Physicochemical Criteria for Reverse Osmosis Separation of Aldehydes, Ketones, Ethers, Esters, and Amines in Aqueous Solutions Using Porous Cellulose Acetate Membranes

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Synopsis

Reverse osmosis separation of 62 different proton acceptor compounds (bases) including 7 aldehydes, 8 ketones, 12 ethers, 11 esters, and 24 amines in aqueous solutions in the concentration range 0.00075 to 0.003 g mole/l. (~100 ppm in most cases) have been studied using porous cellulose acetate membranes at 250 psig. All reverse osmosis data are for single solute systems. Solute separation data for aldehydes, ketones, ethers, and esters are correlated with $\Delta\nu_s$ (basicity) (shift in the OD band maximum in the IR spectra of CH_3OD in benzene and other solvents used as solutes in reverse osmosis experiments), and those for the amines are correlated with dissociation constant (given as pK_a) and the degree of dissociation of the molecule. Solute separation increases with increase in $\Delta\nu_s$ (basicity) for aldehydes, ketones, ethers, and esters and with increase in degree of dissociation for amines. The separation data and the basicity parameters for the above classes of compounds are also correlated with Taft numbers. The results are consistent with those reported earlier for alcohols, phenols, and monocarboxylic acids in aqueous solutions and show that data on $\Delta\nu_s$ (basicity), pK_a, and Taft numbers are valid physicochemical criteria governing reverse osmosis separation of aldehydes, ketones, ethers, esters, and amines.

INTRODUCTION

The physiochemical criteria for reverse osmosis separation of alcohols, phenols, and monocarboxylic acids in aqueous solutions using porous cellulose acetate membranes have been discussed.[1] With respect to the above solution types, it has been shown that solute separation is governed by the polar effect of the molecule as represented by its hydrogen-bonding ability when the molecule is essentially undissociated and by the electrostatic repulsion of ions when the molecule is partially or completely dissociated. Alcohols and phenols exist in aqueous solution practically as undissociated molecules; further, they are primarily proton donors and hence acids. The hydrogen-bonding ability of a molecule is an expression of the stretching of the OH bond. For alcohols and phenols, the stretching of the OH bond may be quantitatively expressed by the shift in the OH band maximum ($\Delta\nu_s$, cm^{-1}) in the IR spectra of the solute in CCl_4 and

ether solutions. For monocarboxylic acids in aqueous solutions, the
stretching of the OH bond can be far enough to dissociate the molecule
into ions, depending on the dissociation constant K_a of the molecule and
its concentration in solution. Thus, the acidity parameter $\Delta\nu_s$ or K_a
gives a measure of the polar effect of the molecule with respect to alcohols,
phenols, and monocarboxylic acids. The contribution of the substituent
group to the total polar effect of the molecule is quantitatively expressed
by the Taft (σ^*) or Hammett (σ) number. Consequently, data on solute
separation could be correlated with those on $\Delta\nu_s$ and K_a, or σ^* or σ. Such
correlations have shown that an increase in acidity decreases solute sep-
aration with respect to alcohols and phenols, and an increase in K_a and
degree of dissociation increases solute separation with respect to mono-
carboxylic acids in aqueous solution–cellulose acetate membrane systems.
This paper extends the applicability of the above physicochemical criteria
for the separation of aldehydes, ketones, ethers, esters, and amines in such
reverse osmosis systems.

Aldehydes, ketones, ethers, and esters exist in aqueous solution prac-
tically as undissociated molecules; further, they are proton acceptors, and
hence bases. The strength of a hydrogen bond increases with the acidity
(proton-donating power) of a proton donor and with the basicity (proton-
accepting power) of a proton acceptor. The basicity of a proton acceptor
can be quantitatively expressed by the magnitude of a shift in the OD
band maximum in the IR spectra of CH_3OD in benzene and the particu-
lar proton-accepting solvent.[2] This shift in IR spectra is referred in this
paper as $\Delta\nu_s$ (basicity). The amines are also predominantly proton ac-
ceptors, and hence bases, and they undergo dissociation to different extents
in aqueous solutions depending on their dissociation constants and con-
centrations.

Thus, the basicity parameter $\Delta\nu_s$ (basicity) or dissociation constant gives
a measure of the polar effect of the molecule with respect to aldehydes,
ketones, ethers, esters, and amines; the contribution of the substituent
groups to the total polar effect of the molecule can again be quantitatively
expressed by the Taft numbers. Consequently, in this work, data on
solute separation are correlated with those on the basicity parameters and
Taft numbers. Such correlations lead to precise physicochemical criteria
for reverse osmosis separation of aldehydes, ketones, ethers, esters, and
amines, consistent with those given earlier for alcohols, phenols, and mono-
carboxylic acids, in aqueous solutions using porous cellulose acetate mem-
branes.

EXPERIMENTAL

Reverse Osmosis Experiments

The organic solute substances in aqueous solutions in the concentration
range 0.00075 to 0.003 g mole/l. and laboratory-made Batch 316-type
porous cellulose acetate membranes were used. The apparatus, mem-

branes, and the experimental procedure employed were the same as those reported earlier.[1] All experiments were carried out at the laboratory temperature (23–25°C) at 250 psig. Five different membrane samples were used in each experiment, and the data obtained with two of them (films 1 and 3) are reported here for each case to emphasize the point that the data are only illustrative of the principles involved; they do not represent limiting values in reverse osmosis. In all cases, similar results were obtained with the other films tested. The specifications of films 1 and 3 were as follows: pure water permeability constant, A, in g mole H_2O/-cm^2 sec atm, $= 2.48 \times 10^{-6}$ for film 1 and 5.35×10^{-6} for film 3; solute transport parameter for sodium chloride, $D_{AM}/K\delta$, in cm/sec, $= 3.22 \times 10^{-5}$ for film 1 and 16.89×10^{-5} for film 3 at 250 psig. The feed flow conditions used in the experiments corresponded to a mass transfer coefficient, k, of 57×10^{-4} cm/sec on the high-pressure side of the membrane for a 1500-ppm $NaCl–H_2O$ feed solution. In each experiment, the pure water permeation rate (PWP) and the product (membrane-permeated solution) rate (PR), in g/hr, for the effective area of film used (7.6 cm^2 in all cases), and the solute separation, defined as

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

were determined. All reverse osmosis data are for single solute systems. Since the feed concentrations used were extremely small (~100 ppm in most cases), the osmotic pressure effects on membrane performance were effectively eliminated, as before.[1] The reported product rates are those corrected to 25°C.

The solute numbers in all figures in this paper are the same as those listed in Table I.

Analysis

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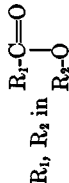
The analysis for sodium chloride in aqueous solutions was done using a conductivity bridge.

IR Spectra

The grating infrared spectrophotometer (Perkin Elmer Model 621), used before,[1] was again used in this work to obtain quantitative data on the shift in the OD band maximum, $\Delta\nu_s$ (basicity), in cm^{-1}, for the solutions of CH_3OD in benzene and other solvents (used as solutes in reverse osmosis experiments) following the method of Gordy.[2] A cell length of

TABLE I
Basicity Parameters for Aldehydes, Ketones, Ethers, Esters, and Amines

Solute No.	Name	Formula	Mol. wt	$\Delta\nu_s$ (Basicity), cm^{-1}				pK_a (refs. 15, 17–19)	σ^* or $\Sigma\sigma^*$ (ref. 21)
				This work	Ref. 7	Ref. 4	Refs. 8 & 9		
Aldehydes		R in R_2>C=O (H)							
1	Isobutyl aldehyde	iC$_3$H$_7$	72.1	130					−0.19
2	n-Butyl aldehyde	n-C$_3$H$_7$	72.1	140		117			−0.115
3	Propionaldehyde	C$_2$H$_5$	58.1	144	83				−0.10
4	Acetaldehyde	CH$_3$	44.1	100	85				0
5	Crotonaldehyde	CH$_3$CH=CH	70.1	83	79	97			0.36
6	Benzaldehyde	C$_6$H$_5$	106.1	60	75	84		−6.99	0.60
7	Furfural	C$_4$H$_3$O	96.1	70	53	70			
Ketones		R_1, R_2 in R_1>C=O R_2							
8	Diisopropyl ketone	iC$_3$H$_7$, iC$_3$H$_7$	114.2	48		84			−0.38
9	Diisobutyl ketone	iC$_4$H$_9$, iC$_4$H$_9$	142.2	85		84			−0.25
10	Cyclopentanone	cyclo-C$_4$H$_8$	84.1	85		84			−0.25^b
11	Cyclohexanone	cyclo-C$_5$H$_{10}$	98.1	90	66	177	98		−0.18^b
12	Methyl ethyl ketone	CH$_3$, C$_2$H$_5$	72.1	76	57	77			−0.10
13	Acetone	CH$_3$, CH$_3$	58.1	79	64	97	78		0
14	Benzyl methyl ketone	C$_6$H$_5$(CH$_2$), CH$_3$	134.2	80					0.215
15	Acetophenone	C$_6$H$_5$, CH$_3$	120.1	66	56	77		−6.04	0.60
Ethers (Noncyclic)		R_1, R_2 in R_1>O R_2							

No.	Compound	R_1, R_2 / Structure							
16	Diisopropyl ether	iC_3H_7, iC_3H_7	102.2	96	75	123	110	-4.30	-0.38
17	Diethyl ether	C_2H_5, C_2H_5	74.1	95	78	130	96	-3.59	-0.20
18	Anisole	CH_3, C_6H_5	108.1	42	26	70	70	-6.54	0.60
19	Ethyl vinyl ether	C_2H_5, $H_2C=CH$	72.1	38[a]	31				
20	Phenetole	C_2H_5, C_6H_5	122.2	30[a]	25	57		-6.44	0.50
21	Methyl benzyl ether	CH_3, $C_6H_5(CH_2)$	122.2			110			0.215
	Ethers (Cyclic)	cyclo $>$O							
22	Tetrahydropyran	cyclo-C_5H_{10}	86.1	104[a]	93		115	-2.79	-0.18[b]
23	Tetrahydrofuran	cyclo-C_4H_8	72.1	100	90		117	-2.08	-0.25[b]
24	1,4-Dioxane	C_4H_8O	88.1	86	77	97	111	-2.92	0.67
25	Propylene oxide	H_3C—HC (epoxide)	58.1	76[a]	59	100	99		
26	Styrene oxide	H_3C—HC (epoxide), C_6H_5	120.1	60[a]	51	85			
27	Epichlorohydrin	H_2C—HC—CH_2Cl (epoxide)	92.5	57	45	104	80		
	Esters	R_1, R_2 in $\begin{array}{c}R_1\text{—}C=O\\ R_2\text{—}O\end{array}$							

(continued)

TABLE I (continued)

Solute No.	Solute Name	Formula	Mol. wt	Δν$_s$ (Basicity), cm^{-1}				pK$_a$ (refs. 15, 17–19)	σ* or Σσ* (ref. 21)
				This work	Ref. 7	Ref. 4	Refs. 8 & 9		
28	Ethyl propionate	C$_2$H$_5$, C$_2$H$_5$	102.1	40	32				−0.20
29	n-Amyl acetate	CH$_3$, n-C$_5$H$_9$	130.2	79		90			−0.133[c]
30	Methyl n-butyrate	C$_3$H$_7$, CH$_3$	102.1	46					−0.115
31	Ethyl acetate	CH$_3$, C$_2$H$_5$	88.1	48	39	84	51		−0.10
32	Methyl acetate	CH$_3$, CH$_3$	74.1	47	36	84	51		0
33	Methyl benzoate	C$_6$H$_5$, CH$_3$	136.1	40		63			0.60
34	Ethyl chloroacetate	ClCH$_2$, C$_2$H$_5$	122.6	21		70			0.95
35	Methyl chloroacetate	ClCH$_2$, CH$_3$	108.5	21	27				1.05
36	Vinyl acetate	CH$_3$, H$_2$C=CH	86.1	25	21				
37	Methyl acrylate	H$_2$C=CH, CH$_3$	86.1	33	30				
38	Methyl methacrylate	H$_2$C=CCH$_3$, CH$_3$	100.1	40	33				
	Amines, Primary	R in RNH$_2$							
39	Ethylamine	C$_2$H$_5$	45.1		233			10.75	0.88
40	Benzylamine	C$_6$H$_5$(CH$_2$)	107.2		224			9.34	1.195
41	Aniline	C$_6$H$_5$	93.1	170	158	181		4.58	1.58
42	p-Anisidine	p-CH$_3$OC$_6$H$_4$	123.2					5.29	
43	p-Toluidine	p-CH$_3$C$_6$H$_4$	107.2					5.07	
44	m-Phenylenediamine	m-NH$_2$C$_6$H$_4$	108.2					4.88	
45	m-Toluidine	m-CH$_3$C$_6$H$_4$	107.2			175		4.67	
46	o-Anisidine	o-CH$_3$OC$_6$H$_4$	123.2					4.49	
47	o-Phenylenediamine	o-NH$_2$C$_6$H$_4$	108.2					4.47	

No.	Name	Substituents					pKa	
48	o-Toluidine	$o\text{-}CH_3C_6H_4$	107.2			175	4.39	
49	p-Chloroaniline	$p\text{-}ClC_6H_4$	127.6				3.81	0.23
50	m-Chloroaniline	$m\text{-}ClC_6H_4$	127.6			162	3.32	0.31
51	o-Chloroaniline	$o\text{-}ClC_6H_4$	127.6			156	2.62	0.49
52	m-Nitroaniline	$m\text{-}NO_2C_6H_4$	138.1				2.45	1.09
	Amines, Secondary	R_1, R_2 in $\frac{R_1}{R_2}{>}NH$						
53	Di-n-Butylamine	$n\text{-}C_4H_9,\ n\text{-}C_4H_9$	129.5	261			11.25	
54	Piperidine	$cyclo\text{-}C_5H_{10}$	85.2		240	242	11.22	
55	Dimethylamine	$CH_3,\ CH_3$	45.1				10.87	
56	N-Methylaniline	$C_6H_5,\ CH_3$	107.2		151	156	4.70	
	Amines, Tertiary	R_1, R_2, R_3 in $\frac{R_1}{R_2}{>}N\text{-}R_3$						
57	Triethylamine	$C_2H_5,\ C_2H_5,\ C_2H_5$	101.2		238		10.76	−0.30
58	Trimethylamine	$CH_3,\ CH_3,\ CH_3$	59.1				9.76	0
59	N,N-Dimethyl-benzylamine	$CH_3,\ CH_3,\ C_6H_5(CH_2)$	135.2			218	8.93	0.215
60	N,N-Dimethylaniline	$CH_3,\ CH_3,\ C_6H_5$	121.2		148	143	5.06	0.60
	Amines, Conjugated							
61	Pyridine	$CH{\big<}(CHCH)_2{\big>}N$	79.1	200	168	181	5.23	
62	γ-Picoline	$C_5H_4N\cdot CH_3$	93.1		160		6.00	

a Estimated from Figure 1.
b Estimated by Hall.[22]
c Estimated from Taft.[21]

0.2 mm was used. The chemicals employed were reagent grade, and the concentration of CH_3OD in the solutions used for IR spectra was 0.6 g mol/l. in all cases. All measurements were made at room temperature; the data on $\Delta\nu_s$ (basicity) were reproducible within ± 1 cm^{-1}. However, in some cases of overlapping and asymmetrical bands, the apparent band maximum was shifted so that the total uncertainty in the location of the true band center was somewhat greater than the experimental reproducibility.

RESULTS AND DISCUSSION

Hydrogen-Bonding Parameters

$\Delta\nu_s$ (**Basicity**) **and** $\Delta\nu_s$. The extensive work of Gordy and co-workers[2-5] is the basis for correlating data on $\Delta\nu_s$ (basicity), as measured in this work, with the relative hydrogen-bonding ability of proton acceptor molecules, i.e., those containing electronegative atoms, such as oxygen and nitrogen, with unshared electron pairs. The hydrogen-bonding situation in the experimental measurement of $\Delta\nu_s$ reported earlier,[1] and that of $\Delta\nu_s$ (basicity) reported here, may be represented as follows:
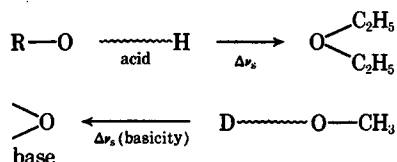
Thus, hydrogen bonding represents the tendency of proton transfer from an acid to a base. A higher hydrogen-bonding ability represents a higher proton-donating power for an acid and a higher proton-accepting power for a base. Values of $\Delta\nu_s$ give a relative measure of the proton-donating power of the acid molecules (alcohols and phenols), and those of $\Delta\nu_s$ (basicity) give a similar measure of the proton-accepting power of the base molecules (aldehydes, ketones, ethers, and esters). Increase in $\Delta\nu_s$ and in $\Delta\nu_s$ (basicity) both represent an increase in the hydrogen-bonding ability with respect to the molecules concerned. However, in terms of effect of structure on reactivity of molecules, the proton-donating and proton-accepting powers represent mutually opposite tendencies. Consequently, for purposes of application to correlation of reverse osmosis data, an increase in the magnitude of $\Delta\nu_s$ can be considered to be equivalent to a decrease in the magnitude of $\Delta\nu_s$ (basicity).[6]

Data on $\Delta\nu_s$ (Basicity). The experimental data on $\Delta\nu_s$ (basicity) obtained in this work for several of the solute substances studied are given in Table I. The corresponding data available in the literature[2-5, 7-9] are also given in Table I for comparison. In many cases, considerable differences exist in the numerical values of $\Delta\nu_s$ (basicity) among the available data including those obtained in this work. These differences are probably
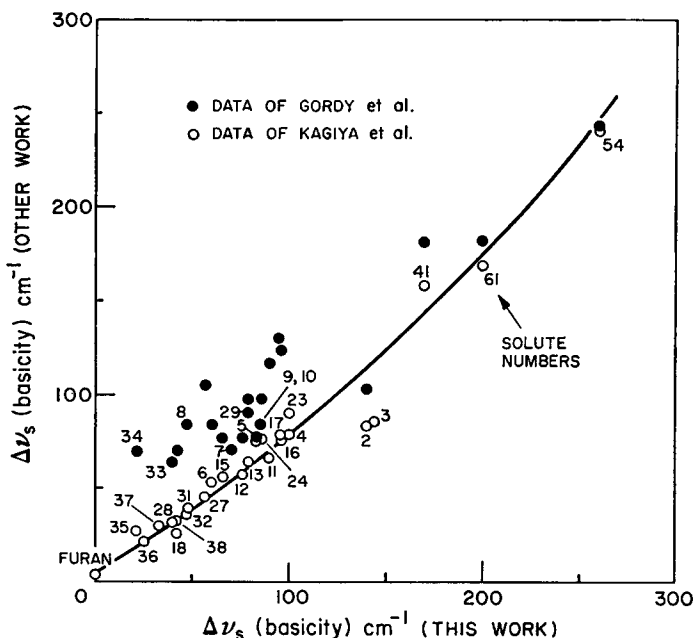
Fig. 1. Comparison of $\Delta\nu_s$ (basicity) data for aldehydes, ketones, ethers, esters, and amines.

attributable to the differences in the apparatus and experimental procedure used by the different workers. To test the consistency of the different sets of available data, those obtained in this work were plotted against those of Kagiya et al.[7] and Gordy et al.[2-5] This plot is given in Figure 1, which shows that a satisfactory correlation exists between the data obtained in this work and those of Kagiya et al. But the data of Gordy et al. are too much scattered in the above plot, suggesting the possible existence of some uncertainties in the latter data as pointed out by Pimentel and McClellan.[10] The data of Searles et al.[8,9] (not plotted in Fig. 1) also show similar scatter. For the sake of internal consistency, the data of $\Delta\nu_s$ (basicity) obtained in this work were used to correlate the basicity parameter with reverse osmosis data. In view of the generally satisfactory correlation obtained with the data of Kagiya et al., the numerical values of $\Delta\nu_s$ (basicity) used for some of the compounds (solutes 19, 20, 22, 25, and 26 in Table I) were obtained by interpolation from Figure 1.

Dissociation Constant of a Base. Data on $\Delta\nu_s$ (basicity) give a relative measure of the stretching of the OD bond corresponding to the incipient ionization of the base.[11-13] When the basicity of the molecule is high enough to stretch the OD bond to the point of rupture, then the molecule dissociates and exists in solution as ions. The amines are significantly dissociated in aqueous solutions, the degree of dissociation depending on their dissociation constants and concentrations in solution. The dissocia-

tion constant of an acid (K_a) and that of a base (K_b) are related[14] by the equation

$$K_a \cdot K_b = K_{auto} \qquad (1)$$

where K_{auto} represents the autoprotolysis constant of water. The value of K_{auto} at 25°C is 10^{-14}. Only the values of K_a are usually listed in the literature for the dissociation constants of both acids and bases; consequently the values of K_b for bases have to be obtained from eq. (1). Often, the above equilibrium constants are given in the form of their negative logarithms such as $pK_a = -\log K_a;$ then eq. (1) becomes

$$pK_a + pK_b = pK_{auto} = 14 \text{ at } 25°C. \qquad (2)$$

Hence an increase in the value of pK_a represents a decrease in acidity for an acid molecule and an increase in basicity for a molecule which is a base.

Using the values of K_b obtained from eq. (1), the initial concentration x_0 of the base in aqueous solution, and the concentration x of the ionic species in solution, the degree of dissociation of the base (x/x_0) can be calculated from the relation

$$\frac{x}{x_0} = \sqrt{\frac{1}{4}\left[\frac{K_b}{x_0}\right]^2 + \left[\frac{K_b}{x_0}\right]} - \frac{1}{2}\left[\frac{K_b}{x_0}\right] \qquad (3)$$

which is just the equivalent expression derived earlier to calculate the degree of dissociation of acids.[1]

Data on pK_a for all the amines[15] and several of the aldehydes and ketones[16] and ethers[17-19] studied in this work are listed in Table I, from the literature. All data are for 25°C.

$\Delta\nu_s$ (**Basicity**) **Versus** pK_a. Since both $\Delta\nu_s$ (basicity) and pK_a are hydrogen-bonding parameters representing the basicity of the molecule, it is only reasonable to expect that they should be uniquely related. The existence of a linear relationship between the above quantities has been shown by several workers.[4,7,20] Using the experimental data of Gordy et al.,[4] Kagiya et al.[7] derived the following equation between pK_b and $\Delta\nu_s$ (basicity):

$$pK_b = -0.102 \, \Delta\nu_s \text{ (basicity)} + 26.8. \qquad (4)$$

In terms of pK_a, the above equation becomes

$$pK_a = 0.102 \, \Delta\nu_s \text{ (basicity)} - 12.8. \qquad (5)$$

From Arnett's results,[20] the following equation can be derived:

$$pK_a = 0.102 \, \Delta\nu_s \text{ (basicity)} - 14.6. \qquad (6)$$

The straight-line relationship represented by eqs. (5) and (6) are given in Figure 2, along with some of the $\Delta\nu_s$ (basicity) data obtained in this work. The latter data include those for one aldehyde, one ketone, five ethers, and one each for primary, secondary, and tertiary amines. In view of the
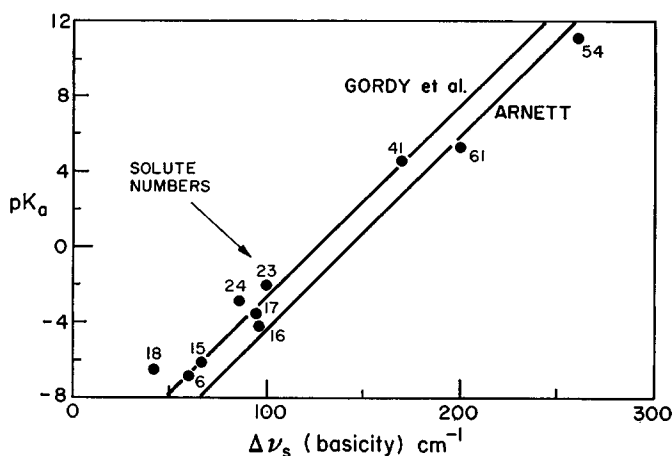
Fig. 2. $\Delta \nu_s$ (Basicity)-vs.-pK_a correlation for some aldehydes, ketones, ethers, and amines.

variety of the compounds involved, the correlation is in reasonable agreement with those represented by eqs. (5) and (6). The scatter in data lends support to the suggestion of Jencks,[12] and the basic approach set in this work, that functional groups should be differentiated in such correlations.

Separation of Aldehydes, Ketones, Ethers, and Esters

$\Delta \nu_s$ **(Basicity) Versus Solute Separation.** Figures 3, 4, and 5 give $\Delta \nu_s$ (basicity)-versus-solute separation correlations for films 1 and 3 with respect to 38 different compounds, including 7 aldehydes and 8 ketones (Fig. 3), 12 ethers (Fig. 4), and 11 esters (Fig. 5), all of which are bases whose dissociation constants are so low that they exist essentially as un-ionized molecules in aqueous solutions. Two important features in the correlations given in Figures 3 to 5 are immediately evident. First, solute separation increases with increase in $\Delta \nu_s$ (basicity); and secondly, beyond a certain value (which is different for each class of compounds), an increase in $\Delta \nu_s$ (basicity) increases solute separation very little. Both these observations are exactly equivalent to those observed earlier[1] with respect to $\Delta \nu_s$-versus-solute separation correlation for alcohols and phenols. Thus, for aqueous solution–cellulose acetate membrane systems, when the relative hydrogen-bonding abilities of the solute molecules are sufficiently small, an increase in hydrogen-bonding ability results in a decrease in solute separation if the solute molecule is an acid (proton donor), or in an increase in solute separation if the solute molecule is a base (proton acceptor). For both acids and bases, with progressive increase in the hydrogen-bonding ability of the solute molecule, the preferential sorption of water in reverse osmosis tends to reach a limiting value, so that beyond a certain value (which is different for different functional groups) any further increase in $\Delta \nu_s$ or $\Delta \nu_s$ (basicity) changes solute separation very little. For
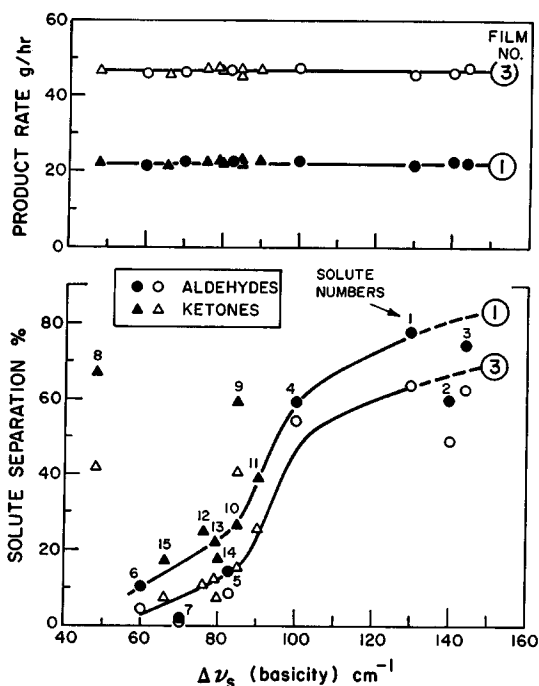
Fig. 3. Effect of $\Delta\nu_s$ (basicity) of aldehydes and ketones on membrane performance. Film type, cellulose acetate (Batch 316); operating pressure, 250 psig; feed concentration, 0.00075 to 0.003 g mole/l.; feed flow rate, 400 cc/min; membrane area, 7.6 cm².

alcohols and phenols, it was shown[1] that the above limiting value for the preferential sorption of water was close to zero, including sometimes negative values. For proton-acceptor solutes (bases) in the increasing range of hydrogen-bonding abilities, the limiting value for the preferential sorption of water is positive, and different for different functional groups. Consequently, for each functional group, solute separation tends to reach some kind of a "saturation value" for a given membrane, with increase in the magnitude of $\Delta\nu_s$ (basicity) for the solutes. In the scale of $\Delta\nu_s$ (basicity) values given in Figures 3 to 5, increases in $\Delta\nu_s$ (basicity) beyond 130 cm^{-1} for aldehydes and ketones, 100 cm^{-1} for ethers, and 80 cm^{-1} for esters seem to result in very little further increase in solute separation.

The data presented in Figures 3 to 5 also confirm the observation made earlier[1] that there is no necessary correlation between solute separation and molecular weight of solute.

Separation of Carbonyl Compounds. Figure 3 gives the $\Delta\nu_s$ (basicity)-versus-solute separation correlation for the aldehydes and ketones tested in the concentration range 0.00075 to 0.003 g mole/l. (~100 ppm in each case). Referring to the performance of film 1, among the aldehydes studied, solute separation was highest (78%) for isobutyl aldehyde (solute 1) and lowest (~2%) for furfural (solute 7). Among the ketones tested, solute
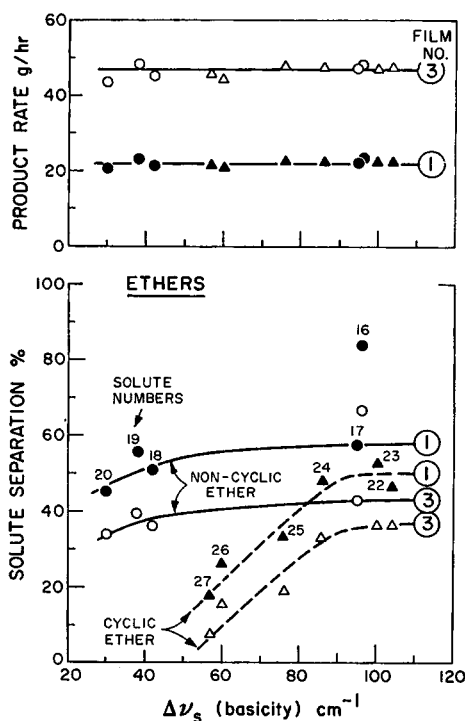
Fig. 4. Effect of $\Delta \nu_s$ (basicity) of ethers on membrane performance. Film type, cellulose acetate (Batch 316); operating pressure, 250 psig; feed concentration, 0.001 to 0.002 g mol/l.; feed flow rate, 400 cc/min; membrane area, 7.6 cm².

separation was highest (67%) for diisopropyl ketone (solute 8) and lowest (17%) for acetophenone (solute 15). Thus, the studies covered a wide range of solute separations. The corresponding separation data with film 3 were lower, but the correlations obtained were similar. Even though the general correlation that solute separation increases with increase in $\Delta \nu_s$ (basicity) is clear in Figure 3, aldehydes and ketones are not clearly distinguishable in the correlation, resulting in a considerable scatter in the data.

A few discrepancies may be mentioned specifically. Low separations obtained for n-butyl aldehyde and propionaldehyde (solutes 2 and 3, respectively) and high separations obtained for diisopropyl ketone and diisobutyl ketone (solutes 8 and 9, respectively) in relation to their respective $\Delta \nu_s$ (basicity) values appear as significant exceptions to the general correlation. These exceptions probably arise by uncertainties inherent in the measure of basicity given by the $\Delta \nu_s$ (basicity) data. The structures of some of the above solutes involve considerable steric interactions. For such solutes, it is possible that the method used in this work does not provide a true measure of the basicity of the molecule. From Figure 3, it would appear that the basicity of n-butyl aldehyde (solute 2) should be
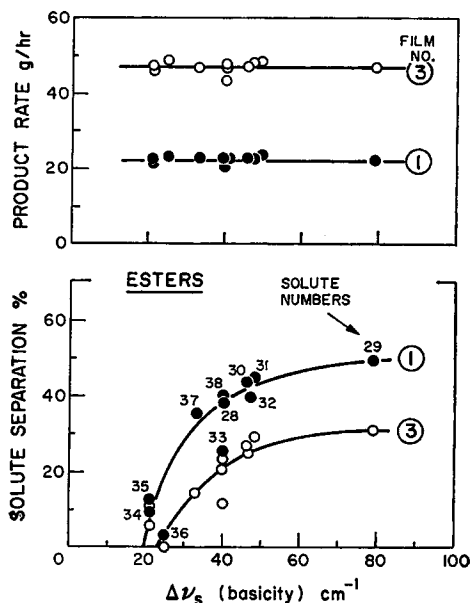
Fig. 5. Effect of $\Delta\nu_s$ (basicity) of esters on membrane performance. Film type, cellulose acetate (Batch 316); operating pressure, 250 psig; feed concentration, 0.001 to 0.002 g mole/l.; feed flow rate, 400 cc/min; membrane area, 7.6 cm².

closer to that of acetaldehyde (solute 4); the corresponding $\Delta\nu_s$ (basicity) data are too far apart. These results will be recalled later in this discussion to point out that they do not represent any fundamental departure in the basis of correlations presented.

Separation of Ethers. Figure 4 gives $\Delta\nu_s$ (basicity)-versus-solute separation correlations for 5 noncyclic and 6 cyclic ethers in the concentration range 0.001 to 0.002 g mol/l. The values of $\Delta\nu_s$ (basicity) for ethyl vinyl ether, phenetole, tetrahydropyran, propylene oxide, and styrene oxide (solutes 19, 20, 22, 25, and 26, respectively) could not be determined experimentally in this work, and hence the data used in Figure 4 are those obtained by interpolation from the correlation given in Figure 1 for the data of Kagiya et al. and those determined in this work. Figure 4 shows that the correlations for the cyclic and noncyclic ethers are functionally distinguishable. Further, the noncyclic ethers are generally better separated than cyclic ethers in the reverse osmosis systems studied. The magnitude of increase in solute separation with increase in $\Delta\nu_s$ (basicity) is far more for cyclic ethers than for noncyclic ethers. For example, the data for film 1 shows that at $\Delta\nu_s$ (basicity) values of 60 and 100 cm⁻¹, solute separations for noncyclic ethers are 56% and 58%, respectively, while the corresponding separations for cyclic ethers are 21% and 50%, respectively. Again, a few apparent discrepancies in correlation are noticeable. For example, for film 1, the solute separation for diisopropyl ether (solute 16) is too high, while that for methyl benzyl ether (solute 21, Gordy et al. $\Delta\nu_s$ (basicity)

= 110 cm^{-1}, solute separation 25.8%, not plotted in Fig. 4) is too low with respect to their $\Delta\nu_s$ (basicity) values.

Separation of Esters. Figure 5 gives $\Delta\nu_s$ (basicity)-versus-solute separation correlations for 11 esters in the concentration range 0.001 to 0.002 g mole/l. Solute separation increases steeply with increase in $\Delta\nu_s$ (basicity) in the range 20 to 40 cm^{-1}. The $\Delta\nu_s$ (basicity) data for methyl benzoate and vinyl acetate (solutes 33 and 36) appear too high compared to what may be expected from their separation data.

Order of Separations. Referring to Figures 3 to 5 together, at lower $\Delta\nu_s$ (basicity) values (for example, at 60 cm^{-1}) solute separations are generally in the order noncyclic ether > ester > cyclic ether > aldehyde and ketone. At the "saturation" levels of solute separation, the corresponding order is aldehyde and ketone > noncyclic ether > cyclic ether and ester. Though there could be individual exceptions to the orders of separation stated above, the important point is that the orders themselves change with the level of basicity of the molecule.

Data on Product Rates. Figures 3 to 5 also give the product rate data obtained with films 1 and 3 for each one of the solutes tested. With respect to each film, the product rate remained essentially constant for all the solution systems tested (with the possible exception of one system), showing thereby that the porous structure of each film remained unaffected under the conditions of the experiments. The product rate obtained for the solution system methyl benzoate (solute 33)–water was a little lower compared to others, indicating some probable change in the porous structure of the membrane; this system needs further investigations.

Data on σ^* and $\Sigma\sigma^*$. The definition and the significance of the Taft number (σ^*) with reference to reverse osmosis separation have been discussed.[1] As pointed out already, σ^* gives a true measure of the polar effect of the substituent group in a molecule. Since polar effects are additive,[21] for polysubstituted derivatives, the total polar effect of the substituent groups is given by the sum of their respective σ^* values; this sum is represented by the quantity $\Sigma\sigma^*$. For example, the Taft number, $\Sigma\sigma^*$, for diisopropyl ketone is -0.38, since σ^* for $iC_3H_7 = -0.19$. The σ^* or $\Sigma\sigma^*$ values for many of the compounds used in this work are given in Table I; most of these data are obtained from reference 21. It was shown earlier[1] that a good straight-line correlation existed between σ^* and pK_a values. Similar correlations were also given by Hall[22] for the base strengths of primary, secondary, and tertiary nonaromatic amines. Such correlations offer a means for estimating σ^* values; some of the data given in Table I were estimated from such correlations.

σ^* or $\Sigma\sigma^*$ Versus Solute Separation. Figure 6 gives the σ^* or $\Sigma\sigma^*$-versus-solute separation correlations for those aldehydes, ketones, ethers, and esters for which Taft numbers are available (Table I). Several aspects of these correlations are significant.

In all cases, solute separation increases with decrease in σ^* or $\Sigma\sigma^*$; in general, solute separations increase steeply at higher negative values of
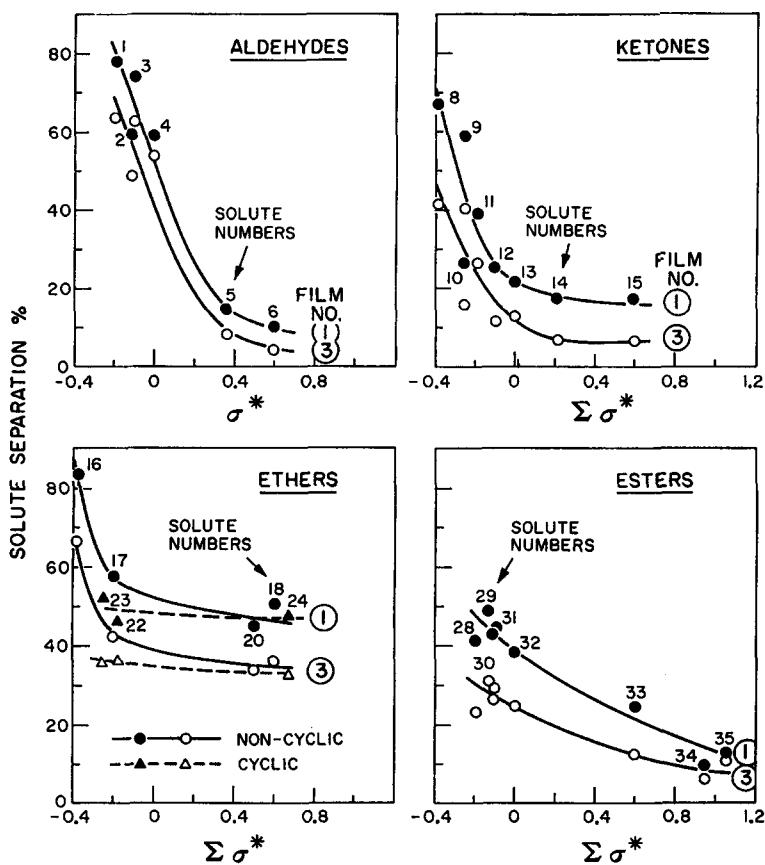
Fig. 6. Taft number vs. solute separation for aldehydes, ketones, ethers, and esters. Film type, cellulose acetate (Batch 316); operating pressure, 250 psig; feed concentration, 0.00075 to 0.003 g mole/l.; feed flow rate, 400 cc/min.

Taft numbers. These observations are identical to those made earlier with respect to the separation of alcohols and phenols.[1] The Taft number is a measure of the electron-withdrawing power of the substituent group or groups in the molecule.[21] Hence a decrease in the value of σ^* or $\Sigma\sigma^*$ is equivalent to a decrease in the acidity or increase in basicity of the molecule. Consequently, with respect to both proton-donor (acid) and proton-acceptor (base) solutes, an increase in solute separation is obtained with decrease in σ^* or $\Sigma\sigma^*$.

The functional groups in aldehydes, ketones, cyclic ethers, noncyclic ethers, and esters are mutually distinguishable with respect to reverse osmosis separation. For a given value of σ^* or $\Sigma\sigma^*$, aldehydes are better separated then ketones. The tendency of solute separation to reach a limiting value with decrease in $\Sigma\sigma^*$ is noticeable only with respect to cyclic ethers in the range of σ^* or $\Sigma\sigma^*$ values studied.
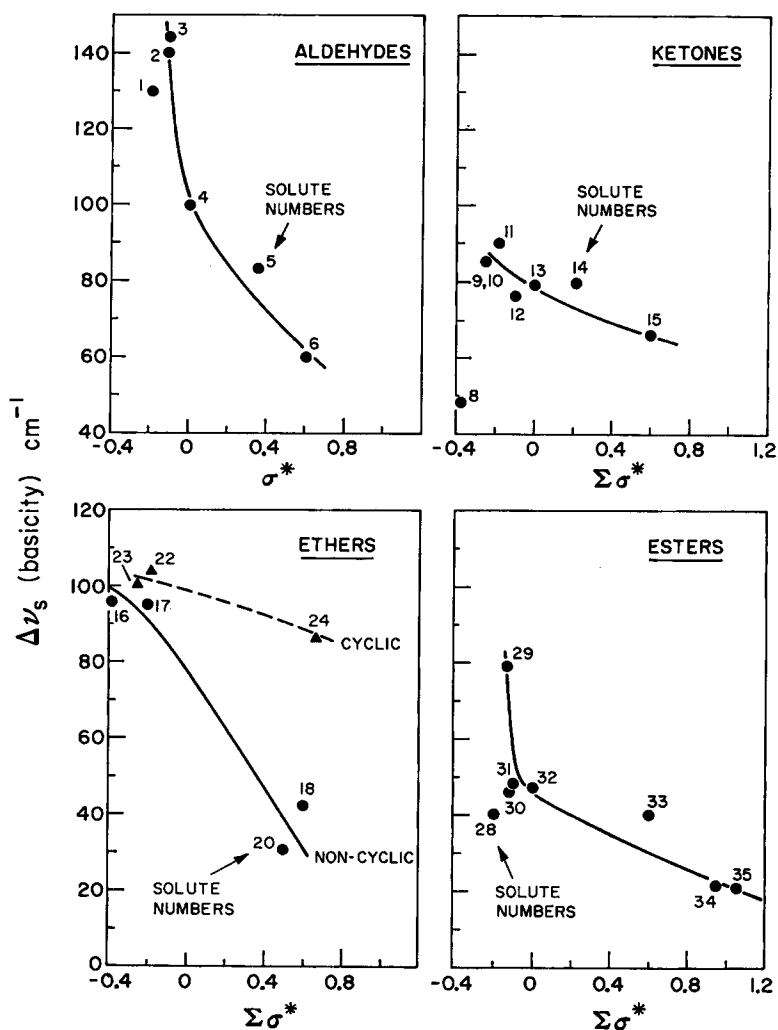
Fig. 7. Taft number vs. $\Delta\nu_s$ (basicity) for aldehydes, ketones, ethers, and esters.

At higher positive values of Taft numbers, the σ^* or $\Sigma\sigma^*$-versus-solute separation curves tend to flatten at positive values for solute separation, indicating preferential sorption of water for proton-acceptor solutes in reverse osmosis process involving cellulose acetate membranes of the type used in this work.

The discrepancies noted earlier with respect to solutes 2, 8, 9, 16, and 33 in the $\Delta\nu_s$ (basicity)-versus-solute separation correlations (Figs. 3, 4, and 5) have virtually vanished in the corresponding σ^* or $\Sigma\sigma^*$-versus-solute separation correlation given in Figure 6, probably because Taft numbers are unaffected by steric effects.   In any case, the consistency of the correlations given in Figure 6 indicates that no fundamental discrepancies exist

in the basis of correlations presented in Figures 3 to 5.   The results further illustrate that σ^* and $\Sigma\sigma^*$ values are effective and useful physicochemical criteria for the reverse osmosis separation of aldehydes, ketones, ethers, and esters.

σ^* **or** $\Sigma\sigma^*$ **Versus** $\Delta\nu_s$ **(Basicity).**   Since $\Delta\nu_s$ (basicity) represents the total polar effect of the molecule and σ^* or $\Sigma\sigma^*$ represents the contribution of the substituent group or groups to this total effect, unique correlations between $\Delta\nu_s$ (basicity) and σ^* or $\Sigma\sigma^*$ should be expected to exist for each functional group as illustrated earlier for alcohols and phenols.[1]   Such correlations are presented in Figure 7 for aldehydes, ketones, ethers, and esters.   An increase in σ^* or $\Sigma\sigma^*$ corresponds to a decrease in the basicity of the molecule; even though there is some scatter in the data, Figure 7 illustrates the relative effect of each functional group on the total basicity of the molecule in the range of σ^* or $\Sigma\sigma^*$ values investigated.   It might be interesting to study whether other methods of expressing basicity[23] result in better or different correlations.

Separation of Amines

Effect of Structure on Solute Separation.   The dissociation constants of amines are high enough to partially ionize the molecules in aqueous solutions and offer a means of expressing the relative basicities of the solutes. As pointed out earlier,[1] ions are subject to electrostatic repulsion in the vicinity of the cellulose acetate membrane surface, which repulsion contributes to preferential sorption of water in reverse osmosis.[24–26]   Though all amines are generally classified as bases, their basicity effects on reverse osmosis separation should be expected to be different for primary, secondary, and tertiary amines for the following reason.   A tertiary amine does not have any hydrogen atom attached to the electronegative nitrogen atom.   Consequently, a tertiary amine has no acidic character; it is entirely a base.   On the other hand, the hydrogen atoms (or atom) attached to the nitrogen atom in the primary and secondary amines impart in them some acidic character[10,27] which weakens the basicity effect of the solute concerned.   Thus, with respect to amines, the factors governing solute separation in reverse osmosis include pK_a and degree of dissociation, basicity effect, and acidity effect.   Of the above three factors, the first two tend to increase, and the last one tends to decrease, solute separations in reverse osmosis.   Further, only the first two are relevant to the separations of tertiary amines, while all three are relevant to the separations of primary and secondary amines.   Consequently, the primary, secondary, and tertiary amines need to be functionally distinguished in the correlation of reverse osmosis data.

Effect of pK_a and Degree of Dissociation.   Figure 8 shows the effects of pK_a on solute separation and product rate for films 1 and 3 with respect to 14 primary amines (solutes 39 to 52), 4 secondary amines (solutes 53 to 56), and 4 tertiary amines (solutes 57 to 60).   The solute concentrations
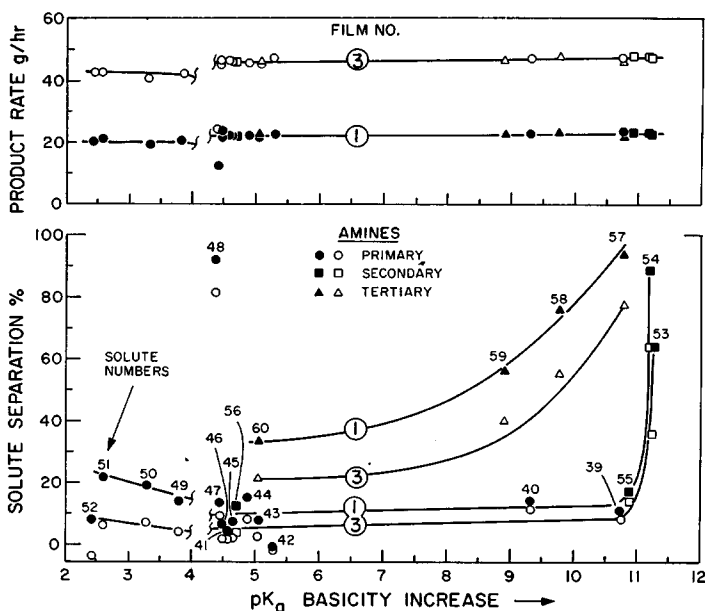
Fig. 8. Effect of pK_a of amines on membrane performance. Film type, cellulose acetate (Batch 316); operating pressure, 250 psig; feed concentration, 0.00075 to 0.003 (0.001 in most cases) g mole/l.; feed flow rate, 400 cc/min; membrane area, 7.6 cm².

used were in the range 0.00075 to 0.003 (in most cases, 0.001) g mole/l. Figure 9 shows explicitly the effects of degree of dissociation, calculated from eq. (6), on solute separation for some of the above amines.

Separation of Tertiary Amines. Referring to the data on tertiary amines (solutes 57, 58, 59, and 60), Figure 8 shows that an increase in pK_a in the range 5.06 to 10.76 increases solute separation. Figure 9 shows that the basicity effect for N,N-dimethylaniline (solute 60, $pK_a = 5.06$) is sufficiently high to give significant solute separation (33% for film 1) even when the solute molecules are practically un-ionized. The data for triethylamine (solute 57, $pK_a = 10.76$, Fig. 9) show that when the solute was only 52% ionized, solute separation with film 1 was 93% showing the combined effects of increase in basicity and increase in ionization on solute separation.

Separation of Secondary Amines. Figure 8 covers pK_a values in the range 4.7 to 11.25 for secondary amines. The pK_a-versus-solute separation correlation shows that at pK_a values <10.8, secondary amines are generally far less separated than tertiary amines, and there is practically very little increase in solute separation with increase in pK_a. At values of pK_a >10.8, solute separation increases very steeply. These results indicate that the acidity effect is the dominating factor governing solute separation at pK_a values <10.8.

Referring to the data of film 1, solute separation was 12% for N-methylaniline (solute 56, $pK_a = 4.7$) and 17% for dimethylamine (solute 55, pK_a
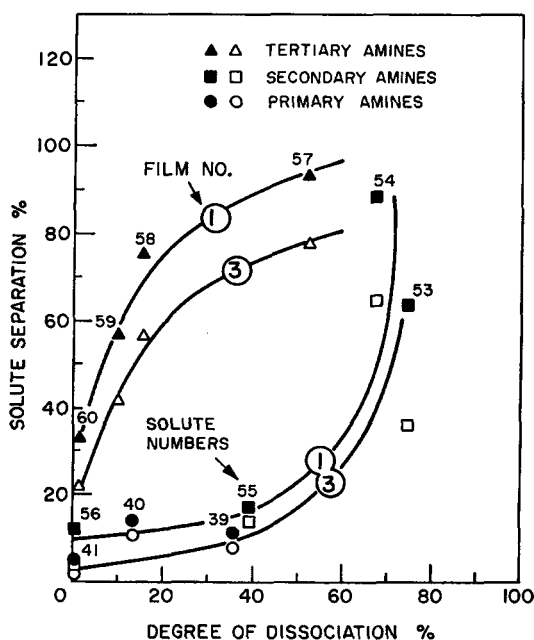
Fig. 9. Effect of degree of dissociation of amines on solute separation. Film type, cellulose acetate (Batch 316); operating pressure, 250 psig; feed concentration, 0.00075 to 0.003 g mole/l.; feed flow rate, 400 cc/min.

= 10.87). Under the conditions of the experiment, the degrees of dissociation for the above solutes were ~0% and 39%, respectively (Fig. 9). Considering the above data, the increase in solute separation obtained for the latter compound (solute 55) was small compared to the increase in degree of dissociation between the two solutes. These results show that the acidity effect of the solute depresses its dissociation effect on solute separation; in other words, the ionic species

$$\begin{matrix} R_1 \\ {} \\ R_2 \end{matrix} \!\!\! > \!\! N^+ H \\ \overset{|}{H}$$
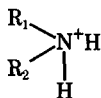
itself acts like a proton donor[22] in the lower ranges of pK_a values (<10.8).

On the other hand, in the range of pK_a values between 10.8 and 11.25, Figure 8 shows that solute separation increases very steeply with increase in pK_a. For example, referring again to the data of film 1, solute separation for piperidine (solute 54, $pK_a = 11.22$) was 88%, whereas its degree of dissociation in the particular experiment was 67% (Fig. 9). These results may be compared with those for dimethylamine (solute 55) given above. The high solute separation obtained for piperidine is due to the combined effects of its basicity and dissociation. These results show that, at pK_a values >10.8, the solute is sufficiently basic that the ionized species no longer acts as a proton donor. These results also show that the degree

of dissociation-versus-solute separation correlation given in Figure 9 for secondary amines is not a unique correlation for all such amines at all concentrations for a given film, but the correlation illustrates the combined effects of acidity, basicity, and dissociation on the separation of secondary amines under the conditions of the experiments used in this study.

Separation of Primary Amines. Figure 8 covers pK_a values in the range 2.45 to 10.75 for primary amines. The solute separation data (Figs. 8 and 9) for ethylamine, benzylamine, and aniline (solutes 39, 40, and 41) show that, in the range of pK_a values from 10.75 to 4.58, the pK_a and degree of dissociation-versus-solute separation correlations are essentially the same as those given for secondary amines in the same range of pK_a values. These results indicate that the comments made earlier with respect to the secondary amines on the dominating effect of the acidity factor and the proton-donating characteristic of the ionic species are also valid, probably more so, to the primary amines in the above range of pK_a values. A steep increase in solute separation at higher pK_a values, similar to that observed in the case of secondary amines at pK_a values >10.8, may also be expected for primary amines, but no experimental data are available at this time to show this trend because primary amines with pK_a values greater than 10.75 could not be obtained for this work.

In the narrow range of pK_a values 5.29 to 4.47 (solutes 42 to 47), solute separations obtained were low ($<15\%$) for both films 1 and 3 (Fig. 8). These results, together with the scatter in the data in the correlation given in Figure 8, appear to reflect the competing effects of acidity and basicity of the solutes and indicate the probable existence of some other factors also (including intramolecular hydrogen-bonding effects) governing solute separation.

pK_a-Versus-Product Rate Correlations. Since the solute concentrations used were very small, the osmotic pressure effects are insignificant. Under such conditions for a given film, the product rates for all solution systems might be expected to be essentially the same. For all feed solution systems involving primary, secondary, and tertiary amines in the pK_a range 4.47 to 11.25, the product rates obtained varied in a very narrow range with respect to each film. The trend in the variation, however, was unmistakable and significant; decrease in product rate corresponded to decrease in solute separation (i.e., less preferential sorption for water) and decrease in pK_a (i.e., decrease in the basicity of the solute). This trend is similar to that observed in the case of alcohol, phenol, and monocarboxylic acid solution systems studied earlier,[1] where the effect was attributed to the probable transient densification of the porous structure of the membrane material as a result of induced intermolecular hydrogen bonding between solute and cellulose acetate molecules.

Some Exceptional Results. The exceptionally high solute separations (92% and 81% for films 1 and 3, respectively) obtained for o-toluidine (solute 48, $pK_a = 4.39$) with about 45% drop in product rates with respect to each film are not in line with the correlations obtained (Fig. 8) with the
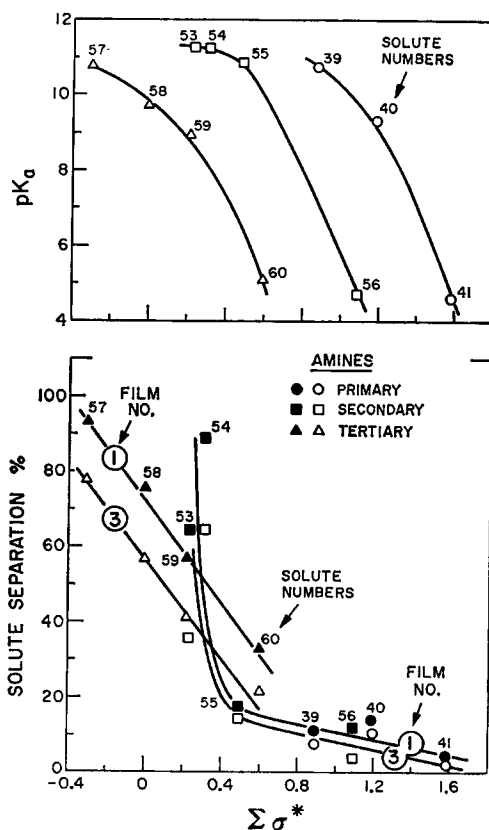
Fig. 10. Taft number vs. pK_a and solute separation for amines.   Solute separation data
under conditions given for Fig. 8.

data for the other primary amines tested in the pK_a range 4.47 to 10.75.
The membrane performance data obtained for p-, m-, and o-chloroaniline
(solutes 49, 50, and 51) and m-nitroaniline (solute 52) in the pK_a range
3.81 to 2.45 also depart significantly from the general correlations presented
in Figure 8 for the other primary amines indicated above.   It may be
recalled that similar exceptional results were reported earlier[1] for p- and
m-chlorophenols and m- and p-nitrophenols.   Such results indicate that
the solute–solvent–membrane material interactions corresponding to such
results are different from those obtained with respect to other solutes,
included in the correlations presented in Figure 8 above and in Figure 1
in reference 1.   The above-mentioned solution systems need further de-
tailed investigations.

Separation of Conjugated Amines. Solute separations for pyridine
(solute 61, $pK_a = 5.23$) and γ-picoline (solute 62, $pK_a = 6.0$) were 4.3%
and 5.3%, respectively, for film 1, and the corresponding product rates
were 22.67 and 23.14 g/hr.   The solute separations were too low compared

to those obtained for tertiary amines with the same pK_a values, and the product rate data indicated no change in the porous structure of the membrane surface. These results show that conjugated amines must be functionally differentiated from tertiary amines for purposes of correlation of reverse osmosis data.

$\Sigma\sigma^*$ **Versus pK_a and Solute Separation.** Since pK_a represents the total polar effect of the molecule and $\Sigma\sigma^*$ represents the contribution of the substituent groups to this total effect, unique correlations between $\Sigma\sigma^*$ and pK_a should exist. This is indeed so, as illustrated in Figure 10, which shows clearly that the correlations are different for primary, secondary, and tertiary amines. Similar correlations have also been given by Hall.[22] Such correlations are useful for estimating pK_a or $\Sigma\sigma^*$ values by interpolation for practical reverse osmosis applications.

The pK_a-versus-solute separation correlations given in Figure 8 for primary, secondary, and tertiary amines may also be represented in the form $\Sigma\sigma^*$ versus solute separation, which is illustrated in Figure 10 for films 1 and 3. The latter correlations show, as before (Fig. 6), that solute separation increases with decrease in $\Sigma\sigma^*$ and that the magnitude of the change is different for the different classes of amines. Compared to tertiary amines, the increase in solute separation with decrease in $\Sigma\sigma^*$ is particularly steep for secondary amines in the $\Sigma\sigma^*$ range 0.6 to 0.3. This is not only due to the decrease in the acidity effect but also due to the increase in pK_a, and hence degree of dissociation, for the secondary amines in the above range of $\Sigma\sigma^*$ values.

CONCLUSIONS

The foregoing results confirm the conclusion stated earlier[1] that 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. The results also justify the basic approach in which the chemical nature of the solute is treated in terms of the different functional groups.

Increase in solute separation with increase in $\Delta\nu_s$ (basicity) for aldehydes, ketones, ethers, and esters (which are proton acceptors) is entirely consistent with decrease in solute separation with increase in $\Delta\nu_s$ for alcohols and phenols (which are proton donors) studied earlier. These results confirm the validity of $\Delta\nu_s$ (basicity) and $\Delta\nu_s$ as relevant physicochemical criteria governing solute separation in reverse osmosis for proton-acceptor and proton-donor solutes, respectively. These results also point out that the cellulose acetate membrane material used in this work has a net proton-acceptor character with respect to solute–membrane interactions.

Increase in solute separation with increase in K_a and degree of dissociation for amines is again entirely consistent with similar results reported earlier[1] for the reverse osmosis separation of monocarboxylic acids in aqueous

solution. These results confirm the concept of electrostatic repulsion of ions in the vicinity of the membrane surface.[24-26]

The excellent correlations of $\Delta \nu_s$ (basicity), $\Delta \nu_s$, pK_a, and solute separation with Taft numbers both in the earlier[1] and this work indicate that Taft numbers are effective and useful physicochemical criteria governing reverse osmosis separations.

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