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Physicochemical Criteria for Reverse Osmosis Separation of Monohydric and Polyhydric Alcohols in Aqueous Solutions Using Porous Cellulose Acetate Membranes

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Synopsis

Reverse osmosis data using different samples of Loeb-Sourirajan-type porous cellulose acetate membranes and single-solute aqueous solution systems involving 16 monohydric alcohols, 4 phenols, 18 polyhydric alcohols, pyrogallol, ethylene glycol monoethyl ether, 6 aldehydes, and 8 carbohydrates (sugars) have been studied. The solute concentrations used were in the range of 0.0005 to 0.003 g mole/l. (~100 ppm), and operating pressure used was 250 psig in all cases. The results show that correlations of acidity and basicity parameters (obtained from IR spectra) with solute separation data are equivalent, and they have predictive capability. A method is given for estimating Taft numbers ($\Sigma\sigma^*$) for monohydric and polyhydric alcohols from available data based on the additive nature of σ^*. Data on solute transport parameters ($D_{AM}/K\delta$) for the different solutes were calculated from membrane performance data. For all the alcohols studied, the $\Sigma\sigma^*$-versus-log ($D_{AM}/K\delta$) correlation was found to be a straight line with a slope different for different ranges of $\Sigma\sigma^*$, but independent of the porous structure of the membrane. Based on this result, it is shown that the parameters of the Taft equation can serve as a basis for expressing solute transport parameter, and this basis offers a means for predicting membrane performance for all alcohol–water systems from a single set of experimental data for a reference solute system. This prediction technique is illustrated using experimental data for 1,3-butanediol taken as the reference solute. The general applicability of the technique has been tested for predicting the separation of some aldehydes and carbohydrates.

INTRODUCTION

The physicochemical criteria for the reverse osmosis separation of alcohols, phenols, aldehydes, ketones, ethers, and esters in aqueous solutions using porous cellulose acetate membranes have been discussed.[1–3] It was shown that in such membrane–solution systems, when the solute molecule was essentially undissociated, preferential sorption of water on the membrane surface (and hence solute separation in reverse osmosis) was governed by the polar effect of the solute molecule. The latter was represented by the hydrogen bonding ability of the solute molecule as given by the relative shift in the OH band maximum in the IR spectra.

An increase in the hydrogen bonding ability resulted in a decrease in solute separation if the solute molecule was an acid (proton donor),[1] or in an increase in solute separation if the solute molecule was a base (proton acceptor).[2] The polar effect of the molecule was also represented by the Taft number for the substituent group in the molecule. Both the acidity parameter and the Taft number proved to be effective physicochemical criteria for the reverse osmosis separation of monohydric alcohols studied earlier.[1] This paper extends the applicability of the above criteria for the reverse osmosis separation of polyhydric alcohols and some related compounds in aqueous solutions using the Loeb-Sourirajan-type porous cellulose acetate membranes.

Since the functional —OH group can behave both as an acid as well as a base, the data for the reverse osmosis separation of alcohols can be correlated equally well by the basicity of the alcohol molecule. Further, it is known[4–6] that ethyl and *n*-propyl alcohols are relatively less separated in reverse osmosis than ethylene glycol and glycerol, which indicates that polyhydric alcohols are relatively more basic than monohydric alcohols. For these reasons, both the acidity and basicity parameters have been determined from IR spectra for all the monohydric and dihydric alcohols studied in this work, and the results are reported and discussed in this paper. The proved effectiveness[1,2] of Taft numbers for correlating data on reverse osmosis separation of acids and bases indicates that the Taft equation can serve as a basis for estimating solute transport parameter and predicting solute separation in reverse osmosis. This is illustrated in this paper with particular reference to monohydric and polyhydric alcohols and some carbohydrates.

EXPERIMENTAL

Reverse Osmosis Experiments

The organic solute substances in aqueous solutions in the concentration range of 0.0005 to 0.003 g mole/l. and laboratory-made Batch 316-type porous cellulose acetate membranes[7] were used. The apparatus, membranes, and the experimental procedure employed were the same as those reported earlier.[1,2] 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 three of them (films 1, 3, and 5) are included in this paper. It is emphasized that the data are only illustrative of the principles involved and do not represent limiting values in reverse osmosis. In all cases, similar results were obtained with all the films tested. The specifications[8a] of films 1, 3, and 5 were as follows: pure water permeability constant A (in g mole H_2O/cm^2 sec atm) = 2.48×10^{-6} for film 1, 5.35×10^{-6} for film 3, and 9.73×10^{-6} for film 5; and solute transport parameter for sodium chloride $D_{AM}/K\delta$ (in cm/sec) = 3.22×10^{-5} for film 1, 16.89×10^{-5} for film 3, and 144.4×10^{-5} for film 5 at 250 psig. The feed flow conditions used in the experiments corre-

sponded 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 grams per hour) for the effective area of film used (7.6 cm^2 in all cases), and solute separation f defined as

$$f = \left[\frac{\text{solute ppm in feed} - \text{solute ppm in product}}{\text{solute ppm in feed}}\right] \quad (1)$$

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. 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.

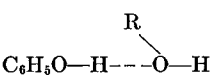
Analysis

A Beckman total carbon analyzer Model 915 was used to measure the concentration of the organic solutes. The analytical procedure was the same as that used before.[1,2] 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

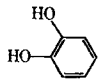
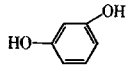
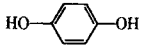
The acidity parameter $\Delta\nu_s$ (cm^{-1}) for monohydric and polyhydric alcohols was determined from measurements of the shift in the OH band maxima in the IR spectra for each solute in CCl_4 and ether solutions following the method of Barrow.[9] The experimental procedure employed for these determinations was exactly the same as before.[1] The frequency measurements had an accuracy of ± 1 cm^{-1} in CCl_4 solutions and ± 2 in ether solutions. Following the method of Kuhn,[10] the basicity parameter $\Delta\nu_s$(basicity) (cm^{-1}) for monohydric and dihydric alcohols was determined from measurements of the shift in the OH band maximum in the IR spectra for phenol in alcohol + phenol + CCl_4 solution using phenol + CCl_4 solution without any alcohol as the reference system; consequently, $\Delta\nu_s$-(basicity) was the difference in frequency between the free OH band of phenol and the bonded OH band of the compound

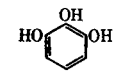


For basicity measurements, a cell length of 1 mm was used. The concentration of phenol and other solutes were 0.05 g mole/l. except for some glycols and hydroxy phenols which were not soluble in CCl_4 to that extent; in such cases, saturated solutions were used. All measurements were made

TABLE I

Acidity, Basicity, and Taft Number for Monohydric and Polyhydric Alcohols

Solute no.	Solute: Name	Solute: Formula	Molecular weight	$\Delta\nu_s$, cm^{-1}	$\Delta\nu_s$(basicity), cm^{-1}	Taft number σ^* or $\Sigma\sigma^*$
	Alcohols	R in ROH				
1	*t*-Butyl alcohol	*t*-C_4H_9	74.1	123	248 (264)[a]	−0.300
2	3-Pentanol	3-C_5H_{11}	88.2	136	244	−0.225
3	*s*-Butyl alcohol	*s*-C_4H_9	74.1	137	236 (242)	−0.210
4	i-Propyl alcohol	i-C_3H_7	60.1	135	238	−0.190
5	Cyclohexanol	*cyclo*-C_6H_{11}	102.2	129	242	−0.250
6	*n*-Butyl alcohol	*n*-C_4H_9	74.1	145	231 (231)	−0.130
7	i-Butyl alcohol	i-C_4H_9	74.1	140	233	−0.125
8	*n*-Propyl alcohol	*n*-C_3H_7	60.1	141	229	−0.115
9	Ethyl alcohol	C_2H_5	46.1	143	228	−0.100
10	Methyl alcohol	CH_3	32.0	149	216 (218)	0
11	Phenethyl alcohol	$C_6H_5(CH_2)_2$	122.2	163	229	0.08
12	Benzyl alcohol	$C_6H_5(CH_2)$	108.1	156	217	0.215
13	Phenol	C_6H_5	94.1	288	136 (136)	0.600
14	*n*-Amyl alcohol	*n*-C_5H_{11}	88.2	142	234	−0.133
15	*n*-Hexyl alcohol	*n*-C_6H_{13}	102.2	144	234	−0.134
16	*n*-Heptyl alcohol	*n*-C_7H_{15}	116.2	145	234	−0.134
17	*n*-Octyl alcohol	*n*-C_8H_{17}	130.2	142	237	−0.134
	Phenols					
18	Pyrocatechol		110.1	291	—	1.200
19	Resorcinol		110.1	284	126	1.200
20	Hydroquinone		110.1	—	130	1.200

	Polyhydric Alcohols and Pyrogallol					
21	D-Sorbitol	$CH_2OH(CHOH)_4CH_2OH$	182.2	—	—	−1.224
22	Dulcitol	$CH_2OH(CHOH)_4CH_2OH$	182.2	—	—	−1.224
23	Arabitol	$CH_2OH(CHOH)_3CH_2OH$	152.2	—	—	−0.951
24	Xylitol	$CH_2OH(CHOH)_3CH_2OH$	152.2	—	—	−0.951
25	Adonitol	$CH_2OH(CHOH)_3CH_2OH$	152.2	—	—	−0.951
26	L-Erythritol	$CH_2OH(CHOH)_2CH_2OH$	122.1	—	—	−0.680
27	Pinacol	$(CH_3)_2COHCOH(CH_3)_2$	118.2	140	261	−0.650
28	1,2,6-Hexanetriol	$CH_2OHCHOH(CH_2)_3CH_2OH$	134.2	—	—	−0.501
29	2,3-Butanediol	$CH_3CHOHCHOHCH_3$	90.1	149	243	−0.420
30	Glycerol	$CH_2OHCHOHCH_2OH$	92.1	—	—	−0.420
31	1,3-Butanediol	$CH_2OHCH_2CHOHCH_3$	90.1	138	245	−0.340
32	Propylene glycol	$CH_2OHCHOHCH_3$	76.1	152	237	−0.305
33	*cis*- and *trans*-1,2-Cyclohexanediol	*cis*- and *trans*- 	116.2	164	244	−0.500
34	*trans*-1,2-Cyclohexanediol	*trans*- 	116.2	165	244	−0.500
35	1,6-Hexanediol	$CH_2OH(CH_2)_4CH_2OH$	118.2	140	235	−0.268
36	1,5-Pentanediol	$CH_2OH(CH_2)_3CH_2OH$	104.2	139	241	−0.266
37	1,3-Propanediol	$CH_2OH(CH_2)CH_2OH$	76.1	140	241	−0.230
38	1,2-Ethanediol (ethylene glycol)	CH_2OHCH_2OH	62.1	156	234	−0.200
39	Pyrogallol		126.1	—	—	1.800

[a] Data in parentheses are those of Kuhn.[10]

at room temperature. The data on $\Delta\nu_s$(basicity) were reproducible within 1 cm^{-1}; however, in some cases of 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

Acidity and Basicity of Alcohols

The acidity ($\Delta\nu_s$, cm^{-1}) and basicity ($\Delta\nu_s$(basicity), cm^{-1}) parameters for 16 monohydric alcohols, 2 phenols, and 10 dihydric alcohols were determined by the method described above, and the data are presented in Table I. Figure 1 gives the $\Delta\nu_s$-versus-$\Delta\nu_s$(basicity) correlations for the compounds studied. Even though there is some scatter in the data, three basic results emerge clearly from Figure 1. First, the $\Delta\nu_s$-versus-$\Delta\nu_s$-(basicity) correlations are different for monohydric and dihydric alcohols; this result indicates that the number of the functional —OH groups and their disposition in the molecule affect the polar effect of the molecule. Secondly, with respect to both monohydric and dihydric alcohols, a decrease in $\Delta\nu_s$ is always accompanied by an increase in $\Delta\nu_s$(basicity), and vice versa; this result illustrates the equivalence of the above changes with respect to the reactivity of molecules and offers direct experimental

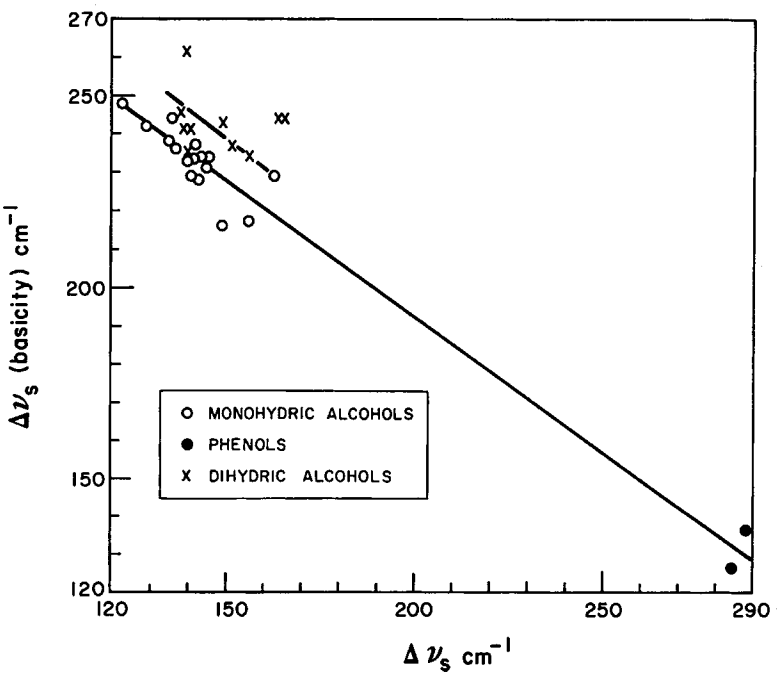


Fig. 1. Acidity-vs.-basicity parameters for monohydric and dihydric alcohols and phenols.

justification for the interpretation of reverse osmosis separation data given earlier[1,2] for proton donor and proton acceptor solutes in terms of their relative acidity and basicity parameters, respectively. Thirdly, the basicity of dihydric alcohols is generally higher than that of monohydric alcohols; this result illustrates the consequence of the susceptibility of the —OH groups in polyhydric alcohols for intramolecular hydrogen bonding[10,11] and explains why dihydric (and polyhydric) alcohols are generally better separated than monohydric alcohols in reverse osmosis.

$\Delta\nu_s$(basicity)-versus-Membrane Performance

Figure 2 gives $\Delta\nu_s$(basicity)-versus-solute separation and product rate correlations for films 1 and 3 with respect to all monohydric and polyhydric alcohols for which data on $\Delta\nu_s$(basicity) are given in Table I. The correlations cover a wide range (< 0 to 93%) of solute separations. Though there is considerable scatter in the $\Delta\nu_s$(basicity)-versus-solute separation correlations, the following results stand out without any ambiguity.

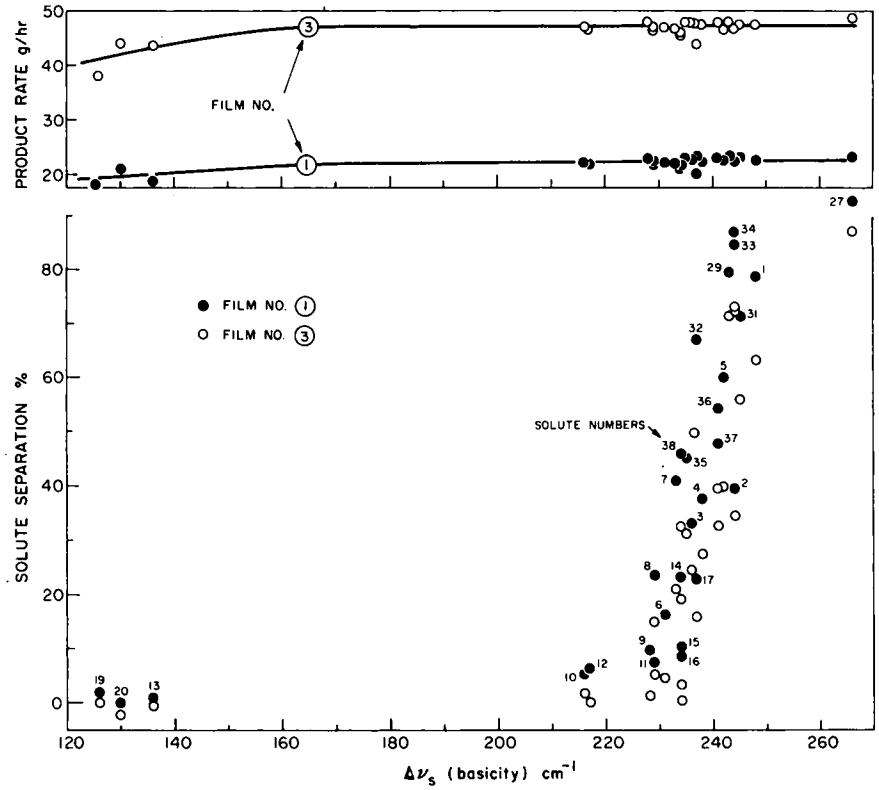


Fig. 2. Effect of $\Delta\nu_s$(basicity) of monohydric and dihydric alcohols and phenols on membrane performance: film type, cellulose acetate (Batch 316); operating pressure, 250 psig; feed concentration, 0.0005 to 0.003 g-mole/l.; feed flow rate, 400 cc/min; membrane area, 7.6 cm²; solute numbers, same as in Table I.

Solute separation increases with increase in $\Delta\nu_s$(basicity); this change is steepest in the $\Delta\nu_s$(basicity) region of 225 to 260 cm^{-1}. In the scale of values obtained in this work, the above region of basicity corresponds to the acidity region where $\Delta\nu_s$ is less than 155 cm^{-1}. The solute separation data in the latter acidity region shows exactly the corresponding correlation as seen in Figure 1 in reference 1.

The value of $\Delta\nu_s$ for water was estimated as 250 cm^{-1} in reference 1. From Figure 1, the corresponding $\Delta\nu_s$(basicity) for water is 156 cm^{-1}. On the basis of the criterion for preferential sorption stated earlier for aqueous solutions of alcohols and phenols,[1,3] one would expect practically negligible separation for solutes whose $\Delta\nu_s$(basicity) is $\sim$156 cm^{-1}. Figure 2 shows that solute separation is indeed relatively very small in the $\Delta\nu_s$(basicity) range 156–225 cm^{-1}, which also indicates that preferential sorption of water is not a linear function of $\Delta\nu_s$(basicity) of solute molecule.

The $\Delta\nu_s$ value for pyrocatechol is 291 cm^{-1}; but no experimental data are available for its $\Delta\nu_s$(basicity) value. The latter, however, can be estimated to be 127 cm^{-1} from Figure 1. Thus $\Delta\nu_s$(basicity) for pyrocatechol is less than that of water; hence the former may be expected to be preferentially sorbed on the membrane surface during reverse osmosis operation.[1,3] On the basis of reverse osmosis data obtained for *p*-chlorophenol discussed earlier,[3] one can expect either negligible or slightly positive or negative separation for pyrocatechol, and slightly lower product rates compared to those obtained in the $\Delta\nu_s$(basicity) region far above 156 cm^{-1}. These expectations were confirmed by experimental reverse osmosis data for the pyrocatechol–water system for which solute separations were 3.8% and -1.4%, respectively for films 1 and 3, and the corresponding product rates were 21.7 and 44.9 g/hr (per 7.6 cm^2 of film area) which fitted well with the correlations presented in Figure 2.

Ethylene glycol monoethyl ether ($CH_2OHCH_2OC_2H_5$) has in its structure both an alcoholic group and an ether linkage. Its $\Delta\nu_s$(basicity) was experimentally determined to be 231 cm^{-1}. Reverse osmosis experiments with aqueous solution of the above compound gave solute separations of 38% and 32%, respectively, for films 1 and 3, with corresponding product rates of 23 and 48 g/hr (per 7.6 cm^2 of film area). These data fit well with the correlations presented in Figure 2.

The $\Delta\nu_s$-versus-product rate correlations (Fig. 1 in reference 1) showed that the porous structure on the membrane surface was affected, and the product rates decreased for $\Delta\nu_s$ values greater than $\sim$175 cm^{-1}. The same tendency is shown by the $\Delta\nu_s$(basicity)-versus-product rate correlations in Figure 2 for the corresponding $\Delta\nu_s$(basicity) region of <220 cm^{-1}.

The foregoing results establish the equivalence of correlations of acidity and basicity parameters with reverse osmosis experimental data, and the predictive capability of such correlations for the separation of monohydric and polyhydric alcohols and related compounds in aqueous solutions using porous cellulose acetate membranes.

Taft Numbers for Monohydric and Polyhydric Alcohols

The definition and significance of the Taft number (σ^* or $\Sigma\sigma^*$) and its relevance to reverse osmosis separation have been discussed.[1,2] In view of the effectiveness of σ^* or $\Sigma\sigma^*$ for correlating acidity and basicity parameters, and also the experimental reverse osmosis separation data, it is important to develop appropriate techniques for estimating Taft numbers to express the polar effect of the substituents in a wide variety of organic molecules of practical interest in reverse osmosis applications. The σ^* values of Taft[12] constitute the basis for all such estimations. The procedure for estimating Taft numbers is a problem with respect to substituent groups for which valid σ^* data are not available in the literature, and with respect to substituent groups in molecules whose structures involve polyfunctional groups. Some monohydric alcohols and all the polyhydric alcohols studied in this work involve such substituent groups for the estimation of whose Taft numbers an empirical method has been developed. The method is based on the additive nature of σ^* and follows the technique illustrated by Taft[12] for estimating the Taft numbers for $(C_6H_5)_2CH$ ($\sigma^* = 0.430$) and $C_6H_5CH_3CH$ ($\sigma^* = 0.115$) from those of $C_6H_5CH_2$ ($\sigma^* = 0.215$) and C_2H_5 ($\sigma^* = -0.100$). Following the same technique, the Taft number for the substituent group in a polyhydric alcohol is considered equal to the sum of the Taft numbers for each of the substituent groups obtained by replacing by hydrogen atom all the —OH groups in the molecule except the —OH group under consideration and carrying out the summation to cover all the —OH groups in the molecule. The following comments and method of calculation give the basis for the numerical data on Taft number (σ^* or $\Sigma\sigma^*$) listed in Table I for all the monohydric and polyhydric alcohols studied in this work.

The σ^* values for compounds 1 to 4 and 6 to 13 are the same as those listed by Taft.[12] For cyclo-C_6H_{11} (solute 5), the Taft table gives σ^* as -0.15. On the basis of the correlation of reverse osmosis separation data for cyclohexanol with $\Delta\nu_s$ and σ^* reported earlier,[1] σ^* for cyclo-C_6H_{11} has been changed to -0.25 for the purpose of this work.

According to Taft,[12] interposing a CH_2 group between a hydrogen atom or an alkyl group and the functional center changes the difference in σ^* values by a factor of 5. The values of σ^* for n-C_3H_7 and n-C_4H_9 are -0.115 and -0.130, respectively. On the above basis, the difference between the σ^* values for n-C_4H_9 and n-C_5H_{11} is one-fifth of the difference of σ^* values for n-C_3H_7 and n-C_4H_9, i.e., $^1/_5 \times 0.015 = 0.003$; consequently σ^* for n-C_5H_{11} (solute 14) $= -0.133$. On the same basis, σ^* for n-$C_6H_{13} = -0.1336$, or -0.134. Further addition of CH_2 groups to n-C_6H_{13} may be assumed to change the corresponding σ^* values insignificantly. Therefore, a σ^* value of -0.134 is assigned for n-C_nH_{2n+1}, where the subscript n is equal to or greater than 6 (solutes 15, 16, and 17).

The Taft numbers ($\Sigma\sigma^*$) for solutes 18 to 39 were calculated as follows:

$\Sigma\sigma^*$ for pyrocatechol (solute 18) $= 2 \times \sigma^*$ for $C_6H_5(0.600) = 1.200$.

On the same basis, $\Sigma\sigma^*$ is the same for solutes 18, 19 and 20.

$\Sigma\sigma^*$ for D-sorbitol (solute 21) $= 2 \times [\sigma^*$ for n-$C_6H_{13}(-0.134)$ $+ \sigma^*$ for n-$C_4H_9CHCH_3 + \sigma^*$ for n-$C_3H_7CHC_2H_5]$.

Since

σ^* for n-$C_4H_9CHCH_3 = \sigma^*$ for n-$C_5H_{11}(-0.133) + \sigma^*$ for $C_2H_5(-0.100)$

and

σ^* for n-$C_3H_7CHC_2H_5 = \sigma^*$ for n-C_4H_9 (-0.130) $+ \sigma^*$ for n-$C_3H_7(-0.115)$,

$\Sigma\sigma^*$ for D-sorbitol $= 2 \times (-0.134-0.133-0.100-0.130-0.115) = -1.224$.

On the same basis, $\Sigma\sigma^*$ for dulcitol (solute 22) is the same as that of D-sorbitol.

$\Sigma\sigma^*$ for arabitol (solute 23) $= 2 \times \sigma^*$ for n-$C_5H_{11}(-0.133) + 2 \times \sigma^*$ for $C_3H_7CHCH_3$ $(-0.230) + \sigma^*$ for $(C_2H_5)_2CH(-0.225) = -0.951$.

On the same basis, -0.951 is also the Taft number for xylitol and adonitol (solutes 24 and 25).

$\Sigma\sigma^*$ for L-erythritol (solute 26) $= 2\times[\sigma^*$ for n-$C_4H_9(-0.130) + \sigma^*$ for s-$C_4H_9(-0.210)] = -0.680$,

$\Sigma\sigma^*$ for pinacol (solute 27) $= 2 \times \sigma^*$ for $(CH_3)_2CHC(CH_3)_2$ $(-0.325) = -0.650$,

$\Sigma\sigma^*$ for 1,2,6-hexanetriol (solute 28) $= 2 \times \sigma^*$ for n-C_6H_{13} (-0.134) $+ \sigma^*$ for $C_4H_9CHCH_3(-0.233) = -0.501$,

$\Sigma\sigma^*$ for 2,3-butanediol (solute 29) $= 2 \times \sigma^*$ for s-C_4H_9 $(-0.210) = -0.420$,

$\Sigma\sigma^*$ for glycerol (solute 30) $= 2 \times \sigma^*$ for n-$C_3H_7(-0.115) + \sigma^*$ for i-C_3H_7 $(-0.190) = -0.420$,

$\Sigma\sigma^*$ for 1,3-butanediol (solute 31) $= \sigma^*$ for n-C_4H_9 $(-0.130) + \sigma^*$ for s-C_4H_9 $(-0.210) = -0.340$,

$\Sigma\sigma^*$ for propylene glycol (solute 32) $= \sigma^*$ for n-C_3H_7 (-0.115) $+ \sigma^*$ for i-C_3H_7 $(-0.190) = -0.305$.

$\Sigma\sigma^*$ for *cis*- and *trans*-1,2, cyclohexanediol (solute 33) $= 2 \times \sigma^*$ for *cyclo*-$C_6H_{11}(-0.250) = -0.500$.

On the same basis, $\Sigma\sigma^*$ for *trans*-1,2,cyclohexanediol (solute 34) is also -0.500.

$\Sigma\sigma^*$ for 1,6-hexanediol (solute 35) $= 2 \times \sigma^*$ for n-C_6H_{13}

$(-0.134) = -0.268,$

$\Sigma\sigma^*$ for 1,5-pentanediol (solute 36) $= 2 \times \sigma^*$ for n-C_5H_{11}

$(-0.133) = -0.266,$

$\Sigma\sigma^*$ for 1,3-propanediol (solute 37) $= 2 \times \sigma^*$ for n-C_3H_7

$(-0.115) = -0.230,$

$\Sigma\sigma^*$ for 1,2-ethanediol (solute 38) $= 2 \times \sigma^*$ for $C_2H_5(-0.100) = -0.200,$

$\Sigma\sigma^*$ for pyrogallol (solute 39) $= 3 \times \sigma^*$ for $C_6H_5(0.600 = 1.800.$

Taft Number versus Net Basicity

Since $\Delta\nu_s$ and $\Delta\nu_s$(basicity) represent the total polar effect of the molecule and the Taft number ($\Sigma\sigma^*$) represents the contribution of the substituent group to this total polar effect, unique correlations between $\Delta\nu_s$ and $\Sigma\sigma^*$, or $\Delta\nu_s$(basicity) and $\Sigma\sigma^*$, must exist for each functional group as illustrated earlier for alcohols and phenols[1] and aldehydes, ketones, ethers, and esters.[2] Further, since basicity may be treated as negative acidity, and the membrane material used has a net basicity character with respect to solute–membrane interactions, one may also correlate $\Sigma\sigma^*$ with net basicity of solute obtained by combining appropriately the data on $\Delta\nu_s$ and $\Delta\nu_s$-(basicity) given in Table I. Two adjustments on the numerical values of $\Delta\nu_s$ and $\Delta\nu_s$(basicity) given in Table I are needed before they can be combined to obtain a relative measure for the net basicity of the solute molecule.

The acidity and basicity parameters given in Table I are first transformed into ($\Delta\nu_s$-a) and [$\Delta\nu_s$(basicity)-b], where a and b are arbitrary constants which bring the measures of the respective hydrogen bonding abilities to the same arbitrary scale.

In the —OH functional group of monohydric alcohols, one hydrogen atom is available as a proton donor and one oxygen atom is available as a proton acceptor. Consequently, for monohydric alcohols,

$$\text{net basicity} = \{[\Delta\nu_s(\text{basicity}) - b] - (\Delta\nu_s - a)\} \tag{2}$$

In the functional groups of dihydric alcohols, two oxygen atoms are available as proton acceptors, and the measured $\Delta\nu_s$(basicity) may be considered as the average value for each of the oxygen atoms. On the other hand, with respect to acidity, only one hydrogen atom is available as a proton donor since the other is intramolecularly hydrogen bonded. Consequently, for dihydric alcohols,

$$\text{net basicity} = \{2[\Delta\nu_s(\text{basicity}) - b] - (\Delta\nu_s - a)\}. \tag{3}$$

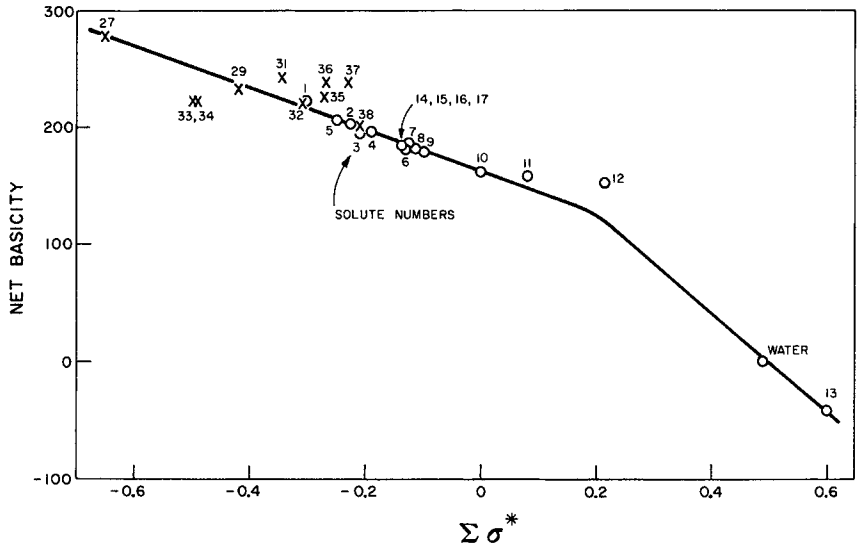


Fig. 3. Effect of Taft number on net basicity for monohydric and dihydric alcohols and phenol. Solute numbers same as in Table I.

In order to use eqs. (2) and (3) to obtain a consistent set of numerical values for net basicity for both monohydric and dihydric alcohols, the applicable values of a and b are needed. The latter can be determined on the following criteria: (i) net basicity for t-butyl alcohol is the same as that of propylene glycol since both compounds have essentially the same $\Sigma\sigma^*$ values (-0.300 and -0.305, respectively); (ii) net basicity for water equals zero. The above criteria bring all data for monohydric and dihydric alcohols in the same scale relative to that of water. Using the above criteria with the numerical values of $\Delta\nu_s$ and $\Delta\nu_s$(basicity), the value of a and b can be calculated to be 291 and 197, respectively.

Figure 3 gives the $\Sigma\sigma^*$-versus-net basicity correlation for all the monohydric and dihydric alcohols used in this work. The results show that the net basicity (and hence, preferential sorption of water in reverse osmosis) increases with decrease in $\Sigma\sigma^*$, which is consistent with all the data reported earlier.[1,2]

Taft Number and Membrane Performance

Figure 4 gives the Taft number ($\Sigma\sigma^*$)-versus-solute separation and product rate correlations for films 1 and 3 for aqueous solution systems involving 38 monohydric and polyhydric alcohols (solutes 1 to 38) listed in Table I. Several aspects of these correlations are significant.

The correlations cover a wide range (<0 to >99%) of solute separations. Hence, these data offer a firm experimental basis for the effect of Taft number on membrane performance.

The scatter of data observed earlier in the $\Delta\nu_s$(basicity)-versus-solute separation correlations (Fig. 2) has largely disappeared in the $\Sigma\sigma^*$-versus-

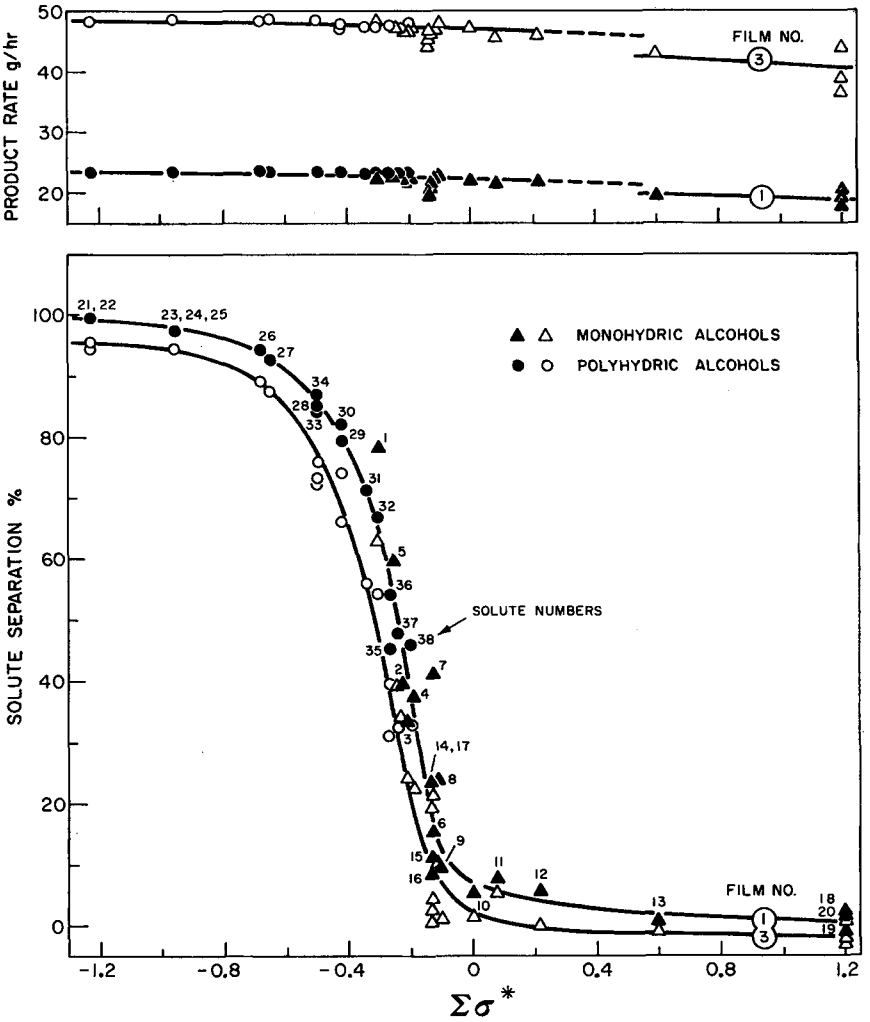


Fig. 4. Effect of Taft number of monohydric and polyhydric alcohols, and phenols on membrane performance: film type, cellulose acetate (Batch 316); operating pressure, 250 psig; feed concentration, 0.0005 to 0.003 g-mole/l.; feed flow rate, 400 cc/min; membrane area, 7.6 cm^2; solute numbers, same as in Table I.

solute separation correlations. For each film, a single line represents reasonably well the $\Sigma\sigma^*$-versus-solute separation correlation for both monohydric and polyhydric alcohols. Solutes whose Taft numbers are the same have also essentially the same separation in reverse osmosis; examples are data for solutes 14 and 17, 18, 19 and 20, 21 and 22, 23, 24 and 25, and 28, 33 and 34. These results show that the method used in this work for calculating $\Sigma\sigma^*$ values is essentially valid and that Taft numbers are effective for correlating reverse osmosis separation data. These results also justify the value of -0.25 assigned to σ^* for *cyclo*-C_5H_{11}

in view of the experimental separation data obtained for cyclohexanediols (solutes 33 and 34).

For both films, solute separations are less than 10% at $\Sigma\sigma^*$ values of zero or more. Solute separation increases with higher negative values of $\Sigma\sigma^*$; this increase is steepest in the $\Sigma\sigma^*$ range of -0.1 to -1.0. At a $\Sigma\sigma^*$ value higher than that of water (0.49), solute separation is either practically zero or negative for all solutes for which data are given in Figure 4. These results confirm the basic physicochemical criteria for separation of alcohols discussed earlier,[1] namely, that positive separations are obtainable for an alcohol whose $\Sigma\sigma^*$ value is less than that of water and higher negative values of $\Sigma\sigma^*$ increase the preferential sorption of water, and hence solute separation, in reverse osmosis.

At zero or negative $\Sigma\sigma^*$ values, there is no change in product rates (and hence, no change in the porous structure of the membrane) except for feed solutions involving solutes 15, 16, and 17 (n-C_6, C_7, and C_8 alcohols, $\Sigma\sigma^* = -0.134$). With respect to the latter feed solutions and those involving solutes whose $\Sigma\sigma^*$ values are positive, the product rates showed a tendency to decrease, and this decrease became significantly more for higher positive values of $\Sigma\sigma^*$. These data indicate that in such feed solution systems, the proximity of the solute molecule to the membrane surface is so close that transient densification of the porous structure of the membrane material due to induced intermolecular hydrogen bonding (as discussed earlier[1]) and/or partial blocking of the pore area available for fluid flow occur.[3]

Figure 4 shows that solute separations for n-C_4, C_6, and C_7 alcohols (solutes 6, 15, and 16) are lower than the separation obtained for n-C_3 alcohol (solute 8) in spite of the more negative $\Sigma\sigma^*$ values for the former alcohols. Further, solute separations for n-C_5 and C_8 alcohols (solutes 14 and 17) are no different from the separation obtained for n-C_3 alcohol; the corresponding product rates, however, were lower for the higher alcohols. These results indicate the possible existence of factors other than polar effects, which simultaneously govern solute separation in reverse osmosis.

The Taft number represents only the polar effect of the substituent group in the solute molecule. Since cellulose acetate membrane material has both polar and nonpolar characters, the extent of solute separation may be expected to be governed both by the polar and nonpolar characters of the solute molecule. No physicochemical parameter has yet been chosen to represent effectively the nonpolar effect (i.e., the hydrophobic character) of the solute molecule. The membrane surface may be expected to attract a molecule which has a significant hydrophobic character. The result of this attraction is either to reduce the preferential sorption of water (and hence reduce solute separation in reverse osmosis) or to promote the preferential sorption of solute at the membrane–solution interface which in turn may result in positive, negative, or zero solute separation in reverse osmosis.[3] Even solute molecules which have polar functional groups may be expected to have some hydrophobic character. The above experimental results with C_4–C_7 alcohols indicate that molecules containing *a*

straight chain involving three or more carbon atoms *not* associated with any polar functional group may be expected to exhibit significant nonpolar effect. With respect to such molecules, solute separation in reverse osmosis may be expected to be governed simultaneously by both polar and nonpolar effects of the solute molecule. This aspect of the subject opens a new area of investigation in reverse osmosis.

Solute separations of 33% and 26% were obtained for pyrogallol (solute 39, not shown in Fig. 4) with films 1 and 3, respectively; the corresponding product rates were 21.1 and 43.4 g/hr (per 7.6 cm^2 of film area). The high positive $\Sigma\sigma^*$ value for pyrogallol would indicate that the latter would be preferentially sorbed on the membrane surface. Consequently, the above separation and product rate data indicate that the case of pyrogallol is probably analogous to the case of *p*-chlorophenol discussed before[3] and calls for further detailed investigations.

Solute Transport Parameter from Membrane Performance Data

The existence of a unique correlation between $\Sigma\sigma^*$ and solute separation of monohydric and polyhydric alcohols (Fig. 4) indicates that such a correlation could also exist between $\Sigma\sigma^*$ and solute transport parameter ($D_{AM}/K\delta$) for the above alcohols with respect to each film. It is important to explore the latter possibility for the following reason. For any membrane, solute separation is not a fixed quantity; it is a function of feed concentration and mass transfer coefficient k on the high pressure side of the membrane; even at the same feed concentration and feed flow rate, k could be different for different solutes. On the other hand, $D_{AM}/K\delta$ is independent of feed concentration and feed flow rate, as illustrated for the systems glycerol–water[5] and ethylene glycol–water,[6] which makes $\Sigma\sigma^*$-versus-$D_{AM}/K\delta$ correlation more useful for practical purposes of predicting membrane performance under different operating conditions. The values of $D_{AM}/K\delta$ for alcohols with respect to each film can be obtained from the membrane performance data following the Kimura-Sourirajan analysis for reverse osmosis transport.[8a] An expression for $D_{AM}/K\delta$ in terms of product rate [PR], solute separation f, and the mass transfer coefficient k is derived below, using the same symbols as those given in reference 8a.

Let [PR] represent product rate in grams per hour per S cm^2 of effective film surface and let Q' represent product rate in grams per sec per cm^2 of film area; and let w_A and w_B be the grams of solute and solvent, respectively, in Q' grams of product solution. Let $(\text{ppm})_{\text{feed}}$ and $(\text{ppm})_{\text{prod}}$ represent parts per million of solute in feed and product solutions, respectively. From eq. (1),

$$(\text{ppm})_{\text{prod}} = (\text{ppm})_{\text{feed}}\,(1 - f). \tag{4}$$

Also,

$$(\text{ppm})_{\text{prod}} = \frac{w_A}{w_A + w_B} \times 10^6 \approx \frac{w_A}{w_B} \times 10^6 \tag{5}$$

$$\frac{w_A}{w_B} = \frac{(\text{ppm})_{\text{feed}}\,(1-f)}{10^6}. \tag{6}$$

Since

$$Q' = w_A + w_B \tag{7}$$

$$= w_B\left[1 + \frac{(\text{ppm})_{\text{feed}}\,(1-f)}{10^6}\right] \tag{8}$$

$$\frac{w_B}{Q'} = 1\Big/\left[1 + \frac{(\text{ppm})_{\text{feed}}\,(1-f)}{10^6}\right] \tag{9}$$

$$w_A = Q' - w_B = Q'\left[1 - \frac{w_B}{Q'}\right] \tag{10}$$

$$\approx \frac{Q'}{10^6}\,(\text{ppm})_{\text{feed}}\,(1-f) \tag{11}$$

since $(\text{ppm})_{\text{feed}}\,(1-f)/10^6$ is $\ll 1$ for $(\text{ppm})_{\text{feed}} \approx 10^2$.

$$\therefore Q' = w_A \times 10^6/(\text{ppm})_{\text{feed}}(1-f) \tag{12}$$

$$= N_A M_A \times 10^6/(\text{ppm})_{\text{feed}}(1-f) \tag{13}$$

where N_A is solute flux through the membrane, in g mole/cm^2 sec, and M_A is the molecular weight of solute.

$$[\text{PR}] = Q' \cdot S \cdot 3600 \tag{14}$$

$$= 3600\,S \cdot N_A M_A\,10^6/(\text{ppm})_{\text{feed}}(1-f) \tag{15}$$

$$\therefore N_A = \frac{[\text{PR}](\text{ppm})_{\text{feed}}\,(1-f)}{3600\,S \cdot M_A \cdot 10^6}. \tag{16}$$

Assuming molar density of the solution (c in g-mole/cm^3) is constant and mole fraction of solute in product solution $X_{A3} \ll 1$, the Kimura-Sourirajan analysis yields the following expressions for solute and water flux through the membrane, N_A and N_B, respectively in g-mole per cm^2 per sec[8a]:

$$N_A = \left[\frac{D_{AM}}{K\delta}\right] c(X_{A2} - X_{A3}) \tag{17}$$

$$N_B = kc \ln\left[\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right] \tag{18}$$

where X_{A1}, X_{A2}, and X_{A3} are the mole fractions of solute in feed solution, concentrated boundary solution on the high pressure side of the membrane, and product solution on the low pressure side of the membrane, respectively.

(The Kimura-Sourirajan analysis is discussed extensively in reference 8a. It may be recalled that the above eq. (17) defines the quantity $D_{AM}/K\delta$ for the transport of any given solute through the membrane. This quantity,

called the solute transport parameter, is a fundamental one for any given membrane–solution system. The above parameter is not a mere proportionality constant, but it is a combination of at least three distinct quantities all of which have important physical significance, but none of which can be precisely measured. These three quantities are the solute diffusivity through the membrane D_{AM}, effective film thickness δ, and the factor K which relates solute concentration in the membrane phase to that in the solution phase in equilibrium with the membrane phase. From the point of view of reverse osmosis process design, it is sufficient to know the overall value of the parameter $D_{AM}/K\delta$ which plays the role of a mass transfer coefficient with respect to solute transport through the membrane; hence the parameter is treated as a single quantity for purposes of analysis.)

Since

$$N_B = \frac{w_B}{M_B} \approx \frac{Q'}{M_B} = \frac{[\mathrm{PR}]}{3600\, S \cdot M_B} \tag{19}$$

where M_B is the molecular weight of water,

$$\frac{[\mathrm{PR}]}{3600\, S \cdot M_B} = kc \ln\left[\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right] \tag{20}$$

$$\therefore\ X_{A2} - X_{A3} = (X_{A1} - X_{A3}) \exp\left[\frac{[\mathrm{PR}]}{3600\, SM_B kc}\right] \tag{21}$$

$$c(X_{A2} - X_{A3}) = c(X_{A1} - X_{A3}) \exp\left[\frac{[\mathrm{PR}]}{3600\, SM_B kc}\right] \tag{22}$$

$$= \{(\mathrm{ppm})_{\mathrm{feed}} - (\mathrm{ppm})_{\mathrm{prod}}\} \frac{d}{10^6 M_A} \exp\left[\frac{[\mathrm{PR}]}{3600\, SM_B kc}\right] \tag{23}$$

$$= (\mathrm{ppm})_{\mathrm{feed}} \frac{fd}{10^6 M_A} \exp\left[\frac{[\mathrm{PR}]}{3600\, SM_B kc}\right] \tag{24}$$

where d is the density (in g/cm^3) of solution. Using eq. (24), and noting that

$$d = cM_B, \tag{25}$$

eq. (17) becomes

$$N_A = \left[\frac{D_{AM}}{K\delta}\right] (\mathrm{ppm})_{\mathrm{feed}} \frac{fd}{10^6 M_A} \exp\left[\frac{[\mathrm{PR}]}{3600\, Skd}\right]. \tag{26}$$

Establishing the identity of eqs. (16) and (26), the expression for $D_{AM}/K\delta$ may be given as

$$\left[\frac{D_{AM}}{K\delta}\right] = \frac{[\mathrm{PR}]}{3600\, Sd} \frac{(1-f)}{f} \left\{\frac{1}{\exp\left[\frac{[\mathrm{PR}]}{3600\, Skd}\right]}\right\}. \tag{27}$$

All quantities on the right-hand side of eq. (27) are known except k, for which reasonably valid data are needed in order to calculate $D_{AM}/K\delta$ values from membrane performance data.

Estimation of Mass Transfer Coefficients

In the Kimura-Sourirajan analysis, the mass transfer coefficient k on the high-pressure side of the membrane is defined (in the conventional manner of the "film theory") as

$$k = \frac{D_{AB}}{l} \tag{28}$$

where D_{AB} and l represent the diffusivity (in cm²/sec) of solute in water and the thickness (in cm) of the concentrated boundary layer, respectively. With respect to a given apparatus, for the same conditions of feed concentration and feed flow rate, if l can be assumed constant for different solutions, then k is directly proportional to D_{AB}. This means that for such experimental conditions, if k for a reference solution system and the applicable values of D_{AB} for all the solutes involved are known, the corresponding values of k can be calculated from the relation

$$k = \left[\frac{k}{D_{AB}}\right]_{\text{ref}} \cdot D_{AB} \tag{29}$$

where the subscript ref refers to the reference solution system. The essential validity of the above assumption regarding l is illustrated by a comparison of the experimental and calculated values of k given in Table II for feed solutions involving 14 different solutes. Table II shows that the experimental and calculated values of k agree within 10% in most cases, which level of agreement is adequate for practical purposes of predicting membrane performance. Hence, one may conclude that eq. (29) offers a reasonable means for estimating mass transfer coefficients for the systems studied in this work.

The solution system 1500 ppm NaCl–H_2O, for which data on k ($= 57 \times 10^{-4}$ cm/sec) and D_{AB} ($= 1.61 \times 10^{-5}$ cm²/sec) are available, is taken as the reference system in this work. The values of D_{AB} (diffusivity of solute in pure water at 25°C) for all the organic solutes considered in this work were calculated from the empirical equation of Wilke and Chang[13]:

$$D_{AB} = 7.4 \times 10^{-8} \frac{(\chi M)^{1/2} T}{\mu V_1^{0.6}} \tag{30}$$

where χ = "association" parameter of solvent (=2.6 for water); M = molecular weight of solvent (= 18.02 for water); T = temperature, °K (= 298); μ = viscosity of solution, centipoises (= 0.8937 for pure water); and V_1 = molal volume of solute at normal boiling point, cm³/g mole.

The values of V_1 were obtained by summation of atomic volume data listed in the literature.[14] The precision of the calculated D_{AB} values is estimated to be about 10%, which is adequate for the present purpose. The

TABLE II
Comparison of Experimental and Calculated Values of k[a]

Solute	$D_{AB} \times 10^5$, cm²/sec	$k \times 10^4$, cm/sec	
		Experimental (ref. 7)	Calculated (using eq. (29))
$MgSO_4$	0.556	23	18.5
Na_2SO_4	0.909	33	30
$BaCl_2$	1.160	40.5	38.3
$CaCl_2$	1.318	43.5	43.5
$MgCl_2$	1.039	36	34.3
LiCl	1.277	43	42.2
NaCl[b]	1.475	48.7	48.7*
KCl	1.849	57.1	61
NH_4Cl	1.860	58	61.4
$LiNO_3$	1.260	44	41.6
KNO_3	1.718	52	56.7
$NaNO_3$	1.403	42.5	46.3
Glycerol	0.896	33.4	29.6
Urea	1.345	45	44.4

[a] Feed concentration: 0.5M; feed flow rate: 300 cc/min in the same apparatus. All D_{AB} data from ref. 8b.
[b] Reference solute.

estimated values of V_1, D_{AB}, and k obtained by the above technique for all the solutes involved in this work are given in Table III.

Taft Number and Solute Transport Parameter

Using the values of the mass transfer coefficient k given in Table III, and solute separation and product rate data given in Figure 4, the solute transport parameter $D_{AM}/K\delta$ for different alcohols were calculated from eq. (27). Figure 5 gives a plot of $\Sigma\sigma^*$ versus log $(D_{AM}/K\delta)$ for films 1, 3, and 5. These data cover a wide range of Taft numbers ($\Sigma\sigma^* = 0$ to -1.224), $D_{AM}/K\delta$ ($<1 \times 10^{-5}$ to $>1000 \times 10^{-5}$ cm/sec), and solute separation (5% to >99%), and hence offer a firm experimental basis for the relation between Taft number and solute transport parameter in reverse osmosis.

Figure 5 shows that the data fall naturally into three distinct ranges of $\Sigma\sigma^*$, which are 0 to -0.3, -0.3 to -0.68, and -0.68 to -1.224. Within each region, the $\Sigma\sigma^*$-versus-log $(D_{AM}/K\delta)$ correlation is essentially a straight line with different slopes characteristic of the particular range of $\Sigma\sigma^*$. Further, in each region of $\Sigma\sigma^*$ values, the above slope is identical for all the three membranes, which shows that the above slope is independent of the porous structure of the membrane.

Following the form of Taft equation, the correlation represented in Figure 5 shows that the solute transport parameter and Taft number are related by the expression

$$\left[\frac{D_{AM}}{K\delta}\right] = Ce^{\rho^*\Sigma\sigma^*} \tag{31}$$

where ρ^* is a polar functional constant applicable to reverse osmosis transport given by the slope of the $\Sigma\sigma^*$-versus-log $(D_{AM}/K\delta)$ correlation, and C is a proportionality constant depending on the porous structure of the membrane surface.

In view of the fundamental thermodynamic basis of the Hammett and Taft equations discussed earlier,[1] it is evident that the quantity $\rho^*\Sigma\sigma^*$ is a measure of the relative free-energy changes involved in solute transport through membrane expressed in arbitrary nondimensional units. While the Taft number $\Sigma\sigma^*$ depends only on the nature of the substituent group in the solute molecule, ρ^* should be expected to depend on the nature of the functional group in the molecule and the reverse osmosis operating conditions such as pressure, temperature, nature of solvent, and chemical nature of the membrane. Figure 5 shows that for the experimental conditions used in this work, values of ρ^* for the functional group —OH are 9.7, 5.8, and 2.5 for $\Sigma\sigma^*$ ranges of 0 to −0.3, −0.3 to −0.68, and −0.68

TABLE III
Estimation of k for Solute-Water Systems Under the Conditions of Experiment Used[a]

No.	Solute	V_1, cm³/g mole	$D_{AB} \times 10^5$, cm²/sec	$k \times 10^4$, cm/sec
	Sodium chloride[b]	—	1.61	57
1	*t*-Butyl alcohol	103.6	1.043	36.9
2	3-Pentanol	125.8	0.929	32.9
3	*s*-Butyl alcohol	103.6	1.043	36.9
4	i-Propyl alcohol	81.4	1.206	42.7
5	Cyclohexanol	125.6	0.930	32.9
6	*n*-Butyl alcohol	103.6	1.043	36.9
7	i-Butyl alcohol	103.6	1.043	36.9
8	*n*-Propyl alcohol	81.4	1.206	42.7
9	Ethyl alcohol	59.2	1.460	51.7
10	Methyl alcohol	37.0	1.935	68.5
11	Phenethyl alcohol	147.8	0.843	29.8
12	Benzyl alcohol	125.6	0.930	32.9
13	Phenol	83.4	1.189	42.1
14	*n*-Amyl alcohol	125.8	0.929	32.9
15	*n*-Hexyl alcohol	148.0	0.842	29.8
16	*n*-Heptyl alcohol	170.2	0.775	27.4
17	*n*-Octyl alcohol	192.4	0.720	25.5
18	Pyrocatechol	110.8	1.002	35.5
19	Resorcinol	110.8	1.002	35.5
20	Hydroquinone	110.8	1.002	35.5
21	D-Sorbitol	185.0	0.737	26.1
22	Dulcitol	185.0	0.737	26.1
23	Arabitol	155.4	0.818	29.0
24	Xylitol	155.4	0.818	29.0
25	Adonitol	155.4	0.818	29.0
26	L-Erythritol	125.8	0.929	32.9
27	Pinacol	155.4	0.818	29.0
28	1,2,6-Hexanetriol	162.8	0.796	28.2
29	2,3-Butanediol	111.0	1.001	35.4

TABLE III (*continued*)

No.	Solute	V_1, cm³/g mole	$D_{AB} \times 10^5$, cm²/sec	$k \times 10^4$, cm/sec
30	Glycerol	96.2	1.091	38.6
31	1,3-Butanediol	111.0	1.001	35.4
32	Propylene glycol	88.0	1.151	40.8
33	*cis*- and *trans*-1,2-Cyclohexanediol	133.0	0.898	31.8
34	*trans*-1,2-Cyclohexanediol	133.0	0.898	31.8
35	1,6-Hexanediol	155.4	0.818	29.0
36	1,5-Pentanediol	133.2	0.897	31.8
37	1,3-Propanediol	88.8	1.145	40.5
38	Ethylene glycol	66.6	1.360	48.2
39	Pyrogallol	133.2	0.897	31.8
	Ethylene glycol monoethyl ether	91.3	1.126	40.0
	L-Arabinose	148.0	0.843	29.8
	D-Glucose	177.6	0.755	26.7
	D-Mannose	177.6	0.755	26.7
	D-Galactose	177.6	0.755	26.7
	D-Fructose	177.6	0.755	26.7
	Sucrose	366.0	0.489	17.3
	Maltose	366.0	0.489	17.3
	Lactose	366.0	0.489	17.3
	i-Butyraldehyde	15.5	1.091	38.6
	n-Butyraldehyde	15.5	1.091	38.6
	Propionaldehyde	13.2	1.277	45.1
	Acetaldehyde	10.7	1.582	56.0
	Crotonaldehyde	14.8	1.145	40.6
	Benzaldehyde	17.5	0.964	34.0

[a] Feed concentration: ~100 ppm of solute; feed flow rate: 400 cc/min in the same apparatus.

[b] Reference solute, D_{AB} data from ref. 8b.

to −1.224, respectively. The changes in the value of ρ^* show that the effect of the functional group on the total polar effect of the molecule under the specified operating conditions is different for different ranges of $\Sigma\sigma^*$. The polar functional constants, together with Taft numbers, offer a means of predicting membrane performance for all monohydric and polyhydric alcohols from a single set of experimental data for any one of the alcohols, taken as the reference solute, as illustrated below.

Predictability of Membrane Performance

To illustrate the applicability of the parameters of the Taft equation (ρ^* and $\Sigma\sigma^*$) to predict membrane performance for different alcohols, the experimental data for 1,3-butanediol is arbitrarily chosen as the reference solute. Its $\Sigma\sigma^*$ value is −0.34, and its separations (f) were 71% with film 1 and 56% with film 3. Under the experimental conditions used, the product rates [PR] were 23.2 g/hr with film 1 and 47.3 g/hr with film 3, the

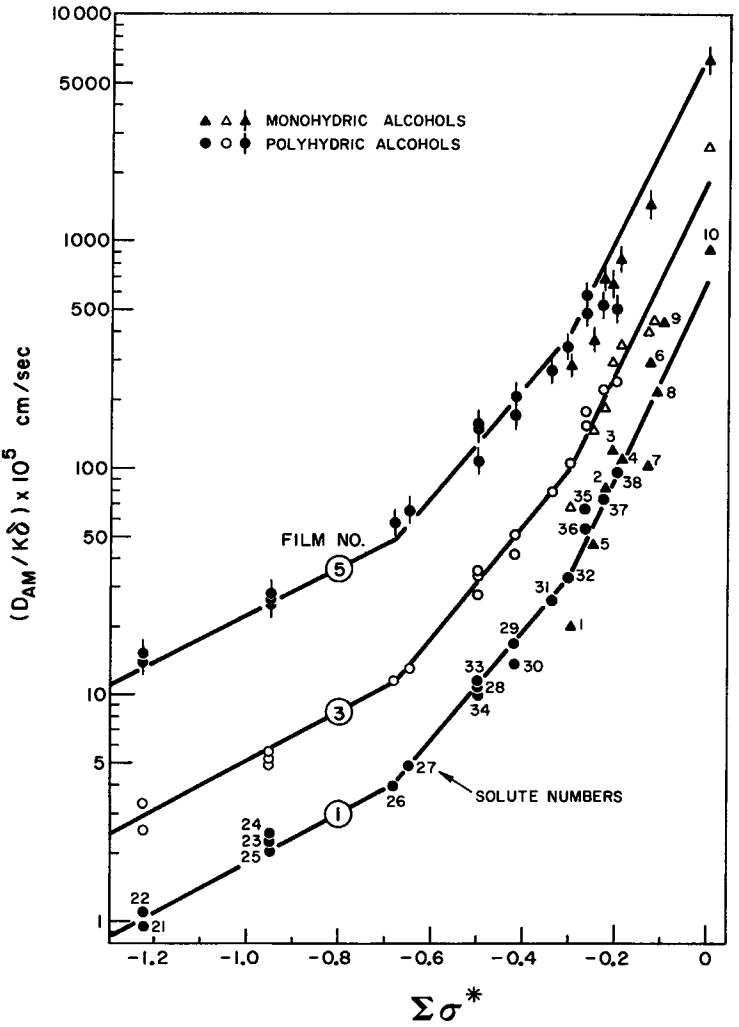


Fig. 5. Effect of Taft number on solute transport parameter for monohydric and polyhydric alcohols: film type, cellulose acetate (Batch 316); operating pressure, 250 psig; solute numbers, same as in Table I.

membrane area S was 7.6 cm^2, the mass transfer coefficient k was 35.4 $\times$ 10^{-4} cm/sec, and the density of the solution was 0.9969 g/cm^3. Using the above data and eq. (25), the values of $D_{AM}/K\delta$ for the reference solute are found to be 26.0 $\times$ 10^{-5} cm/sec for film 1 and 79.6 $\times$ 10^{-5} cm/sec for film 3. In the $\Sigma\sigma^*$-versus-$D_{AM}/K\delta$ correlation, the points corresponding to the reference solute are thus fixed for films 1 and 3. The entire correlation is then generated for each film in the $\Sigma\sigma^*$ regions of -0.30 to -0.68, -0.68 to -1.224, and -0.3 to 0, using the ρ^* values of 5.8, 2.5, and 9.7, respectively (noting that the slope of the $\Sigma\sigma^*$-versus-$\log_{10}$ $(D_{AM}/K\delta)$ straight line is $\rho^*/2.303$). The correlations so generated for films 1 and 3 are given in Figure 6.

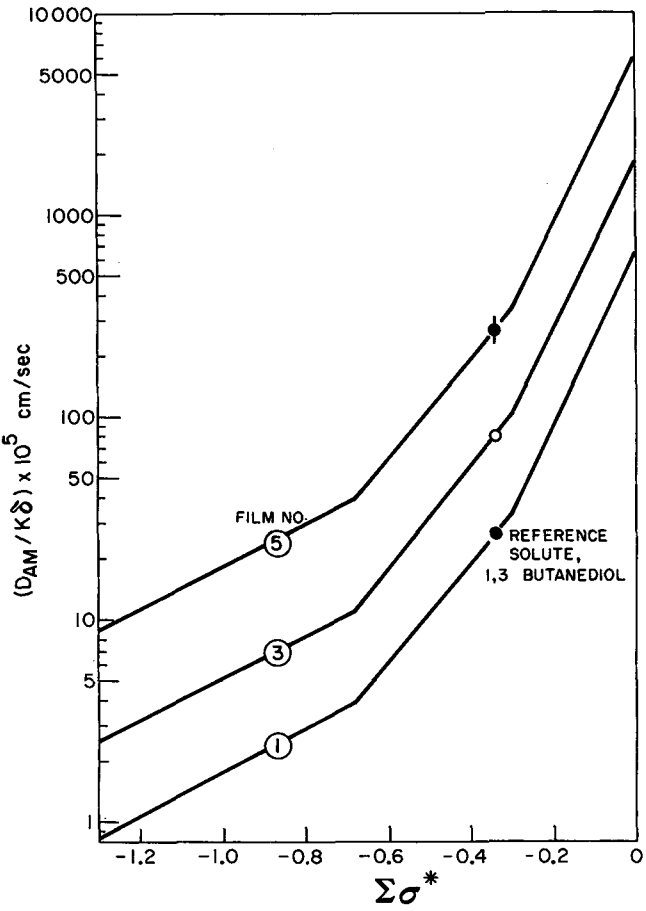


Fig. 6. Taft number-vs.-solute transport parameter correlation for monohydric and polyhydric alcohols based on experimental data for 1,3-butanediol: film type, cellulose acetate (Batch 316); operating pressure, 250 psig.

Since the osmotic pressure effects involved are negligible for the level of solute concentrations used in this work, the product rates may be assumed constant. Therefore, using the same values of [PR], membrane area, solution density, and the applicable $D_{AM}/K\delta$ values taken from Figure 6 and k values taken from Table III, solute separations f for all the monohydric and polyhydric alcohols covered by the range of $\Sigma\sigma^*$ values in Figure 6 can be predicted from eq. (27). The values of f so predicted are represented by the solid line in Figure 7a for film 3. The corresponding experimental data are also plotted in Figure 7a for comparison, which shows excellent agreement between predicted and experimental values.

Since $D_{AM}/K\delta$ is independent of k and [PR] may be assumed constant, eq. (27) can also be used to calculate solute separation at different values of k. The results of such calculations are illustrated in Figure 7b for film 1 which shows solute separation data for all the alcohols involved in the range of $\Sigma\sigma^*$ covered, at k values of ∞, 50×10^{-4}, and 10×10^{-4} cm/sec. These

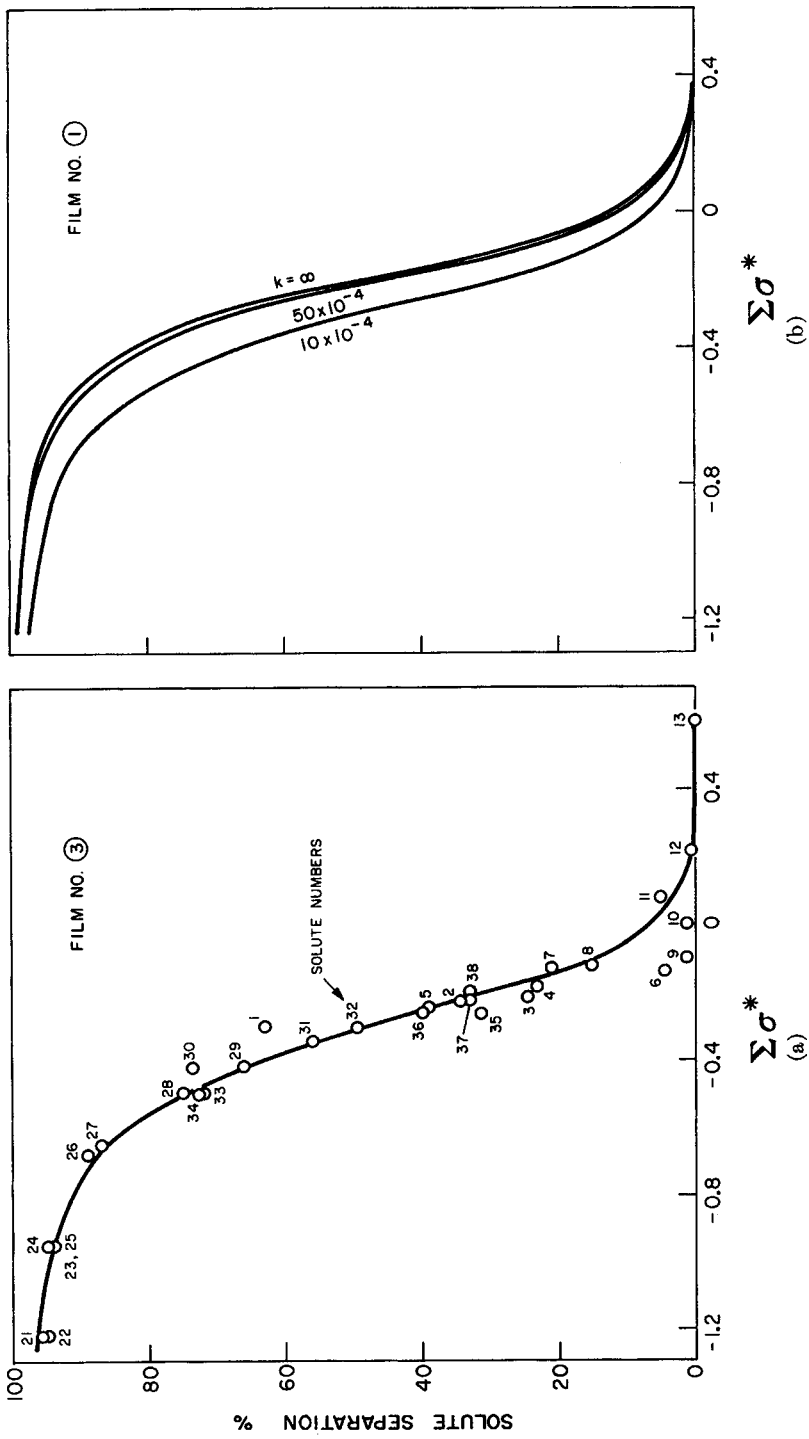


Fig. 7. Effect of Taft number on solute separation for monohydric and polyhydric alcohols: (a) data for film 3, (——) predicted, (O) experimental; (b) data for film 1, (——) predicted for different values of k; film type, cellulose acetate (Batch 316); operating pressure, 250 psig; solute numbers, same as in Table I.

data show that solute separation is particularly sensitive to k when the latter is $<50 \times 10^{-4}$ cm/sec. For example, solute separation for 1,3-butanediol at feed flow conditions corresponding to k values of ∞, 50×10^{-4}, and 10×10^{-4} cm/sec can be predicted to be 76%, 74%, and 58%, respectively. Such sensitivity of solute separation to k can partially account for the apparent scatter in the $\Sigma\sigma^*$-versus-solute separation correlations given in Figure 4.

In the foregoing illustrations, [PR] has been assumed constant. This is not a necessary criterion for the validity of the principles involved in the prediction procedure given above. Once the $\Sigma\sigma^*$-versus-$D_{AM}/K\delta$ correlation is generated by the use of the appropriate ρ^* values, both solute separation and product rate can be predicted from a knowledge of A (pure water permeability constant), $D_{AM}/K\delta$, and k in the usual manner of the Kimura-Sourirajan analysis.[8a]

The principles of the prediction technique illustrated above for alcohols may be expected to be equally applicable to all solute molecules involving polar functional groups. This was tested with respect to six aldehydes, listed in Table III, for which membrane performance data were reported earlier.[2] These data were obtained with the same membranes and experimental conditions used for the alcohol–water systems discussed above. The data on Taft number, diffusivity, and mass transfer coefficient used in this work are also given in Table III. The calculation and correlation techniques used were identical to those used for alcohol-water systems.

Figure 8 gives the $\Sigma\sigma^*$-versus-log $(D_{AM}/K\delta)$ correlations for films 1, 3, and 5 in the $\Sigma\sigma^*$ range of -0.19 to 0.60. Even though there is some scatter in the data, straight-line correlations with constant slope for each film seem reasonable. From Figure 8, the ρ^* value for the functional group —CHO was estimated to be 4.85 for the range of $\Sigma\sigma^*$ (in this case, only σ^*) involved. Using this value of ρ^* and i-butyraldehyde as the reference solute, the data given in Figure 9a and 9b were obtained. Figure 9a gives the predicted $\Sigma\sigma^*$-versus-solute separation correlation (solid line) for film 3, along with the experimental data for the five other solutes studied. The agreement between the calculated and the experimental data is reasonable, particularly in view of Figure 9b, which shows the sensitivity of solute separation to changes in mass transfer coefficient illustrated for film 1.

One may hence conclude that eq. (31) has a firm experimental and theoretical basis relating to solute transport in reverse osmosis; and, in conjunction with the general Kimura-Sourirajan transport equations, eq. (31) offers an effective means for predicting membrane performance for the reverse osmosis separation of a wide variety of solute molecules involving polar functional groups.

Separation of Some Carbohydrates

The reverse osmosis separations of one aldopentose (L-arabinose), three aldohexoses (D-glucose, D-mannose, and D-galactose), one ketohexose (D-

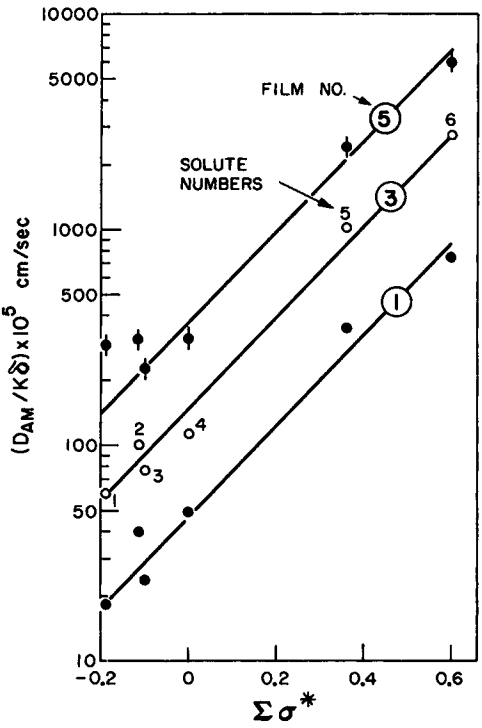


Fig. 8. Taft number-vs.-solute transport parameter correlation for aldehydes: film type, cellulose acetate (Batch 316); operating pressure, 250 psig; solutes, (1) i-butyraldehyde ($\sigma^* = -0.19$), (2) *n*-butyraldehyde ($\sigma^* = -0.115$), (3) propionaldehyde ($\sigma^* = -0.10$), (4) acetaldehyde ($\sigma^* = 0$), (5) crotonaldehyde ($\sigma^* = 0.36$), (6) benzaldehyde ($\sigma^* = 0.60$).

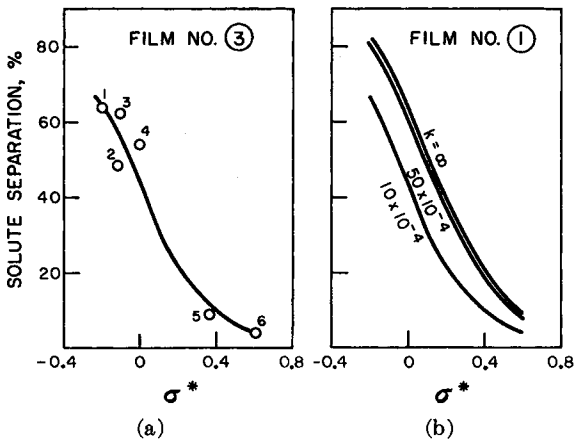


Fig. 9. Effect of Taft number on solute separation for aldehydes: (a) data for film 3' (——) predicted, (O) experimental; (b) data for film 1, (——) predicted for different values of k; film type, cellulose acetate (Batch 316); operating pressure, 250 psig; solute numbers, same as in Figure 8.

fructose), and three disaccharides (sucrose, maltose, and lactose) were also briefly studied in this work. All the above carbohydrates are naturally occurring sugars, and the applicability of reverse osmosis for their separations is of both scientific and practical interest.

The aldopentose and the three aldohexoses mentioned above have both —OH and —CHO functional groups in their molecules, and hence, each of them has two Taft numbers, one with respect to —OH and the other with respect to —CHO. Following the procedure same as that used for polyhydric alcohols, the Taft numbers for the above monosaccharides can be estimated as follows:

L-arabinose ($CH_2OH(CHOH)_3CHO$):

$$\Sigma\sigma^* \text{ with respect to —CHO} = \sigma^* \text{ for } n\text{-}C_4H_9 = -0.130,$$

$$\Sigma\sigma^* \text{ with respect to —OH} = 2[\sigma^* \text{ for } n\text{-}C_4H_9\ (-0.130) + \sigma^* \text{ for } s\text{-}C_4H_9\ (-0.210)] = -0.680.$$

D-glucose, D-mannose, and D-galactose ($CH_2OH(CHOH)_4CHO$):

$$\Sigma\sigma^* \text{ with respect to —CHO} = \sigma^* \text{ for } n\text{-}C_5H_{11} = -0.133,$$

$$\Sigma\sigma^* \text{ with respect to —OH} = 2[\sigma^* \text{ for } n\text{-}C_5H_{11}\ (-0.133) + \sigma^* \text{ for } C_3H_7CHCH_3\ (-0.230)] + \sigma^* \text{ for } (C_2H_5)_2CH\ (-0.225) = -0.951.$$

No method has yet been established to estimate the Taft numbers for D-fructose, sucrose, maltose and lactose which involve —CO— and —O— linkages in their molecules.

Following the method used for the alcohol systems, values of the applicable mass transfer coefficients k were estimated, and they are also listed in Table III.

An empirical technique was tested to predict the reverse osmosis separation of the above aldopentose and aldohexoses. In this technique, it was assumed that, for the above solutes, eq. (31) could be written as

$$(D_{AM}/K\delta)_{\text{carbohydrate}} = C_{\text{carbohydrate}} \exp(\rho^*_{OH}\Sigma\sigma^*_{OH} + \rho^*_{CHO}\Sigma\sigma^*_{CHO}) \quad (32)$$

where $D_{AM}/K\delta$, C, ρ^*, and $\Sigma\sigma^*$ were for the solute or functional group indicated, and

$$C_{\text{carbohydrate}} = \frac{n_{OH}C_{OH} + n_{CHO}C_{CHO}}{n_{OH} + n_{CHO}} \quad (33)$$

where n_{OH} and n_{OHO} were the number of —OH and —CHO groups, respectively, in the solute molecule and C_{OH} and C_{CHO} were the proportionality constants applicable to the —OH and —CHO groups, respec-

tively, corresponding to their $\Sigma\sigma^*$ values. Using the appropriate values of C and ρ^* obtained already for the —OH and —CHO functional groups, and the values of k listed in Table III, the values of $D_{AM}/K\delta$ and solute separation were calculated for films 1, 3, and 5 using eqs. (32) and (27). The results are given in Table IV along with the experimental values. The reasonable agreement between calculated and experimental values indicate that the prediction technique used is essentially valid, and it would be worthwhile to test the applicability of the technique for a wider range of membrane–solution–operating systems.

TABLE IV
Comparison of Calculated and Experimental Data For Solute Transport Parameter and Solute Separation for Carbohydrates[a]

Solute	Film no.	$(D_{AM}/K\delta) \times 10^5$, cm/sec		Solute separation, %	
		Calcd.	Exptl.	Calcd.	Exptl.
L-Arabinose	1	2.6	2.5	96.0	96.1
	3	8.0	5.4	91.9	94.4
	5	28.5	25.4	77.5	79.5
D-Glucose	1	1.3	0.96	97.9	98.4
	3	3.9	2.6	95.6	97.0
	5	14.2	15.8	86.2	84.9
D-Mannose	1	1.3	—	97.9	~100
	3	3.9	1.7	95.6	98.0
	5	14.2	10.3	86.2	89.6
D-Galactose	1	1.3	0.84	97.9	98.6
	3	3.9	2.9	95.6	96.7
	5	14.2	16.2	86.2	84.6
D-Fructose	1	—	0.48	—	99.2
	3	—	2.4	—	97.2
	5	—	12.2	—	87.9
Sucrose	1	—	—	—	~100
	3	—	1.8	—	97.0
	5	—	2.8	—	94.9
Maltose	1	—	—	—	~100
	3	—	0.87	—	98.5
	5	—	4.7	—	91.7
Lactose	1	—	0.35	—	99.3
	3	—	0.75	—	98.7
	5	—	3.4	—	93.9

[a] Operating pressure: 250 psig; solute concentration in feed: ~100 ppm; feed flow concentration: k as in Table III.

Table IV also gives experimental data on $D_{AM}/K\delta$ and solute separation for D-fructose, sucrose, maltose, and lactose obtained with films 1, 3, and 5. These data show that the porous structure of film 1 (as represented by the $D_{AM}/K\delta$ for NaCl = 2.48×10^{-5} cm/sec) is adequate for obtaining essentially complete separation of the above sugars by reverse osmosis.

CONCLUSIONS

Decrease in acidity and increase in basicity are equivalent with respect to the reactivity of polar molecules for reverse osmosis separation. For such molecules, solute transport in reverse osmosis can be expressed in terms of parameters of the Taft equation. The method for estimating Taft numbers for polyhydric alcohols, and the technique for predicting solute transport parameter and solute separation of alcohols, aldehydes, and carbohydrates illustrated in this paper, confirm the physicochemical criteria discussed earlier[1-3] for the reverse osmosis separation of such solutes and offer an experimental basis for extending the scope and utility of such criteria in the further development of the science and engineering of reverse osmosis.

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