preferential sorption of water on the membrane surface (and hence solute separation in reverse osmosis) should decrease with increase in the hydrogen-bonding ability of the molecule.

In any hypothesis concerning reverse osmosis transport, it is the intermediate range of solute separation ($\sim$20 to 80%) which is particularly important for purposes of correlation. This range of separation is given by the data for film 1. With respect to this film, solute separations for *tert*-butyl alcohol and *n*-octyl alcohol are, respectively, 79% and 22%; the corresponding $\Delta\nu_s$ values are 123 and 142 cm^{-1}. In this range of $\Delta\nu_s$ values, the $\Delta\nu_s$-versus-solute separation correlation is linear, and the change in separation with respect to $\Delta\nu_s$ is very steep. The somewhat high separation data for isobutyl alcohol (solute 7) appears as an exception relative to the other solutes in this group. For the same film, solute separations for methyl alcohol and *m*-nitrophenol are, respectively, 6% and 2%; the corresponding $\Delta\nu_s$ values are 149 and 407 cm^{-1}. In this range of $\Delta\nu_s$ values also, the correlation is linear; but the change in separation with respect to $\Delta\nu_s$ is small since the absolute values on solute separations are themselves very small. In the latter range of $\Delta\nu_s$ values, the relatively high solute separations for *p*-aminophenol, *p*-chlorophenol, and *m*-chlorophenol (solutes 18, 25, and 26) appear as apparent exceptions to the correlation; these exceptions probably arise from the fact that in each of the above compounds, the effective functional group is not simply the OH group, and hence the basis for comparison of results needs some modification. All results are similar for film 3.

Aside from the few exceptions noted above, it seems reasonable to conclude from the above results that aliphatic alcohols are in general better separated than the phenols because the former have less hydrogen-bonding ability than the latter as indicated by their relative values of $\Delta\nu_s$. In the scale of $\Delta\nu_s$ values given in this work, alcohols whose values of $\Delta\nu_s$ are less than 145 cm^{-1} can be separated to a significant extent (more than 10%) in practical reverse osmosis operations with porous cellulose acetate membranes of the type used in this work.

Some of the separation data reported in Figure 1 are small negative values, i.e., solute concentration in the product was slightly more than that in the corresponding feed solution. A small negative separation does not necessarily mean that the membrane material has a preferential sorption for the solute molecules. The reported separation data are based on feed concentrations. Even though data on solute separations are negative with respect to feed concentration, they may still be positive with respect to the concentration of the boundary solution, which is usually more for more porous membranes.[22]

The data on the separation of phenol in aqueous solution are particularly significant from the point of view of waste water treatment. Using the Loeb-Sourirajan-type cellulose acetate membranes and aqueous feed solutions containing 70 to 80 ppm of phenol, Lonsdale et al.[23] reported negative separations (i.e., phenol enrichment in permeate) of 10% to 20% in the operating pressure range of 34 to 102 atm at ~30°C; the negative separation increased with increase in operating pressure. In this work, which involves lower operating pressure (17 atm) and temperature (~25°C), the phenol separations obtained with films 1 and 3 were +1% and −2%, respectively; in view of the accuracy of analysis, these data mean that the phenol separation obtained was either negligible or slightly negative with the membranes tested. While these data are qualitatively consistent with those of Lonsdale et al.,[23] they also seem to indicate the need for more extensive studies on the effect of operating conditions on the reverse osmosis separation of phenols in aqueous solutions.

$\Delta\nu_s$ and Product Rates. The $\Delta\nu_s$-versus-product rate data correlation given in Figure 1 is particularly interesting. The product rates show a general decrease with increase in $\Delta\nu_s$ and hence decrease in solute separation. (This change is opposite to that one would expect on the basis of considerations of osmotic pressure whose effect is, in any case, negligible in this work because of the very low feed concentrations.) For $\Delta\nu_s$ values up to ~150 cm^{-1}, the changes in product rate data are within the accuracy of the experimental measurements; even then, the general trend in product rate change is unmistakable. There is, in addition, an abrupt decrease in product rate for systems involving solutes whose $\Delta\nu_s$ values are ~300 cm^{-1} or more; values of $\Delta\nu_s$ higher than 300 cm^{-1} do not seem to result in a further decrease in product rate. The above data on solute separation and product rate were found to be completely reversible for all the films and solutes tested. These results indicate that the solute molecules affect the porous structure of the membrane during reverse osmosis.

According to Wasilewski,[24] almost all the oxygen atoms of the carbonyl groups in the side chains of the cellulose acetate molecule are intramolecularly hydrogen bonded. During heat treatment of the membrane, intramolecular bonds are broken and the carbonyl group rotates about a single bond; this brings two neighboring polymer segments closer together and aids the formation of stronger intermolecular bonds between polymer segments, resulting in a densification of the porous structure of the membrane. A similar phenomenon may be expected to occur when solute molecules capable of intermolecular hydrogen bonding move in sufficiently close proximity to the membrane material. The induced intermolecular hydrogen bonding between the solute and the cellulose acetate molecules may tend to weaken the intramolecular hydrogen bonds in the membrane material and bring the neighboring polymer segments in closer proximity with each other, resulting in a transient densification of the porous structure of the membrane. Such transient densification of the porous structure of the membrane increases its resistance to fluid flow and hence decreases

product rate. This effect may be expected to reach a limiting state, as is evident from the product rate data obtained for solutes whose $\Delta\nu_s$ values are $\sim$300 cm^{-1} or more. When the vicinity of the membrane material is washed free of solute, the solute–membrane interaction is withdrawn and apparently the original porous structure of the membrane is restored.

Thus, the $\Delta\nu_s$-versus-product rate correlation is understandable on the basis of transient densification of the porous structure of the membrane material as a result of induced intermolecular hydrogen bonding between solute and cellulose acetate molecules. It is only reasonable to expect that this effect will be more the closer the solute molecule is to the membrane surface, i.e., when preferential sorption for water, and hence solute separation, is less.

When the transient densification is limited to the porous structure underneath the surface layer of the membrane, the effect is seen only with respect to product rate; if the pore structure on the membrane surface is also affected, then the effect will be seen with respect to solute separation as well. In particular, if the pores on the membrane surface become temporarily smaller during reverse osmosis operation as a result of transient densification on the membrane surface, solute separation will increase significantly. This may also partly explain the apparent exceptions noted earlier with respect to $\Delta\nu_s$-versus-solute separation correlation.

$\Delta\nu_s$ and σ^* or σ. Since $\Delta\nu_s$ represents the total polar effect of the molecule and σ^* and σ represent the contribution of the substituent group to this total effect, unique relationships between $\Delta\nu_s$ and σ^*, and $\Delta\nu_s$ and σ may be expected to exist for a given functional group. This is indeed the case, as illustrated in Figures 2 and 3. Figure 2 is applicable to solutes 1 to 13, and Figure 3 is applicable to solutes 13 and 20 to 27 listed in Table II. Even though there is some scatter of data in Figures 2 and 3, the correlations appear sufficiently satisfactory for practical purposes of estimating $\Delta\nu_s$ by interpolation for compounds for which data on σ^* or σ are available.

One such interpolation offers a pertinent suggestion. According to Taft,[8] the value of σ^* for water is 0.49; from Figure 2, the corresponding value of $\Delta\nu_s$ is $\sim$250 cm^{-1}. It would seem reasonable to suggest that positive separations are obtainable in reverse osmosis for all alcohols and phenols whose $\Delta\nu_s$ values are less than that of water, and negative separations are obtainable for those whose $\Delta\nu_s$ values are greater than that of water. In this work, small values of both positive and negative separations have been obtained for phenols whose $\Delta\nu_s$ values are greater than $\sim$250 cm^{-1}. These results point to some possible limitations on the above suggestion; however, it seems reasonable to conclude that for nondissociated alcohols and phenols, the $\Delta\nu_s$ values should be far less than $\sim$250 cm^{-1} to obtain significant positive solute separation in reverse osmosis.

From Figures 1 and 2, it is clear that a solute whose substituent group has a more negative Taft number is susceptible to a higher level of separa-

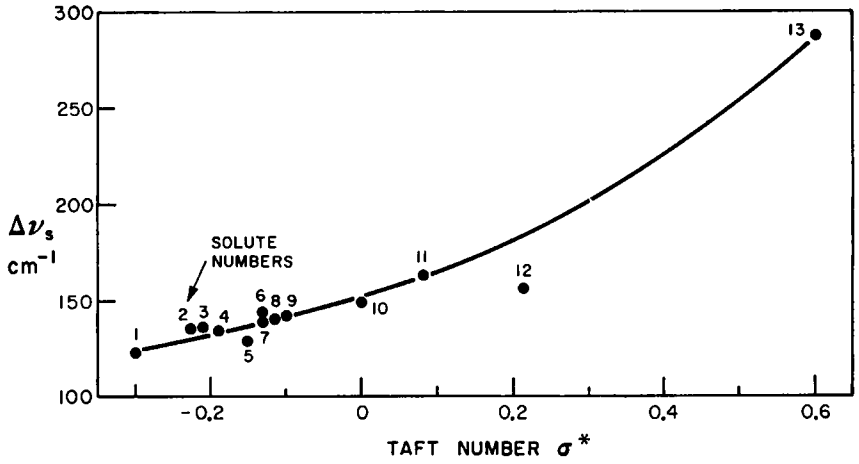


Fig. 2. $\Delta\nu_s$ of solute vs. Taft number of substituent group in alcohols and phenol.

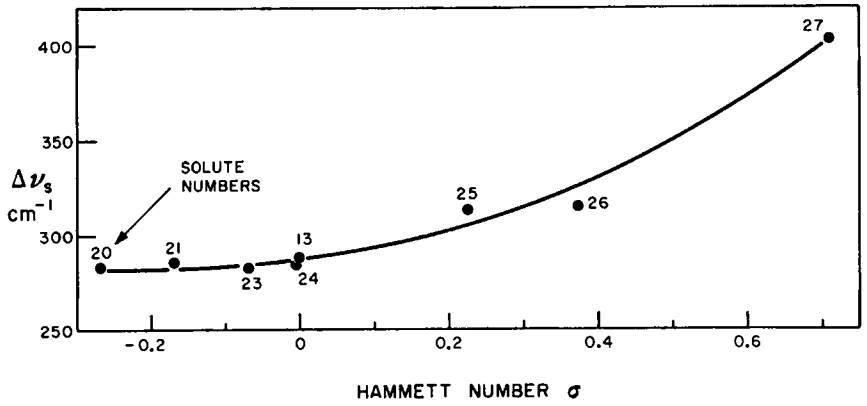


Fig. 3. $\Delta\nu_s$ of solute vs. Hammett number of substituent group in phenols.

tion in reverse osmosis. This is to be expected because a more negative Taft number means that the electron-withdrawing power of the substituent, and hence the hydrogen-bonding ability of the molecule, is less.

Figure 3 can be used for estimating $\Delta\nu_s$ values for compounds whose Hammett numbers are available. For example, the $\Delta\nu_s$ value for *m*-aminophenol estimated from Figure 3 is 291 cm^{-1}. Other methods of estimating $\Delta\nu_s$ are also possible. For example, it was found that $\Delta\nu_s$-versus-dipole moment[7] correlation is essentially linear for solutes 21, 23, 13, 25, 26, and 27; using this correlation, $\Delta\nu_s$ values for *p*-aminophenol, hydroquinone, and *p*-nitrophenol were estimated to be 295, 280, and 462 cm^{-1}, respectively. These estimated values of $\Delta\nu_s$ may not be very accurate, but they appear to be of the right order of magnitude as shown by their separation data. Solutes 19, 20, 21, 22, 23, 24, 28, and 13 have all high values of $\Delta\nu_s$ (more than 250 cm^{-1}) and essentially the same very

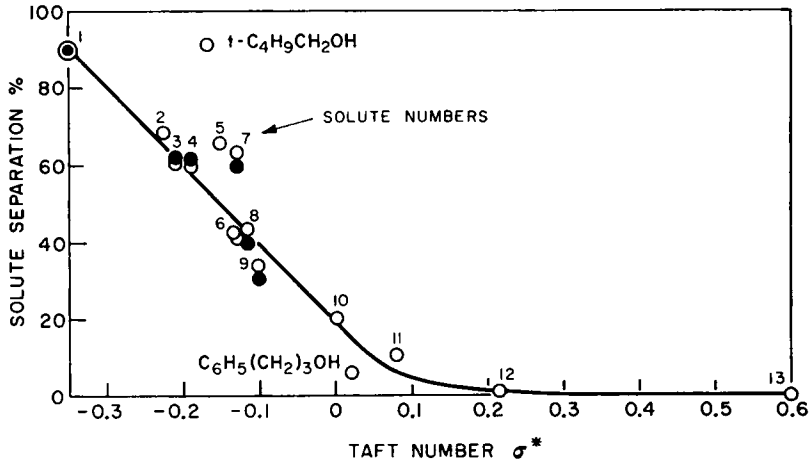


Fig. 4. Taft number vs. solute separation: (●) data of Sourirajan[2]; (○) data of Dufel et al.[5]

low values for separation; the separation of *p*-aminophenol is a notable exception.

Solute Separation and σ^*. The existence of a unique correlation between $\Delta\nu_s$ and σ^* (Fig. 2) makes it possible to correlate solute separation directly with σ^*. Such a correlation is illustrated in Figure 4 for the data of Sourirajan[2] and those of Duvel et al.[5] Even though these data refer to two different types of membranes of the same material (Schleicher and Schuell type and Loeb-Sourirajan type), to two different levels of feed concentrations (0.5*M* and 0.001 to 0.01*M*), and to two different operating pressures (1500 and 600 psig), all data are correlated in Figure 4 just as well as in Figure 1; fortuitously, the correlating line seems essentially the same for both the membranes. These results show that the type of correlations presented in Figures 1 and 4 is independent of feed concentration and operating pressure for all applicable solutes.

Separation of Ortho-Substituted Phenols. For film 1, solute separations for *o*-cresol, *o*-chlorophenol, *o*-nitrophenol, and pyrocatechol (solutes 29, 30, 31, and 32) were 4.2, 14.3, 19.1, and 3.8%, respectively; the corresponding product rates were in the range 18.8 to 20.4 g/hr per given area (7.6 cm^2) of film surface. The low separations obtained for *o*-cresol and pyrocatechol are understandable on the basis of their high values for $\Delta\nu_s$. The relatively high separations obtained for *o*-chlorophenol and *o*-nitrophenol seem to indicate that the intramolecular hydrogen bonding possible in these compounds weaken their ability for intermolecular hydrogen bonding considerably.[6]

Separation of Monocarboxylic Acids

pK_a and Solute Separations. The dissociation constant K_a, conveniently expressed as pK_a = $-\log K_a$, is a quantitative measure of the

total acidity of the molecule. A decrease in the value of pK_a represents an increase in the acidity of the molecule. On the basis of the foregoing discussion with respect to the separation of alcohols and phenols, it is clear that an increase in the acidity of the solute molecule tends to increase its hydrogen-bonding ability which, in turn, tends to decrease the preferential sorption of water and hence solute separation in reverse osmosis. On the other hand, when the acidity of the molecule is high enough to stretch the OH bond to the point of rupture, then the molecule dissociates and exists in solution as ions. These ions are subject to electrostatic repulsion in the vicinity of the membrane surface in reverse osmosis, as postulated by Sourirajan[1] and theoretically analyzed and confirmed by Glueckauf[25] and Bean.[12] The consequence of the above electrostatic repulsion for ions is greater preferential sorption for water and higher solute separation in reverse osmosis, depending on the chemical nature of the solute and the degree of dissociation. Therefore one should conclude that, up to a certain level, an increase in acidity of the molecule decreases solute separation and that, beyond that level, an increase in acidity increases solute separation. Thus, one would expect a point, or region, of minimum separation in the pK_a-versus-solute separation correlation. This is confirmed experimentally by the results illustrated in Figure 5.

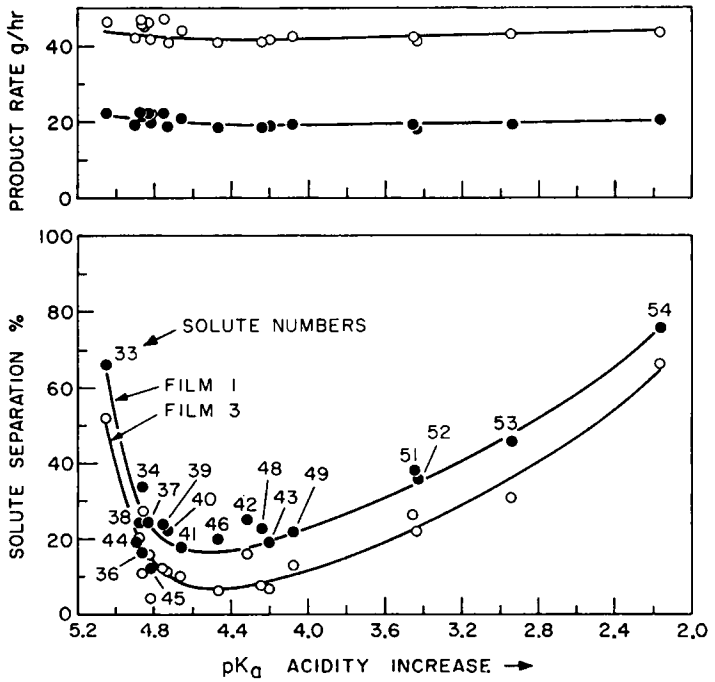


Fig. 5. Effect of pK_a of solute on reverse osmosis separation of monocarboxylic acids in aqueous solution using porous cellulose acetate membranes. Film type, Batch 316; operating pressure, 250 psig; feed concentration, 0.0006–0.0008 g-mole/l., feed flow rate, 400 cc/min; membrane area, 7.6 cm²; (●) film 1; (○) film 3.

Figure 5 illustrates the data obtained with films 1 and 3. The results obtained with the other films used were similar. These results involve 19 different aliphatic and aromatic carboxylic acids, listed in Table III, in the concentration range 0.0006 to 0.0008 g-mole/l. in aqueous solution. The range of pK_a values involved is 2.17 to 5.05, and the range of solute separations involved is 11% to 76% for film 1 and 4% to 67% for film 3. The correlation shows minimum separation in the region of pK_a values between 4.2 and 4.8; the dissociation effect is progressively more dominant for pK_a values less than 4.2, and the hydrogen-bonding effect is relatively more dominant for pK_a values greater than 4.8.

To be more specific, at the concentration level used in this work, the degree of dissociation for *p*-aminobenzoic acid (pK_a 4.82) is 12.7%; for solutes whose pK_a values are greater than 4.82, the degree of dissociation is less, and consequently the hydrogen-bonding effect is more. The scatter is correlation in a relatively narrow range of high pK_a values appears only reasonable in view of the accuracy of pK_a values in this region and possibly also the effect of changes in the feed concentrations used in each experiment. The experimental results and the form of correlation presented in Figure 5 offer unequivocal evidence for the mechanism of reverse osmosis separation postulated above for the class of solutes under discussion.

pK_a and Product Rates. The product rate data shown in Figure 5 above exhibit a tendency for minima in the region of minimum solute separations. That this tendency is real is confirmed by the product rate data given in Figures 7, 9, 10, and 11 discussed below. In all cases, the higher hydrogen-bonding effect and the lower degree of dissociation corresponded to lower product rates, and the changes in solute separation and product rate were reversible. These data are consistent with the concepts discussed earlier on the possible effect of the hydrogen-bonding ability of the molecule and its proximity to the membrane material on the porous structure of the membrane. This effect should be expected to be progressively less with increasing degree of dissociation or decreasing values of pK_a. This is indeed seen to be the case.

pK_a and σ^* or σ. Since pK_a represents the total polar effect of the acid molecule, and σ^* and σ represent the contribution of the substituent group to this total effect, again one may expect unique relationships to exist between pK_a and σ^* and pK_a and σ for aliphatic and aromatic monocarboxylic acids. This is the case, as illustrated in Figure 6. Similar correlations have been shown and discussed by Taft.[8] Figure 6 is useful for purposes of estimating either pK_a or σ^* and σ values for practical reverse osmosis applications.

Solute Separation and σ^* or σ. The existence of unique relationships between pK_a and σ^* and pK_a and σ makes it possible to make direct correlations between solute separation and σ^* or σ. Such correlations are illustrated in Figures 7 and 8. These correlations are essentially for the same feed concentration (0.0006–0.0008 g-mole/l.) and operating

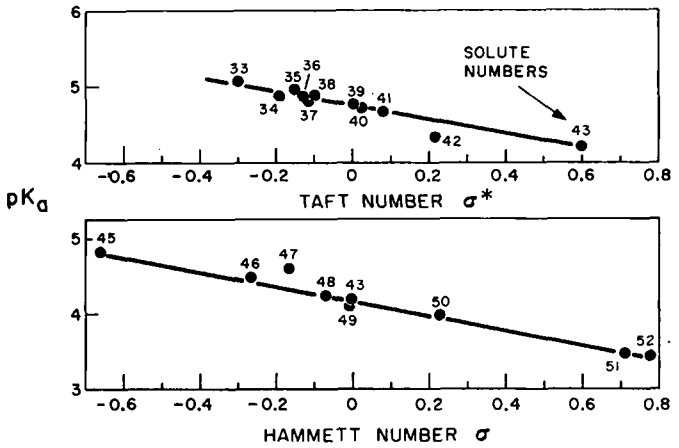


Fig. 6. Taft or Hammett number vs. pK_a for monocarboxylic acids.

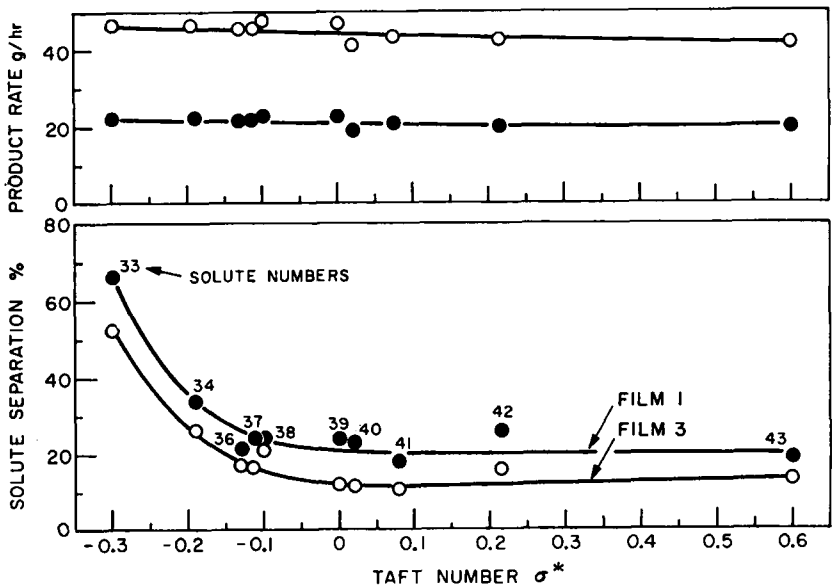


Fig. 7. Effect of Taft number on reverse osmosis separation of aliphatic monocarboxylic acids in aqueous solution using porous cellulose acetate membranes. Film type, Batch 316; operating pressure, 250 psig; feed concentration, 0.0006–0.0007 g-mole/l.; feed flow rate, 400 cc/min; membrane area, 7.6 cm²; (●) film 1; (○) film 3.

pressure (250 psig). Similar correlations can be expected to exist for different feed concentrations and operating pressures.

Effect of Degree of Dissociation on Membrane Performance. As pointed out already, a higher degree of dissociation of the solute molecule increases preferential sorption for water, and hence solute separation, in reverse osmosis. Under these conditions, the possible solute–polymer

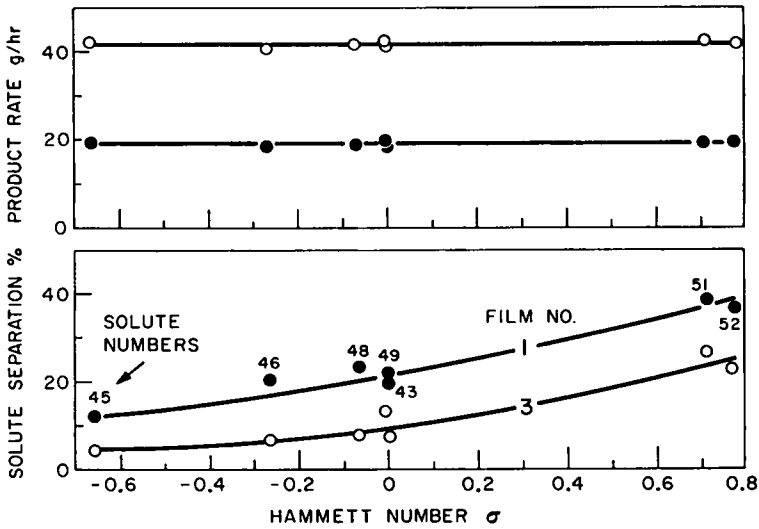


Fig. 8. Effect of Hammett number on reverse osmosis separation of substituted benzoic acids in aqueous solution using porous cellulose acetate membranes. Film type, Batch 316; operating pressure, 250 psig; feed concentration, 0.0006–0.0008 g-mole/l.; feed flow rate, 400 cc/min; membrane area, 7.6 cm²; (●) film 1; (○) film 3.

intermolecular hydrogen-bonding effects affecting the porous structure of the membrane are also less. Equation (3) shows that the degree of dissociation is higher when the dissociation constant K_a is higher and/or the feed concentration x_0 is lower. The degree of dissociation can also be increased by increasing the pH of the solution. Figures 9, 10, and 11 illustrate the effect of changes of K_a, x_0, and pH on membrane performance. Data are given for three films of different surface pore structures. The results obtained with all the films are similar.

Figure 9 shows the effects of changes in dissociation constant and feed concentration on membrane performance with respect to *o*-nitrobenzoic acid (K_a 671×10^{-5}), *m*-nitrobenzoic acid (K_a 32.1×10^{-5}), and *p*-aminobenzoic acid (K_a 1.37×10^{-5}) in the concentration range 0.0001 to 0.007 g-mole/l. The results demonstrate explicitly the dominant effects of K_a and x_0 on solute separation. At any given feed concentration, solute separation is higher the higher the value of K_a. For each solute (K_a constant) separation decreases with increase in feed concentration; this change is particularly steep at lower feed concentrations. Therefore, for solutes for which the dissociation effect is the governing factor in reverse osmosis separation, lower feed concentrations result in higher separation. This situation is particularly relevant to the separation of organics in waste water treatment.

Figure 9 also gives the separation data obtained with film 1 for pivalic acid (K_a 0.89×10^{-5}) at two different feed concentrations. Comparing these data with those of the other three solutes discussed above, two observations are significant. Even though the dissociation constant of pivalic

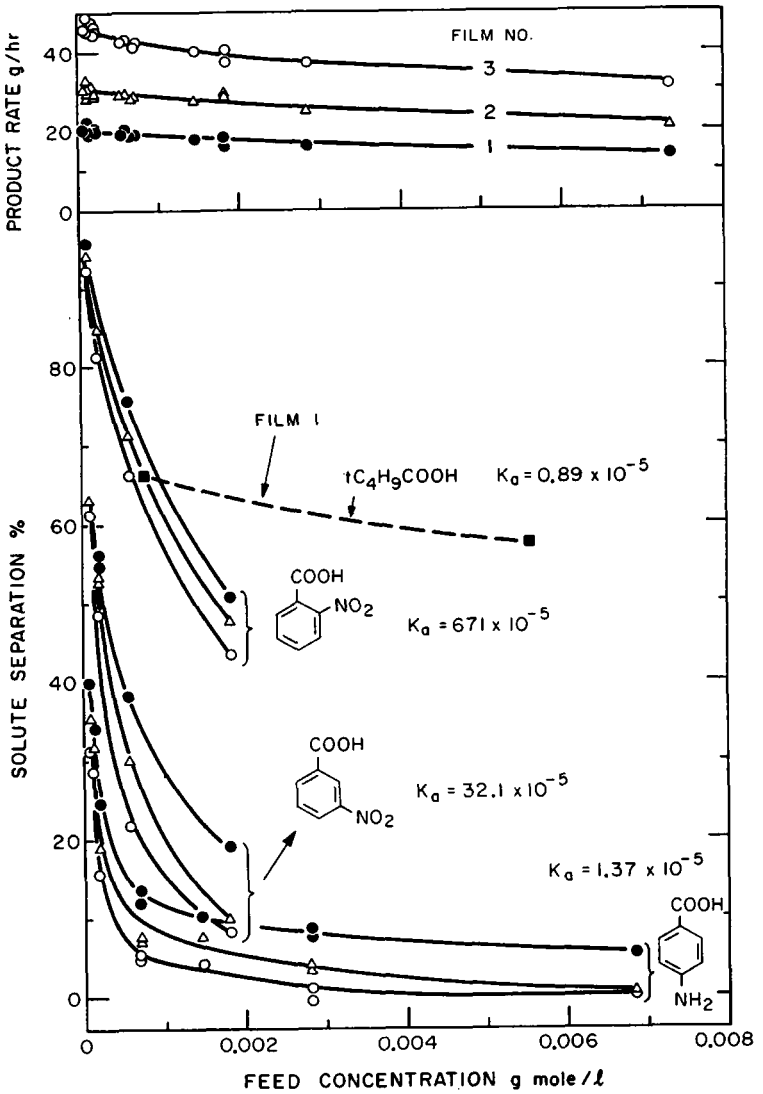


Fig. 9. Effect of K_a and feed concentration on reverse osmosis separation of some monocarboxylic acids in aqueous solution using porous cellulose acetate membranes. Film type, Batch 316; operating pressure, 250 psig; feed concentration, 0.0001–0.007 g-mole/l; feed flow rate, 400 cc/min; membrane area, 7.6 cm²; (●) film 1; (Δ) film 2; (○) film 3.

acid is very small (even smaller than that of *p*-aminobenzoic acid), its separation is relatively high; secondly, its decrease in separation as a consequence of several-fold increase in feed concentration is relatively low. The reason for the above difference in results is clear from a reference to the location of this solute (solute 33) in Figure 5. The acidity of pivalic

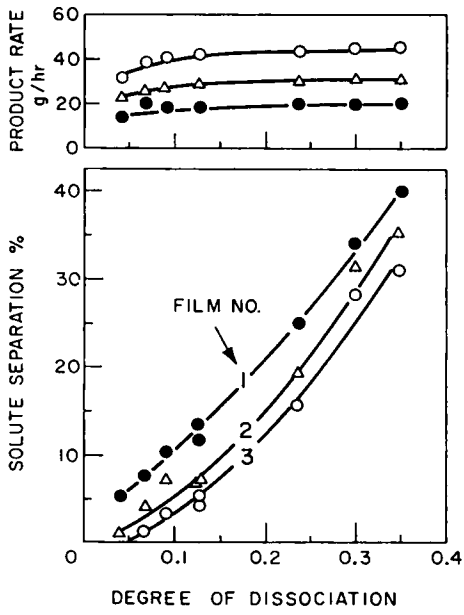


Fig. 10. Effect of degree of dissociation of solute on reverse osmosis separation of *p*-aminobenzoic acid in aqueous solution using porous cellulose acetate membranes. Film type, Batch 316; operating pressure, 250 psig; feed concentration, 0.0001–0.007 g-mole/l.; feed flow rate, 400 cc/min; membrane area, 7.6 cm²; (●) film 1; (△) film 2; (○) film 3.

acid is so low that the hydrogen-bonding effect is the factor governing its separation in reverse osmosis; even at the highest feed concentration used, its degree of dissociation is only 3.9%. The results on pivalic acid separation indicate that monocarboxylic acids whose acidities are sufficiently low (pK_a less than 5) can be separated to a significantly high extent by reverse osmosis throughout a wide range of feed concentrations.

Membrane performance data given in Figure 10 illustrate the effect of change in the degree of dissociation of solute brought about by changes in feed concentration (x_0) with respect to *p*-aminobenzoic acid; the data given in Figure 11 illustrate the effect of change in the degree of dissociation brought about by changes in the pH of a solution of constant concentration with respect to benzoic acid. These results show explicitly that solute separation increases with increase in degree of dissociation; and depending on the value of the latter, a very wide range of solute separation is obtainable for a given monocarboxylic acid.

With respect to product rate data, Figures 9, 10, and 11 show the same trend, namely, lower product rates at lower solute separations corresponding to lower degrees of dissociation of solute. The possible reason for this trend has already been discussed.

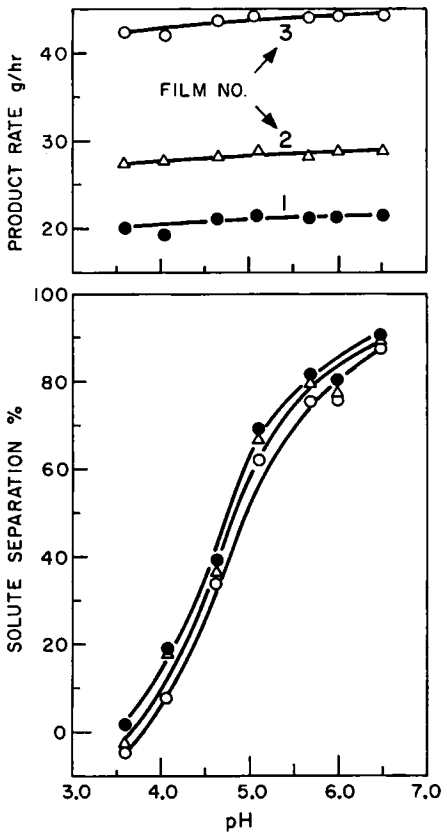


Fig. 11. Effect of pH on reverse osmosis separation of benzoic acid in aqueous solution using porous cellulose acetate membranes. Film type, Batch 316; operating pressure, 250 psig; feed concentration, 0.001 g-mole/l.; feed flow rate, 400 cc/min; membrane area, 7.6 cm^2; (●) film 1; (△) film 2; (○) film 3.

CONCLUSION

Preferential sorption of water, and hence solute separation, in reverse osmosis is governed by the hydrogen-bonding ability of the organic molecule when it is essentially undissociated, and by electrostatic repulsion of ions when the molecule is partially or completely dissociated. This mechanism is supported by correlations of reverse osmosis experimental data with $\Delta\nu_s$ for alcohols and phenols, and K_a and degree of dissociation for monocarboxylic acids in binary aqueous solution systems used in conjunction with asymmetric porous cellulose acetate membranes. These results offer a new and useful approach to the science and engineering of reverse osmosis.

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