

## Polar and Nonpolar Parameters for Polymeric Reverse Osmosis Membrane Materials from Liquid Chromatographic Data

TAKESHI MATSUURA, P. BLAIS, and S. SOURIRAJAN, *Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R9*

### Synopsis

Polar ( $\alpha_p$ ) and nonpolar ( $\alpha_n$ ) parameters to characterize a variety of cellulosic and noncellulosic polymers have been developed from liquid chromatographic data on retention times for selected reference solutes in aqueous solutions. The above parameters give relative quantitative measures for the hydrogen bonding and nonpolar (hydrophobic) forces inherent in the chemical structure of the polymer molecule. Unique correlations are also shown to exist between the above parameters and Hansen's solubility parameters  $\delta_h$  and  $\delta_d$  for the polymers. These parameters and correlations offer significant guidelines for the choice of membrane material for reverse osmosis.

### INTRODUCTION

Since early in the development of reverse osmosis, it has been recognized<sup>1</sup> that both the polar character and the nonpolar character of the membrane material affect solute separations. Recent researches<sup>2-4</sup> on the analysis of solute separation data using polar and nonpolar parameters to characterize solutes have contributed significantly to our understanding of the physiochemical basis of reverse osmosis separations. It is hence reasonable to expect that development of similar polar and nonpolar parameters to characterize membrane materials can yield useful results. Therefore, the object of this work is to develop appropriate polar and nonpolar parameters to characterize a variety of cellulosic and noncellulosic membrane materials. Such parameters may be expected to suggest possible guidelines for the choice of suitable membrane materials capable of yielding higher reverse osmosis separations for nonionized polar organic solutes in aqueous solutions in the light of the available experimental data.

This work utilizes the technique of liquid chromatography for developing the appropriate polar and nonpolar parameters characterizing the polymeric materials tested. The polymeric material was packed in the chromatographic column, and water was used as the carrier solvent. Dilute aqueous solutions of some suitably selected reference solutes were injected into the chromatographic column, and the retention times for each solute for each column were experimentally determined. Benzyl alcohol, phenol, and phenethyl al-

cohol were used as reference solutes in this work. The solvent front was established in each case by the retention time for potassium biphthalate, which was practically unretained in the column. The retention times for the reference solutes could be expected to represent the polar and nonpolar effects involved in the solute-solvent-polymer interactions. These interactions are totally analogous to those prevailing under reverse osmosis conditions. Thus, the technique of liquid chromatography offers a means of simulating the effects of interfacial forces governing reverse osmosis separations. Thus, this work serves also to illustrate the utility of the data obtained by liquid chromatography in the further development of reverse osmosis.

## EXPERIMENTAL

### Column Materials Used

Thirty-three different chromatographic columns listed and designated in Table I were used in this work. Details of the materials used in these columns are given in Tables II and III. The cellulose acetates used in columns 1 to 4, cellulose triacetate used in column 5, cellulose acetate butyrates used in columns 8 to 11, and cellulose tridecanoate used in column 12 were obtained from Eastman chemicals. The cellulose acetate propionate used in column 6 and the ethyl celluloses used in columns 14 and 15 were obtained from K & K Laboratories and Hercules Inc., respectively. Cellulose propionate used in column 7 was obtained by the esterification of ether-extracted cotton linters with propionyl chloride in anhydrous *N,N*-dimethylformamide according to the procedure described in the literature.<sup>5</sup> Cellulose benzoate used in column 13 was synthesized using a similar procedure with benzoyl chloride. The cellulose for column 16 was obtained from linters which were powdered, milled, ether extracted, and sieved.

The structures and syntheses of the noncellulosic polymers used in columns 17 to 31 are given in Table III; more details on them are available in the literature.<sup>6-12</sup> Commercially available Zytel (nylon 66, supplied by du Pont), Udel (bisphenol A polysulfone, supplied by Union Carbide), and Profax 6701 (isotactic polypropylene, supplied by Hercules) were used in columns 28, 29, and 30, respectively. The polyurea material used in column 31 consisted of acetone- and water-washed pulverized (100–200  $\mu$ ) product of the reaction between polyethylenimine and tolylene 2,4-diisocyanate in chloroform, which was allowed to evaporate to dryness and cured at 80°C for 3 hr; the above material may be considered to be chemically equivalent to the NS-1 material described in the literature.<sup>13</sup> The corasil used in column 32 and Bondapak C<sub>18</sub>/corasil used in column 33 were obtained from Waters Associates, Inc.

### Preparation of Columns

The commercially available cellulose acetate (polymer 1) and cellulose tridecanoate (polymer 12) were packed directly into the column. In the case of the other cellulosic materials, the particle size for the column was kept in the range of 31 to 53  $\mu$  by sieving. When the appropriate powder for the column material was not commercially available, it was obtained either by crushing

TABLE I  
 Polymers and Their Polar and Nonpolar Parameters

Polymer no. ≡ column no.	Name of column	Polymer	$r_1$	$r_2$	$\alpha_p$	$\alpha_n$
Cellulosic						
1	CA-398-3-C	cellulose acetate	0.310	1.18	-1.09	-0.085
2	CA-398-3	cellulose acetate	0.361	1.24	-1.00	-0.017
3	CA-383-40	cellulose acetate	0.318	1.28	-1.13	-0.014
4	CA-394-45	cellulose acetate	0.363	1.29	-1.03	0.017
5	CTA	cellulose triacetate	0.243	1.23	-1.32	-0.098
6	CAP	cellulose acetate propionate	0.305	1.57	-1.33	0.143
7	CP	cellulose propionate	0.214	1.30	-1.47	-0.077
8	CAB-171-2	cellulose acetate butyrate	0.207	0.983	-1.27	-0.310
9	CAB-171-40	cellulose acetate butyrate	0.190	0.923	-1.28	-0.377
10	CAB-381-2	cellulose acetate butyrate	0.278	1.46	-1.35	0.066
11	CAB-500-5	cellulose acetate butyrate	0.236	1.52	-1.51	0.069
12	CTD	cellulose tridecanoate	0.474	2.50	-1.35	0.604
13	CB	cellulose benzoate	0.589	1.53	-0.78	0.246
14	ECG	ethyl cellulose	0.222	1.54	-1.57	0.068
15	ECT	ethyl cellulose	0.203	1.47	-1.61	0.013
16	C	cellulose	—	—	—	—
Noncellulosic						
17	31B	copolyamide	0.842	1.43	-0.43	0.259
18	69B	copolyamide	0.646	0.961	-0.32	-0.114
19	80B	copolyamidohydrazide	0.818	1.61	-0.55	0.349
20	81B	copolyamidohydrazide	0.933	1.22	-0.22	0.149
21	79B	copolyamidohydrazide	0.746	1.04	-0.27	-0.023
22	117B	copolyhydrazide	0.607	1.18	-0.54	0.041
23	107B	copolyamidohydrazide	0.849	1.24	-0.31	0.144
24	94B	polysemicarbazide	0.659	0.813	-0.17	-0.246
25	86B	polythiosemicarbazide	0.520	1.00	-0.53	-0.123
26	101B	polypiperazineamide	—	—	—	—
27	49B	nylon 4	0.416	1.12	-0.80	-0.073
28	N66	nylon 66 (Zytel)	—	—	—	—
29	PS	bisphenol A polysulfone (Udel)	—	—	—	—
30	PP	isotactic polypropylene (Profax 6701)	—	—	—	—
31	NS-1	crosslinked polyurea	—	—	—	—
32	Corasil		2.00	1.70	0.13	0.561
33	Bondapak C <sub>18</sub>		1.53	1.97	-0.21	0.631

the material in a ball mill with Dry Ice or by precipitating the material in agitated water from the polymer solution in an appropriate solvent. In all cases, the column material was packed dry into stainless steel tubes,  $\frac{1}{8}$  in. o.d. and  $\frac{1}{16}$  in. i.d. The column length was 2 ft for cellulosic polymers and 1.6 ft for noncellulosic polymers.

Polymers 17 to 26, 29, and 31 (Table I) were reprecipitated in water from 1% solutions in N,N-dimethylacetamide containing 0.5% calcium chloride, using a high-speed blender. The resulting suspensions, containing about 2 g solids per liter, were filtered, and the solids were repeatedly washed with

TABLE II  
 Structure of Polymer Repeat Unit—Cellulosic Polymers

Column no. ≡ polymer no.	Structure of polymer repeat unit <sup>a</sup>	Ester or ether content <sup>b</sup> , %	Viscosity, <sup>c</sup> poises
1	$(\text{CH}_2)_4(\text{CH})_{20}(\text{O})_8(\text{OH})_{2.19}(\text{OCCH}_3)_{9.81}$	acetyl, 39.8	6.8–14.8
2	$(\text{CH}_2)_4(\text{CH})_{20}(\text{O})_8(\text{OH})_{2.19}(\text{OCCH}_3)_{9.81}$	acetyl, 39.8	6.8–14.8
3	$(\text{CH}_2)_4(\text{CH})_{20}(\text{O})_8(\text{OH})_{2.78}(\text{OCCH}_3)_{9.22}$	acetyl, 38.3	132–208
4	$(\text{CH}_2)_4(\text{CH})_{20}(\text{O})_8(\text{OH})_{2.35}(\text{OCCH}_3)_{9.65}$	acetyl, 39.4	147–197
5	$(\text{CH}_2)_4(\text{CH})_{20}(\text{O})_8(\text{OH})(\text{OCCH}_3)_{11}$	—	—
6	$(\text{CH}_2)_4(\text{CH})_{20}(\text{O})_8(\text{OH})_{0.8}(\text{OCCH}_3)_{8.25}(\text{OCC}_2\text{H}_5)_{2.95}$	acetyl, 30.6; propionyl, 14.5	—
7	$(\text{CH}_2)_4(\text{CH})_{20}(\text{O})_8(\text{OH})_{0.39}(\text{OCC}_2\text{H}_5)_{11.61}$	propionyl, 51.0	0.8
8	$(\text{CH}_2)_4(\text{CH})_{20}(\text{O})_8(\text{OH})_{1.0}(\text{OCCH}_3)_{8.15}(\text{OCC}_3\text{H}_7)_{2.85}$	acetyl, 29.5; butyryl, 17	5.6–9.4
9	$(\text{CH}_2)_4(\text{CH})_{20}(\text{O})_8(\text{OH})_{1.0}(\text{OCCH}_3)_{8.15}(\text{OCC}_3\text{H}_7)_{2.85}$	acetyl, 29.5; butyryl, 17	115–188
10	$(\text{CH}_2)_4(\text{CH})_{20}(\text{O})_8(\text{OH})_{1.50}(\text{OCCH}_3)_{3.85}(\text{OCC}_3\text{H}_7)_{6.65}$	acetyl, 13; butyryl, 37	3.8–13.1
11	$(\text{CH}_2)_4(\text{CH})_{20}(\text{O})_8(\text{OH})_{0.58}(\text{OCCH}_3)_{1.95}(\text{OCC}_3\text{H}_7)_{9.47}$	acetyl, 6; butyryl, 48	15.0–22.5
12	$(\text{CH}_2)_4(\text{CH})_{20}(\text{O})_8(\text{OCC}_5\text{H}_9)_{1.2}$	—	—
13	$(\text{CH}_2)_4(\text{CH})_{20}(\text{O})_8(\text{OH})_{9.95}(\text{OCC}_6\text{H}_5)_{2.05}$	benzoyl, 25.0	—
14	$(\text{CH}_2)_4(\text{CH})_{20}(\text{O})_8(\text{OH})_{3.06}(\text{OC}_2\text{H}_5)_{8.94}$	ethoxyl, 44.8	0.45
15	$(\text{CH}_2)_4(\text{CH})_{20}(\text{O})_8(\text{OH})_{1.64}(\text{OC}_2\text{H}_5)_{10.36}$	ethoxyl, 49.7	0.10
16	$(\text{CH}_2)_4(\text{CH})_{20}(\text{O})_8(\text{OH})_{1.2}$	—	—

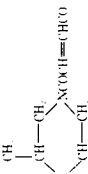

<sup>a</sup> Four anhydroglucose units were taken as a repeat unit. The numbers of functional groups are average values.

<sup>b</sup> Ester contents of polymer numbers 6, 7, and 13 were laboratory determined. Others were given by manufacturers.

<sup>c</sup> Viscosity of polymer number 7 is intrinsic viscosity in acetone and was laboratory determined. Others were given by manufacturers.

large volumes of water and twice with redistilled acetone before drying at 50°C. This procedure yielded agglomerated particles which were subsequently broken by gentle grinding (glass pestle and mortar), and the columns were packed dry with continuous 60 cycles/sec vibration using particles which passed a 400- $\mu$  sieve. A similar procedure was used for nylon 4 (polymer 27) and Zytel (polymer 28), except that formic acid solutions were employed for the reprecipitation steps. The Profax 6701 (polymer 30) sample consisted of 20- to 100- $\mu$  particles as supplied; it was sieved and packed directly into columns without further treatment. All the columns were water washed under

TABLE III  
Structure of Polymer Repeat Unit—Noncellulosic Polymers

Column no. = poly- mer no.	Structure of polymer repeat unit <sup>a</sup>	Reactant				mole	mole	4	mole	Polymer- ization solvent	[ $\eta$ ] <sup>d</sup>	Refer- ence
		1	2	3	3							
17	NH $\phi_m$ NHCO $\phi_r$ CO	$\phi_m$ (NH $_2$ ) $_2$	2.00	$\phi_m$ (COCl) $_2$	1.40	$\phi_p$ (COCl) $_2$	0.60	DMA	0.73	6		
18	NH $\phi_m$ NHCO $\phi_r$ CO	$\phi_m$ (NH $_2$ ) $_2$	2.00	$\phi_m$ (CONHNH $_2$ ) $_2$ <sup>b</sup>	0.00	$\phi_p$ (COCl) $_2$	1.00	DMA	0.80	6		
19	NH $\phi_m$ NHCO $\phi_r$ CO and NHNHCO $\phi_m$ CONHNHCO $\phi_r$ CO	$\phi_m$ (NH $_2$ ) $_2$	1.79	$\phi_m$ (CONHNH $_2$ ) $_2$ <sup>b</sup>	0.21	$\phi_p$ (COCl) $_2$	1.00	DMA	1.25	6		
20	NH $\phi_m$ NHCO $\phi_r$ CO and NHNHCO $\phi_m$ CONHNHCO $\phi_r$ CO	$\phi_m$ (NH $_2$ ) $_2$	1.54	$\phi_m$ (CONHNH $_2$ ) $_2$ <sup>b</sup>	0.46	$\phi_p$ (COCl) $_2$	1.00	DMA	1.11	6		
21	NH $\phi_m$ NHCO $\phi_r$ CO and NHNHCO $\phi_m$ CONHNHCO $\phi_r$ CO	$\phi_m$ (NH $_2$ ) $_2$	1.44	$\phi_m$ (CONHNH $_2$ ) $_2$ <sup>b</sup>	0.56	$\phi_p$ (COCl) $_2$	1.00	DMA	0.69	6		
22	NHNHCO $\phi_m$ CONHNHCO $\phi_r$ CO	$\phi_m$ (NH $_2$ ) $_2$	0.00	$\phi_m$ (CONHNH $_2$ ) $_2$ <sup>b</sup>	2.00	$\phi_p$ (COCl) $_2$	1.00	NMP	0.79	6		
23	NHNHCO $\phi_m$ CONHNHCO $\phi_r$ CO	H $_2$ N $\phi_p$ CONHNH $_2$	1.60	H $_2$ N $\phi_p$ CONHNH $_2$	0.40	$\phi_p$ (COCl) $_2$	1.40	DMA	0.70	7		
24	NHNHCO $\phi_m$ CONHNHCO $\phi_r$ CH $_2$ $\phi_p$ NHCO	$\phi_m$ (CONHNH $_2$ ) $_2$ <sup>b</sup>	1.00	$\phi_m$ (CONHNH $_2$ ) $_2$ <sup>b</sup>	1.00	CH $_2$ ( $\phi_p$ NHCO) $_2$	1.00	DMSO	0.75	8		
25	NHNHCO $\phi_m$ CONHNHCSNH $\phi_r$ CH $_2$ $\phi_p$ NHCS	$\phi_m$ (CONHNH $_2$ ) $_2$ <sup>b</sup>	1.00	$\phi_m$ (CONHNH $_2$ ) $_2$ <sup>b</sup>	1.00	CH $_2$ ( $\phi_p$ NHCS) $_2$ <sup>c</sup>	1.00	DMSO	0.36	8		
26			1.00	ClCOCH=CHCOCl	1.00				0.85 <sup>e</sup>	9		
27	NH(CH $_2$ ) $_2$ CO	NH(CH $_2$ ) $_2$ CO								10		
28	NH(CH $_2$ ) $_2$ NHCO(CH $_2$ ) $_2$ CO											
29	O $\phi_r$ CH(CH $_2$ ) $\phi_p$ O $\phi_r$ SO $_2$ $\phi_p$											
30	CH(CH $_2$ )CH $_2$											
31	crosslinked polyurea											

<sup>a</sup>  $\phi_m = m-C_6H_4$ ;  $\phi_p = p-C_6H_4$ ;  $\phi_r =$  random mixture of  $\phi_m$  and  $\phi_p$ ; DMA = N,N-dimethylacetamide; NMP = N-methylpyrrolidone, DMSO = dimethyl sulfoxide.

<sup>b</sup> Preparation of isophthalic dihydrazide in ref. 11.

<sup>c</sup> Preparation of methylenebis(4-phenyl isothiocyanate) in ref. 12.

<sup>d</sup> In DMSO.

<sup>e</sup> In formic acid.

Trade name  
Zytel (du Pont)  
Udel (Union Carbide)  
Profax 6701 (Hercules)

pressure (at 500 to 2000 psi) until the effluent became free of UV-detectable contaminants.

### Chromatography Experiments

The liquid chromatograph Model ALC 202 of Waters Associates, Inc., was used in this work. All experiments were made at the laboratory temperature (23–25°C). The solvent (water) velocity through the column was fixed at 1 cm/sec. Typical pressure drop in the column ranged from 450 to 3000 psig, depending on column and packing method. The concentration of each of the reference solutes, benzyl alcohol, phenol, and phenethyl alcohol, was 1000 ppm in water. Potassium biphthalate (800 ppm in water) was used as the unretained solute ( $t_{uc}$ ) to establish the position of solvent front in all the columns except the nylon 4 column. Since the latter column showed significant adsorption for potassium biphthalate, sodium benzoate was used instead to establish the solvent front. Twenty to 100  $\mu$ l of the above solutions were used for each injection, and retention time for each solute in each column was determined using an in-line ultraviolet photometer for solute detection. The retention time measurement was repeated several times for each solute and the average value was taken for analysis. The reproducibility of retention time measurement was usually good, and no more than two injections were necessary in most cases. Under the experimental conditions used in this work, the retention time for the unretained compound ( $t_{uc}$ ) was usually about 2 min, whereas the retention time for the reference solutes used was in the range of 5 to 200 min. Through preliminary experiments, it was established that changes in column length, particle size, and packing density of column material, solvent velocity through the column, operating pressure, and sample size do not affect the *retention time ratio* for two different solutes obtained under otherwise identical experimental conditions.

## RESULTS AND DISCUSSION

### A Scale for Polar Parameter $\alpha_p$ and Nonpolar Parameter $\alpha_n$ for Polymer Material in Terms of Retention Time Ratios for Reference Solutes

The retention time ratio  $r$  for any two solutes 1 and 2 may be defined as

$$r = \frac{t_{s1} - t_{uc}}{t_{s2} - t_{uc}} \quad (1)$$

where  $t_{s1}$  and  $t_{s2}$  represent retention time  $t$  for solutes 1 and 2, respectively, and  $t_{uc}$  represents retention time for the unretained component (solvent front). The values of  $r$  are determined experimentally from data on retention time for the solutes under consideration.

Further, in liquid chromatography,<sup>14</sup>

$$r = \frac{K_{s1}}{K_{s2}} \quad (2)$$

where  $K_{s1}$  and  $K_{s2}$  are equilibrium adsorption coefficients for solutes 1 and 2,

respectively, at the packing material-solution interface. Hence, for the reference solutes benzyl alcohol (denoted as benz alc), phenol, and phenethyl alcohol (denoted as phen alc), eqs. (1) and (2) may be written as

$$r_1 = \frac{t_{\text{benz alc}} - t_{uc}}{t_{\text{phenol}} - t_{uc}} = \frac{K_{\text{benz alc}}}{K_{\text{phenol}}} \quad (3)$$

$$r_2 = \frac{t_{\text{phen alc}} - t_{uc}}{t_{\text{benz alc}} - t_{uc}} = \frac{K_{\text{phen alc}}}{K_{\text{benz alc}}} \quad (4)$$

Let  $\Delta G$  represent the free-energy change involved in the adsorption equilibrium, and let  $R$  and  $T$  represent gas constant and absolute temperature, respectively. Then the adsorption equilibrium coefficient in eqs. (3) and (4) can be expressed in terms of the equivalent free-energy term ( $-\Delta G/RT$ ), so that eqs. (3) and (4) can be rewritten as

$$\ln r_1 = \left(-\frac{\Delta G}{RT}\right)_{\text{benz alc}} - \left(-\frac{\Delta G}{RT}\right)_{\text{phenol}} \quad (5)$$

$$\ln r_2 = \left(-\frac{\Delta G}{RT}\right)_{\text{phen alc}} - \left(-\frac{\Delta G}{RT}\right)_{\text{benz alc}} \quad (6)$$

Let  $\alpha_p$  and  $a_{p(\text{solute})}$  be parameters representing the polar part only (i.e., hydrogen bonding effect only) for the polymer material and the solute material respectively. Likewise, let  $\alpha_n$  and  $a_{n(\text{solute})}$  be parameters representing the nonpolar part only (i.e., the effect of dispersion force only) for the polymer material and the solute material, respectively. The free-energy change in the adsorption equilibrium ( $-\Delta G/RT$ ) may then be expected to be a function of  $\alpha_p$ ,  $a_{p(\text{solute})}$ ,  $\alpha_n$ , and  $a_{n(\text{solute})}$ .

Linear free-energy relationships, and the simple additivity principle with respect to such relationships, have been shown to be valid and useful both in physical organic chemistry<sup>15,16</sup> and in chromatography.<sup>17</sup> On the basis of such validity, it is reasonable to express  $-\Delta G/RT$  terms in eqs. (5) and (6) in the general form

$$\left(-\frac{\Delta G}{RT}\right)_{\text{solute}} = \alpha_p a_{p(\text{solute})} + \alpha_n a_{n(\text{solute})} + \beta \quad (7)$$

where  $\beta$  is a constant independent of the nature of the polymer or solute, i.e., dependent only on the nature of the solvent used. Using eq. (7), eqs. (5) and (6) can be rewritten as

$$\ln r_1 = \alpha_p [a_{p(\text{benz alc})} - a_{p(\text{phenol})}] + \alpha_n [a_{n(\text{benz alc})} - a_{n(\text{phenol})}] \quad (8)$$

$$\ln r_2 = \alpha_p [a_{p(\text{phen alc})} - a_{p(\text{benz alc})}] + \alpha_n [a_{n(\text{phen alc})} - a_{n(\text{benz alc})}] \quad (9)$$

The object of the foregoing analysis is to develop relative scales for  $\alpha_p$  and  $\alpha_n$  for different polymeric materials in terms of  $\ln r_1$  and  $\ln r_2$ . For this purpose, let each of the differences in the  $a_p$  and  $a_n$  values for the reference solutes benzyl alcohol and phenol be arbitrarily defined as unity, i.e., let

$$a_{p(\text{benz alc})} - a_{p(\text{phenol})} = 1 \quad (10)$$

$$a_{n(\text{benz alc})} - a_{n(\text{phenol})} = 1. \quad (11)$$

Since the difference in  $a_n$  values of benzyl alcohol and phenol is due to one

TABLE IV  
 Solubility Parameters of Polymers

Polymer no. ≡ column no.	Formula weight	Density, g/cc	$V_{ms}$ , cc/mole	$\Sigma E_h$ , cal/mole	$\Sigma F_{id}$ , cal <sup>1/2</sup> /cc <sup>1/2</sup> /mole	$\delta_h$ , cal <sup>1/2</sup> /cc <sup>1/2</sup>	$\delta_d$ , cal <sup>1/2</sup> /cc <sup>1/2</sup>
Cellulosic							
1	1061.06	1.30	816.2	27613	6219.4	5.82	7.62
2	1061.06	1.30	816.2	27613	6219.4	5.82	7.62
3	1036.24	1.30	797.1	29825	6043.09	6.12	7.58
4	1054.32	1.30	811.0	28213	6170.75	5.90	7.61
5	1110.07	1.29	860.5	23150	6569	5.19	7.63
6	1160.87	1.27	914.1	22400	7038.1	4.95	7.70
7	1299.61	1.27	1023.3	20863	8362.7	4.52	8.17
8	1190.65	1.25	952.5	23150	7361.3	4.93	7.73
9	1190.65	1.25	952.5	23150	7361.3	4.93	7.73
10	1277.25	1.20	1064.4	25025	8272.2	4.85	7.77
11	1394.46	1.17	1191.8	21575	9319.9	4.25	7.82
12	2500.00	~1.20	2083.3	19400	20208	3.05	9.70
13	862.06	~1.20	718.38	—	—	—	—
14	899.50	~1.20	749.6	24617	6105.7	5.73	8.15
15	939.98	~1.20	783.3	18298	6546.0	4.83	8.36
16	162.16	~1.20	135.1	16100	831	10.92	6.15
Noncellulosic							
17	238.26	~1.20	198.6	13200	1776	8.15	8.94
18	238.26	~1.20	198.6	13200	1776	8.15	8.94
19	247.47	~1.20	206.2	13714	1825.3	8.16	8.85
20	258.12	~1.20	215.1	14307	1881.6	8.16	8.75
21	262.40	~1.20	218.7	14547	1904.9	8.16	8.70
22	324.32	~1.20	270.3	18000	2234	8.16	8.26
23	281.29	~1.20	234.4	15600	2005	8.16	8.55
24	444.49	~1.20	370.4	—	—	—	—
25	476.63	~1.20	397.2	—	—	—	—
26	168.22	~1.20	140.2	—	—	—	—
27	99.15	~1.20	82.6	3900	785	6.87	9.50
28	226.36	1.12	202.1	7800	1848	6.21	9.14
29	428.53	~1.20	357.1	4200	3324	3.43	9.31
30	42.09	0.91	46.3	0	391	0	8.45
31	—	—	—	—	—	—	—
32	—	—	—	—	—	—	—
33	—	—	—	—	—	—	—

—CH<sub>2</sub>— group and the same is the case with the difference in  $a_n$  values of phenethyl alcohol and benzyl alcohol,

$$a_n(\text{phen alc}) - a_n(\text{benz alc}) = 1. \quad (12)$$

Let

$$\left[ \frac{a_p(\text{phen alc}) - a_p(\text{benz alc})}{a_p(\text{benz alc}) - a_p(\text{phenol})} \right] = x. \quad (13)$$

Using eqs. (10) to (13), eqs. (8) and (9) can be rewritten as

$$\ln r_1 = \alpha_p + \alpha_n \quad (14)$$

$$\ln r_2 = x\alpha_p + \alpha_n. \quad (15)$$



The numerical value of  $x$  in eq. (15) is not known. This value, however, can be estimated from a consideration of solubility parameter  $\delta$  of polymers. Hansen showed<sup>18,19</sup> that  $\delta$  can be divided into three parts as follows:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (16)$$

where  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$  represent the components of  $\delta$  due to dispersion forces, dipole forces, and hydrogen bonding effects (donor-acceptor interactions), respectively. Such division of  $\delta$  into different components is particularly relevant to this work. The quantity  $\delta_d$  in eq. (16) is analogous to the quantity  $\alpha_n$  in eqs. (14) and (15). Therefore, it is reasonable to consider that  $\alpha_n$  values are identical for polymers whose  $\delta_d$  values are the same. Following the method shown by Koenhen and Smolders<sup>20</sup> (see discussion below), the values of  $\delta_d$  were calculated for all the polymeric materials used in this work. The results, given in Table IV, showed that the values of  $\delta_d$  for the two ethyl cellulose samples (column numbers 14 and 15) and the aromatic polyhydrazide sample (column 22) used were 8.15, 8.36, and 8.26, respectively. These values are so close to each other that the  $\delta_d$  values for the polymers involved may be considered to be essentially the same. Consequently, the above three polymers may be considered to have the same  $\alpha_n$  value, on the basis of which the value of  $x$  in eq. (15) can be calculated as follows.

Denoting the polymers used in columns 14, 15, and 22 by the numbers 14, 15, and 22, respectively, and using the values of  $r_1$  and  $r_2$  given in Table I, the following relationships can be written:

For polymer 14,

$$\ln 0.222 = \alpha_{p(14)} + \alpha_{n(14)} \quad (17)$$

and

$$\ln 1.54 = x \alpha_{p(14)} + \alpha_{n(14)} \quad (18)$$

For polymer 22,

$$\ln 0.607 = \alpha_{p(22)} + \alpha_{n(22)} \quad (19)$$

and

$$\ln 1.18 = x \alpha_{p(22)} + \alpha_{n(22)}. \quad (20)$$

Also,

$$\alpha_{n(14)} = \alpha_{n(22)}. \quad (21)$$

Combining eqs. (17) to (21), the value of  $x$  can be calculated to be  $-0.264$ . Similarly, combining the data for  $r_1$  and  $r_2$  for polymers 15 and 22, and using the identity

$$\alpha_{n(15)} = \alpha_{n(22)} \quad (22)$$

the value of  $x$  can be calculated to be  $-0.200$ . Therefore, an average value of  $-0.232$  for  $x$  is a reasonable estimate for the purpose of this work. Using this value of  $x$ , eqs. (14) and (15) can be solved to give

$$\alpha_p = 0.812 (\ln r_1 - \ln r_2) \quad (23)$$

$$\alpha_n = 0.188 \ln r_1 + 0.812 \ln r_2. \quad (24)$$

Equations (23) and (24) establish independent scales for each of the quantities  $\alpha_p$  and  $\alpha_n$  representing the intrinsic polar character and nonpolar character of the polymer in terms of  $r_1$  and  $r_2$  which can be obtained from the experimental chromatographic data.

The polar parameter  $\alpha_p$  for the polymer is similar to Taft's polar parameter  $\sigma^*$  used earlier for solutes.<sup>2,3</sup> This means that an increase in the value of  $\alpha_p$ , just as an increase in the value of  $\sigma^*$ , represents an increase in the average acidity of the polymer segments. Therefore, it is convenient to consider  $\alpha_p$  as the acidity parameter for the polymer material.

### Correlations of $\alpha_p$ and $\alpha_n$

**$\alpha_p$  Versus  $\alpha_n$ .** Figure 1 is a plot of the data on  $\alpha_p$  and  $\alpha_n$  obtained for most of the polymers tested in chromatographic experiments. These data show a fair range of values for  $\alpha_p$  and  $\alpha_n$ . In view of the availability of reverse osmosis data for cellulose acetate (polymer 1) and aromatic polyamide (polymer 17) membranes for comparison, the values of  $\alpha_p$  and  $\alpha_n$  for these two polymers are of particular interest. The data show that both  $\alpha_p$  and  $\alpha_n$  are higher for the aromatic polyamide material than for the cellulose acetate material, which means that aromatic polyamide is both more acid and more nonpolar (hydrophobic) than cellulose acetate. These results are consistent with the conclusion arrived at earlier on the basis of reverse osmosis data for membranes made of the above materials.<sup>3</sup> Figure 1 also shows that while the noncellulosic materials are generally more acidic than cellulose acetate, there is considerable overlap in their  $\alpha_n$  values.

Though ( $\alpha_p$ ,  $\alpha_n$ ) values of (-1.34, -0.20) and (0.18, -0.63) were obtained for polymers 26 and 31, respectively, these data are not reliable since reliable retention time data for both the columns could not be obtained because of significant column elution. Some further studies are needed with respect to the above two polymers.

**Effects of Variations in Polymer Structure on  $\alpha_p$  and  $\alpha_n$ .** These effects are illustrated in Figure 2. The cellulose acetates used in this work (polymers 1 to 4) have acetyl contents in the range of 38.3% to 39.8% in the viscosity grades of 6.8 to 197 poises. This range of viscosities has been shown<sup>21</sup> to correspond to an average molecular weight of 30,270 to 55,980. Figure 2a shows that  $\alpha_p$  and  $\alpha_n$  values are essentially unaffected by the above change in acetyl content.

The data for cellulose triacetate, cellulose propionate, and cellulose tridecanoate (polymers 5, 7, and 12) show that while  $\alpha_n$  increases linearly with increase in carbon number in the substituent group of the cellulose ester molecule, the values of  $\alpha_p$  are essentially unaffected by such change (Fig. 2b).

The data for the cellulose acetate butyrates used (polymers 8 to 11) show that  $\alpha_n$  tends to increase, and simultaneously  $\alpha_p$  tends to decrease with increase in butyryl content in the polymer (Fig. 2c). These changes are only to be expected.

The data for the polyamide-hydrazide copolymers (polymers 17 to 23) show that the  $\alpha_p$  and  $\alpha_n$  values are comparable for all the copolymers tested, and these values are not significantly affected by the hydrazide/(amide + hydrazide) ratio in the copolymer (Fig. 2d). This result is not surprising in

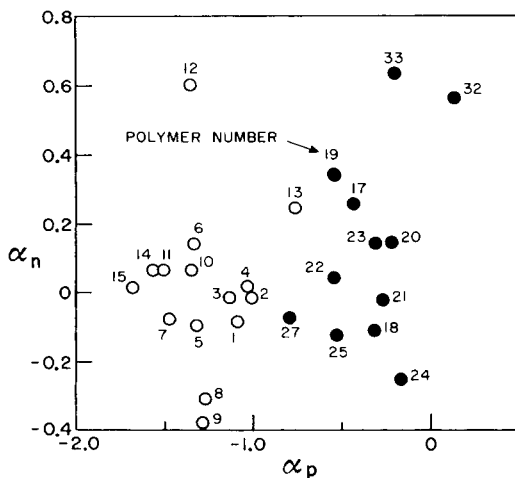


Fig. 1. Plot of data on  $\alpha_p$  and  $\alpha_n$  for (O) cellulose and (●) noncellulosic polymers.

view of the structural similarity of amide ( $-\text{CONH}-$ ) and hydrazide ( $-\text{CONHNHCO}-$ ) linkages.

A comparison of  $\alpha_n$  and  $\alpha_p$  for polysemicarbazide (polymer 24) and polythiosemicarbazide (polymer 25) (Table I) indicates that substantial changes in the  $\alpha_p$  parameter are possible by simply replacing an oxygen atom in the link  $-\text{CONHNHCONH}-$  to make the sulfur analog  $-\text{CONHNHCSNH}-$ ; this substitution, however, leaves the  $\alpha_n$  parameter nearly unchanged.

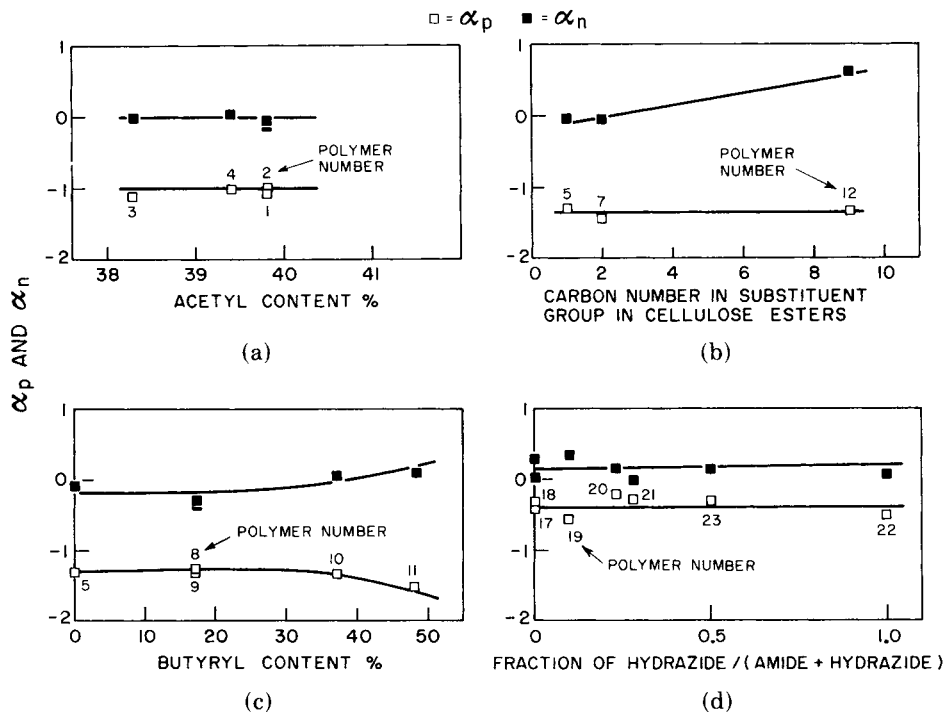


Fig. 2. Effects of variations in polymer side chains or copolymer ratios on  $\alpha_p$  and  $\alpha_n$ .

**Correlations of  $\alpha_p$  and  $\alpha_n$  with Corresponding Solubility Parameters.** Reference has already been made to Hansen's solubility parameters<sup>18,19</sup>  $\delta_h$  and  $\delta_d$ . Since these parameters are analogous to the parameters  $\alpha_p$  and  $\alpha_n$ , respectively, it is reasonable to expect some correlations between them.

The values of  $\delta_h$  and  $\delta_d$  for all the polymers tested were calculated from the molecular structure of the polymer repeat unit using the following relations given by Koenhen and Smolders<sup>20</sup>:

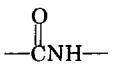
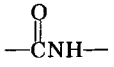

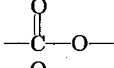
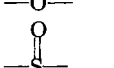
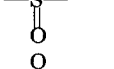
$$\delta_h = [\sum E_h/V_{ms}]^{1/2} \quad (25)$$

and

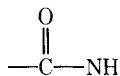
$$\delta_d = \sum F_{id}/V_{ms} \quad (26)$$

where  $E_h$  = enthalpy for the polar (donor or acceptor) group (cal/mole),  $V_{ms}$  = molar volume of polymer (formula wt of polymer repeat unit/density, cc/mole), and  $F_{id}$  = molar attraction constant for the structural group (cal<sup>1/2</sup>·cc<sup>1/2</sup>/mole). The values of  $E_h$  and  $F_{id}$  used in this work are listed in Table V.

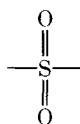
TABLE V  
 $E_h$  and  $F_{id}$  of Structural Components

		$E_h$ , cal/mole	$F_{id}$ , cal <sup>1/2</sup> ·cc <sup>1/2</sup> /mole
—CH <sub>3</sub>			201
>CH <sub>2</sub>			139
>CH			51
—OH		5000	99
	aliphatic	3900	229
	aromatic	6500	229
		8900	
		1250	193
—O—		550	70
		2700	296
			200
—CN		500	218
—NO <sub>2</sub>			215
—CF <sub>2</sub> —			160
—Cl		100	
C <sub>6</sub> H <sub>6</sub>			800
—C <sub>6</sub> H <sub>3</sub>			738
—C <sub>6</sub> H <sub>4</sub> —		100	659

Some brief comments on the values of  $E_h$ ,  $F_{id}$ , and  $V_{ms}$  used are in order. The value of  $E_h$  for the aromatic



group was estimated as 6500 cal/mole on the basis that  $E_h$  values for aliphatic —CONH, aromatic —NH<sub>2</sub>, and aliphatic —NH<sub>2</sub> groups are 3900, 2250, and 1310 cal/mole, respectively ( $3900 \times 2250/1310 = 6500$ ).<sup>19</sup> The  $E_h$  value for the aromatic hydrazide group was estimated as 8900 cal/mole on the basis that  $\delta_h$  for aromatic amide group =  $\delta_h$  for aromatic hydrazide group, as indicated by the chromatographic data (Fig. 2d). The value of  $F_{id}$  for the ether group was taken as 70, which is the molar attraction constant given by Small.<sup>22</sup> The data on  $E_h$  and  $F_{id}$  for the structural group



were calculated from the data on  $\delta_h$  and  $\delta_d$  for dimethyl sulfone<sup>19</sup> to be 2700 cal/mole and 296 cal<sup>1/2</sup>cc<sup>1/2</sup>/mole, respectively. All other data on  $E_h$  and  $F_{id}$  are the same as those given Koenhen and Smolders.<sup>20</sup> The values for  $V_{ms}$  were calculated from the corresponding molecular weight and density data (Table IV); whenever accurate density data were not available, a value of 1.2 g/cc for density was arbitrarily assumed, which was considered to be not too far from the actual value.

The procedure for calculation of  $\delta_h$  and  $\delta_d$  values is illustrated below for three polymer materials used.

*Polymer 1 (Cellulose Acetate):*

$$\sum E_h = 2.19(\text{OH}) + 9.81(\text{COO}) + 8(\text{O}) = 27613$$

$$\begin{aligned} \sum F_{id} &= 9.81(\text{CH}_3) + 4(\text{CH}_2) + 20(\text{CH}) + 2.19(\text{OH}) \\ &\quad + 9.81(\text{COO}) + 8(\text{O}) = 6217.95 \end{aligned}$$

$$V_{ms} = 816.2 \text{ (Table IV)}$$

$$\delta_h = [27613/816.2]^{1/2} = 5.82$$

$$\delta_d = 6217.95/816.2 = 7.62.$$

*Polymer 17 (Aromatic Polyamide):*

$$\sum E_h = 2(\text{CONH}) + 2(\text{C}_6\text{H}_4) = 13200$$

$$\sum F_{id} = 2(\text{CONH}) + 2(\text{C}_6\text{H}_4) = 1776$$

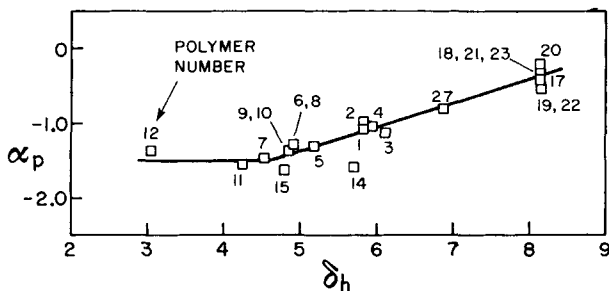
$$V_{ms} = 198.6 \text{ (Table IV)}$$

$$\delta_h = [13200/198.6]^{1/2} = 8.15$$

$$\delta_d = 1776/198.6 = 8.94$$

*Polymer 19 (Aromatic Polyamide-Hydrazide Copolymer):*

In this polymer, the fraction of polyamide is 0.8929 and that of polyhydrazide is 0.1071. Therefore,

Fig. 3. Correlation of  $\delta_h$  vs.  $\alpha_p$ .

formula wt of polymer repeat unit =  $(238.26 \times 0.8929)$

$$+ (324.32 \times 0.1071) = 247.47$$

$$V_{ms} = 247.47/1.2 = 206.2$$

$$\sum E_h = (13200 \times 0.8929) + (18000 \times 0.1071) = 13714$$

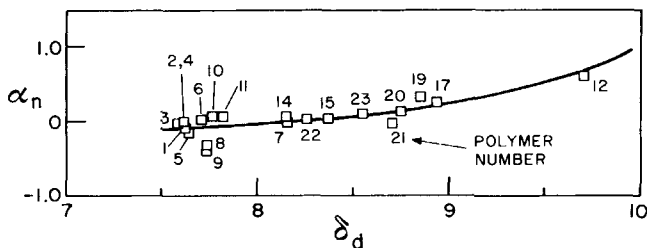
$$\sum F_{id} = (1776 \times 0.8929) + (2234 \times 0.1071) = 1825$$

$$\delta_h = 8.16$$

$$\delta_d = 8.85.$$

Figures 3 and 4 give the plots of  $\delta_h$  versus  $\alpha_p$  and  $\delta_d$  versus  $\alpha_n$ , respectively, for all the polymers for which the data are available from this study. Considering the fact that the numerical values used for  $E_h$ ,  $F_{id}$ , and  $V_{ms}$  are not precise, the correlations obtained are surprisingly good;  $\alpha_p$  increases with increase in  $\delta_h$ , and, similarly,  $\alpha_n$  increases with increase in  $\delta_d$ . The results further show that unique correlations exist between  $\delta_h$  and  $\alpha_p$ , and, similarly, between  $\delta_d$  and  $\alpha_n$ . These results confirm that  $\alpha_p$  and  $\alpha_n$  uniquely represent the hydrogen bonding ability and the nonpolar character, respectively, of the polymer material.

Figure 5 gives a plot of  $\delta_h$  and  $\delta_d$  data for all the polymers for which reliable  $\alpha_p$  and  $\alpha_n$  values were obtained, as well as for a few additional polymers (numbers 16 and 28 to 30 in Table I) for which reliable  $\alpha_p$  and  $\alpha_n$  values could not be obtained because of either significant column elution or extremely short or long retention times for solutes (see discussion below), or both. Figure 5 shows that a wide range of  $\delta_h$  and  $\delta_d$  values is obtainable for noncellulosic polymers; values of  $\delta_h$  for all the cellulose ester polymers are less than those for all the aromatic polyamide polymers included in this

Fig. 4. Correlation of  $\delta_d$  vs.  $\alpha_n$ .

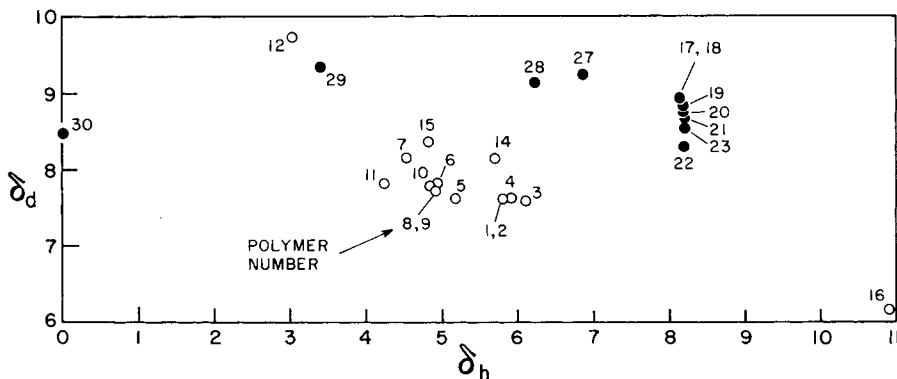


Fig. 5. Plot of data on  $\delta_h$  and  $\delta_d$  for (O) cellulosic and (●) noncellulosic polymers.

study; and, with respect to cellulosic polymers, an increase in nonpolar character ( $\delta_d$ ) always seems to be accompanied by a decrease in the hydrogen bonding ability ( $\delta_h$ ) for the polymer.

The absolute retention times for solutes in different columns are affected by operational details; hence, they cannot be compared in a strict sense. However, a correlation was found to exist between retention time and  $\delta_d$  values. Figure 6 illustrates such a correlation of the retention time for benzyl alcohol and  $\delta_d$  for the polymer used in the column. As Figure 6 shows, the retention time was extremely short both at very low and at very high  $\delta_d$  values, and it passed through a maximum at some intermediate  $\delta_d$  value. This result can be explained on the basis of small hydrophobic interaction between the solute and the polymer surface at small  $\delta_d$  values and very low wettability of the polymer at very high  $\delta_d$  values. In any case, when the retention times are extremely short, the numerical values of both  $\alpha_p$  and  $\alpha_n$  for the polymers become unreliable. This only means that one will have to choose different reference solutes for obtaining reliable  $\alpha_p$  and  $\alpha_n$  values for such polymers.

### CONCLUSIONS

The parameters  $\alpha_p$  and  $\alpha_n$  give relative quantitative measures for the hydrogen bonding and nonpolar (hydrophobic) forces inherent in the polymer

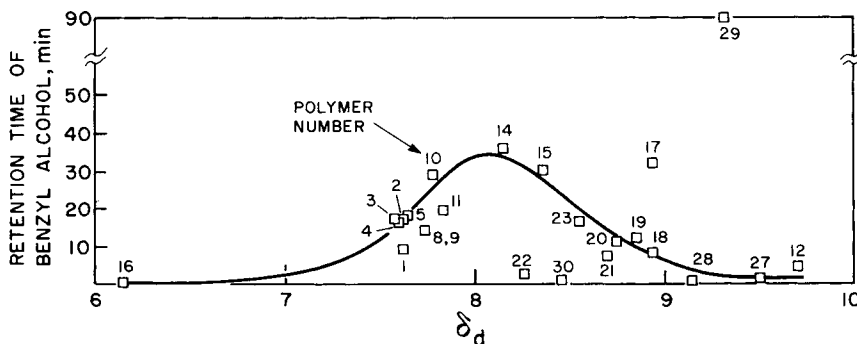


Fig. 6. Plot of retention time of benzyl alcohol vs.  $\delta_d$ .

molecule because of its chemical structure. These parameters are relevant to reverse osmosis. This can be seen from a consideration of reverse osmosis separations of nonionized polar organic solutes in aqueous solutions using membranes made of different materials.

The polar parameter  $\alpha_p$  can either be an attractive force or repulsive force for the solute at the membrane-solution interface depending on the polar (acid or the base) nature of the solute; on the other hand, the nonpolar parameter  $\alpha_n$  is always an attractive force for the solute. The net repulsion of solute at the membrane-solution interface is the combined effect of the hydrogen bonding, nonpolar, and possibly other forces in the polymer-solute-solvent system. This combined effect confers an apparent charged character for the membrane material in reverse osmosis. The net basic character attributed to cellulose acetate material<sup>23</sup> and the net acidic character attributed to the aromatic polyamide material<sup>3</sup> in earlier reports must be viewed in this context.

Reverse osmosis separations of nonionized polar organic solutes have been shown to be higher with the aromatic polyamide membranes than with cellulose acetate membranes of comparable surface pore structure.<sup>3</sup> These results, combined with those of this work, indicate that an increase in both  $\alpha_p$  and  $\alpha_n$  tends to increase reverse osmosis separations for nonionized polar organic solutes. This conclusion suggests a possible guideline for the choice of membrane material for such separations. The existence of unique correlations between  $\alpha_p$  and  $\delta_h$ , and  $\alpha_n$  and  $\delta_d$ , and the possibility of calculating  $\delta_h$  and  $\delta_d$  values on the basis of the structure of the polymer repeat unit enable the exploration of the above guideline without the need for further chromatographic data.

The nonpolar (hydrophobic) force of the polymer material, besides being an attractive force for the organic solute, has an additional effect on reverse osmosis transport. An increase in the value of  $\alpha_n$  tends to increase the mobility of the preferentially sorbed water through the membrane pores when water is preferentially sorbed and to decrease the mobility of the solute when the latter is preferentially sorbed. Both these effects contribute to higher solute separation in reverse osmosis. Higher separations for organics obtainable with aromatic polyamide membranes than with comparable cellulose acetate membranes is understandable on the basis that  $\alpha_n$  for the polyamide material is higher than that for cellulose acetate material. On the basis of this guideline, it is reasonable to expect similar higher separations for organics with more nonpolar cellulosic membranes also. The same guideline can also serve as a basis for the choice of membrane materials for reverse osmosis applications where solute is preferentially sorbed.

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