SOLVENT COMPOSITION EFFECTS ON THE RETENTION CHARACTERISTICS OF AROMATIC HYDROXYL COMPOUNDS WITH SILICA AND POLAR MOBILE PHASES AND INTERPRETATION BY THE SNYDER MODEL

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SUMMARY

Equations from the Snyder chromatographic model were used to interpret the retention data of aromatic hydroxyl compounds on a high-performance silica column. A number of *n*-heptane–2-propanol and *n*-heptane–ethyl acetate mobile phases were used to obtain retention data. It was found that plots of log capacity factor (k') *vs.* solvent strength and log k' *vs.* log mole fraction of the strong solvent showed good linearity for all solutes studied. The slopes of log k' *vs.* solvent strength were used to show that the solutes localized or were hydrogen bonding on the stationary phase. Also, the slopes from various plots were used to obtain experimental molecular areas (A_s) of the solutes. The A_s values were compared a number of ways and the results showed that it was important to consider both the localization of the solutes and the polar mobile phases. In addition, the theoretical chromatographic models correlated better with the data from the ethyl acetate binary mobile phases compared to the data from the 2-propanol binary mobile phases.

INTRODUCTION

High-performance liquid chromatography is a very useful tool in the separation of complex organic mixtures. While reversed-phase systems (non-polar bonded-phase columns and polar mobile phases) are more commonly used, normal-phase systems are also important. Normal-phase systems frequently offer better resolution of isomers and functional classes than reversed-phase systems[1]. A particular advantage of normal-phase systems is in separating coal-derived liquids, since the coal liquids are often insoluble in the water-based solvents frequently used in reversed-phase liquid chromatography[2].

Mobile phase composition in normal-phase liquid chromatography plays a vital role in selectivity and retention of solutes[1,3,4]. A number of authors have developed models to explain solvent, solute, and stationary phase interactions in normal-phase liquid chromatography[5–18]. If a model can describe the interactions in a given chromatographic system, the model can be used to predict retention of solutes at

different mobile phase compositions. This information would be useful in obtaining a mobile phase composition that would give the best separation.

Snyder and co-workers[10,11] have developed an adsorption model based on the displacement of solvent molecules by solute molecules from sites on the stationary phase. A similar model has been proposed by Soczewinski and co-workers[5-9] for adsorption chromatography.

These models have been used to predict retention in normal-phase chromatographic systems. Hurtubise et al.[19] concluded that the Snyder–Soczewinski model described the retention for alkyl phenols on an aminopropyl bonded-phase column. Hussain et al.[20] found that the Snyder–Soczewinski model basically described the retention for alkyl phenols on silica and cyanopropyl bonded-phase columns for certain mobile phase compositions. Ruckmick and Hurtubise[21] concluded that the Snyder model could be used to describe the behavior of polar solutes on a silica stationary phase. Ruckmick and Hurtubise[22] used the Snyder model to describe solvent composition effects for nitrogen heterocycles and hydroxyl aromatics on a nitrophenyl stationary phase. Scolla and Hurtubise[23] were able to use the Snyder model to relate the retention of aromatic nitrogen compounds on an aminopropyl bonded-phase column. Snyder[24] used his model to predict the retention characteristics of diastereomers on a silica column. Snyder and Schunk[25] used the displacement model to describe the behavior of solutes on an amino bonded-phase column. The Soczewinski model was used by Hara et al.[26] to interpret the retention results of steroids on a silica stationary phase. Using the displacement model of Snyder, Hammers et al.[27] concluded that an amino bonded-phase column behaved like partially deactivated silica gel. Wieser et al.[28], using the Snyder model, concluded that a cyanopropyl bonded-phase column acts like deactivated silica gel. Smith and Cooper[29] applied Snyder's model to an amino, cyano, and diol bonded-phase columns to explain the behavior of solutes in several different solvents.

The model by Scott[12] and Scott and Kucera[13-15] views the retention mechanism to be a sorption process emphasizing solute-mobile phase interactions. The models of Snyder, Soczewinski, and Scott have been reviewed by Snyder and co-workers[10,25,30].

Hennion et al.[16] proposed a retention model for normal-phase aminopropyl bonded silica. The Hennion model contains elements of the Snyder, Soczewinski, and Scott models. These models were reviewed and summarized by Snyder and Schunk[25].

Chang and co-workers[17,18] have postulated hydrogen bonding as well as other types of interactions to explain the retention of phenolic and amine type compounds on an amino bonded-phase column.

Most of the earlier investigations that have considered theoretical adsorption models for normal-phase liquid chromatography have used low-molecular-weight standards and relatively weak mobile phases. In this study, we investigated a silica column with various polar compositions of n-heptane–2-propanol and n-heptane–ethyl acetate mobile phases. In addition, a set of aromatic hydroxyl standards were used that had specific structural features.

EXPERIMENTAL

High-performance liquid chromatograph
The liquid chromatograph consisted of mainly Waters Assoc. (Milford, MA,

U.S.A.) equipment. A Model 510 pump and a UK6 injector were used along with a Model 450 variable-wavelength detector set at 280 nm. Also a Linear 1200 strip chart recorder was employed.

Column

The column used was a 30 cm × 3.9 mm I.D. prepacked μPorasil column obtained from Waters Assoc. The μPorasil column consisted of 10-μm porous silica. The column was kept at a constant temperature with a Haake Model FE water circulator set at 25°C.

Reagents

J. T. Baker HPLC-grade *n*-heptane, 2-propanol, and ethyl acetate were obtained from VWR Scientific (Denver, CO, U.S.A.). These solvents were prefiltered through MAGNA Nylon 66 membrane filters of 0.47 μm which were obtained from Fisher Scientific (Denver, CO, U.S.A.).

Chromatographic systems

All chromatographic systems investigated were normal-phase systems using a silica column and various *n*-heptane–2-propanol or *n*-heptane–ethyl acetate mobile phase compositions at a flow-rate of 1.5 ml/min. The *n*-heptane–2-propanol mobile phases consisted of the following compositions: 99.8:0.2, 99.5:0.5, 99:1, 98:2, 97:3, 96:4, and 95:5 (v/v). The *n*-heptane–ethyl acetate mobile phases consisted of the following compositions: 98:2, 96:4, 94:6, 92:8, 90:10, 88:12, 86:14, 84:16, 82:18, and 80:20 (v/v).

Standard compounds

Standard compounds were selected based on their similar structure and size but differing polarity, acidities, and hydrogen bonding abilities. The standards were obtained from commercially available sources. Solutions of 1 mg/ml of the standards were prepared in the mobile phase composition that was used to elute the solute. The retention volumes of the standards were determined from duplicate injections of 5 μl of the standard solutions. The capacity factors (k') were calculated using the equation $k' = (V_R - V_M)/V_M$, where V_R (ml) is the measured retention volume and V_M (ml) is the column void volume. The column void volume was determined for each mobile phase composition by injecting 0.5 μl toluene and measuring its retention volume.

RESULTS AND DISCUSSION

Theoretical considerations

The model developed by Snyder[11] involves the following equation

$$X_m + nS_a \rightleftarrows X_a + nS_m \tag{1}$$
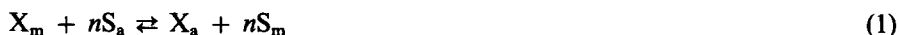
where the subscripts m and a refer to the mobile phase and adsorbed phase, respectively. The adsorption of a solute molecule X results in the displacement of n solvent molecules S. Using the Snyder model the following equation can be derived

$$\log k' = \log(V_A W/V_M) + \alpha'(S^0 - \varepsilon^0 A_s) \tag{2}$$

where k' is the capacity factor, V_A is the adsorbent surface volume, W (g) is the weight of adsorbent in the column, V_M is the void volume of the column, α' is the adsorbent activity, S^0 is the solute adsorption energy, ε^0 is the solvent strength parameter, and A_s is the normalized molecular area of the solute.

If plots of log k' vs. S^0 for standard polycyclic aromatic hydrocarbons are made using heptane as the eluent, α' and log $(V_A W/V_M)$ are the slope and intercept, respectively, from eqn. 2. The solvent strengths of binary eluents can be calculated if α' is known according to Snyder and Schunk[25] and Snyder[31] using

$$\varepsilon_{AB} = \varepsilon_A + \log[N_B 10^{\alpha' n_b}(\varepsilon_A - \varepsilon_B) + 1 - N_B]/\alpha' n_b \tag{3}$$

where ε_{AB} is the solvent strength of the binary eluent, ε_A and ε_B are the solvent strengths of the pure weak and strong solvent respectively, N_B is the mole fraction of solvent B, and n_b is the relative molecular area of a molecule of solvent B. Snyder[4] and Snyder and Schunk[25] have concluded that ε_B can vary with N_B due to restricted-access delocalization of the strong solvent on silica.

According to Snyder[30], the variation of retention of a solute with two mobile phases can be described by the following equation

$$\log(k'_2/k'_1) = \alpha' A_s(\varepsilon_1 - \varepsilon_2) \tag{4}$$

where k'_1 is the capacity factor of the solute in mobile phase 1 that has a solvent strength of ε_1, and k'_2 is the capacity factor for the solute in the second mobile phase of solvent strength ε_2. If n-heptane is used as mobile phase 1, the solvent strength (ε_1) is zero. If plots of log k'_2 vs. ε_2 are made, the slope is equal to $\alpha' A_s$ and the intercept is log k'_1. From the slopes of the log k'_2 vs. ε_2 plots, experimental A_s values can be determined if α' is known. Snyder and Glajch[32] have stated that for high-performance chromatographic silica α' can be considered as a constant equal to 0.57. Experimental A_s values are expected to be larger than calculated A_s values if solutes are polar and can localize and/or hydrogen bond with the adsorbent. These factors cause site-competition delocalization of the solute to occur on silica stationary phases[11,25,32].

With the Snyder[30] approach and very polar binary mobile phases the following equation can be derived
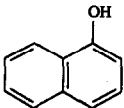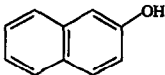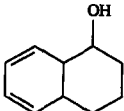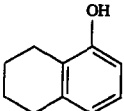
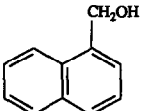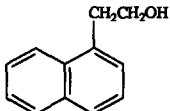$$\log k' = \log k'_0 - (A_s/n_b) \log X_s \tag{5}$$
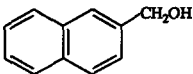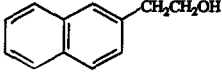
where A_s is the molecular area of the solute, n_b is the strong solvent molecular area, k' is the capacity factor of the solute eluted in the binary mobile phase, k'_0 is the capacity factor of the solute eluted in the pure strong solvent, and X_s is the mole fraction of the strong solvent in the binary mobile phase. For plots of log k' vs. log X_s, Snyder[24,30] has indicated that the slope (A_s/n_b) for monofunctional solutes is equal to the ratio of the number of solute molecules to polar solvent molecules which are displaced from the adsorbent surface. Snyder[24,30] has concluded that the experimental A_s values for a solute molecule can be a function of the solute's configuration on the adsorbent.

In this work, the A_s values were calculated using the following equation developed by Snyder[33] for unsubstituted aromatic hydrocarbons

$$A_s = 6 + 0.80(h - 6) + 0.25(c - h) \tag{6}$$

where h is the number of aromatic hydrogens in the solute and c is the number of aromatic carbons in the solute. The A_s values increase by 7.6 units and 8.5 units for aromatic –OH groups and aliphatic –OH groups, respectively[33].

TABLE I

COMPOUNDS STUDIED ON SILICA

No.	Compound	Structure	pK_a
1	1-Naphthol		9.3^a
2	2-Naphthol		9.6^a
3	1,2,3,4-Tetrahydro-1-naphthol		15.7^b
4	5,6,7,8-Tetrahydro-1-naphthol		10.3^a
5	1-Naphthalenemethanol		15.3^b
6	1-Naphthaleneethanol		15.2^b
7	2-Naphthalenemethanol		15.3^b
8	2-Naphthaleneethanol		15.2^b

^{a} From ref. 34.
^{b} Calculated from information in ref. 35.

Plots of log k' vs. solvent strength

The hydroxyl standards studied in this work appear in Table I along with their pK_a values[34,35]. The solvent strength values used in this study were determined from solvent strength data published by Snyder and Glajch[32]. Snyder and Glajch[32] listed solvent strength values for *n*-hexane–2-propanol and *n*-hexane–ethyl acetate mobile phases. Since *n*-heptane and *n*-hexane both have a solvent strength of zero on silica and both solvents give essentially the same selectivity, the solvent strength of a given mole fraction of strong solvent should be the same whether in *n*-hexane or *n*-heptane. For this work, solvent strengths were determined by graphing solvent strength values[32] *vs.* mole fraction of the strong solvent and then by knowing the mole fraction of the strong solvent used in this study the solvent strength values were obtained from the graphs. Table II gives a listing of various mobile phase compositions of *n*-heptane–2-propanol, log k' for the solutes, and solvent strength values used in this work. Similar information can be found in Table III for *n*-heptane–ethyl acetate mobile phases.

Using eqn. 4, plots of log k' *vs.* solvent strength for the solutes listed in Table I yielded linear correlation coefficients ranging from -0.994 to -1.00 for the *n*-heptane–2-propanol mobile phases, and the correlation coefficients were all -1.00 for *n*-heptane–ethyl acetate mobile phases. The results for *n*-heptane–2-propanol mobile phases were based on five compositions since results for the 96:4 and 95:5 mobile phases showed deviation from the log k' *vs.* solvent strength line. This is possibly due to the small k' values, ranging from 0.34 to 1.56, obtained at these compositions or to errors in determining the solvent strength in these solvent mixtures. The slope, intercept, and correlation coefficient values obtained are shown in Table IV. The linearity of the plots is shown by the high correlation coefficient values obtained. The lowest correlation coefficient was -0.994 for 1-naphthaleneethanol in the

TABLE II

LOG k' VALUES FOR THE MODEL COMPOUNDS ON SILICA WITH *n*-HEPTANE-2-PROPANOL MOBILE PHASES

Compound No.	Mole fraction 2-propanol						
	0.004	0.010	0.019	0.038	0.056	0.074	0.092
	n-Heptane–2-propanol (v/v)						
	99.8:0.2	99.5:0.5	99:1	98:2	97:3	96:4	95:5
1	1.224	0.760	0.387	0.039	-0.14	-0.28	-0.36
2	0.982	0.571	0.248	-0.07	-0.23	-0.36	-0.47
3	1.137	0.743	0.456	0.185	0.000	-0.11	-0.21
4	0.762	0.389	0.097	-0.18	-0.33	-0.47	-0.55
5	—	0.974	0.681	0.398	0.228	0.097	0.013
6	—	1.054	0.750	0.453	0.281	0.152	0.061
7	—	1.082	0.776	0.480	0.301	0.176	0.076
8	—	1.067	0.774	0.486	0.314	0.193	0.097
$\log X_s$	-2.398	-2.000	-1.721	-1.420	-1.252	-1.131	-1.036
ε_{AB}	0.270	0.291	0.308	0.323	0.338	0.348	0.360

TABLE III

LOG k' VALUES FOR THE MODEL COMPOUNDS ON SILICA WITH n-HEPTANE–ETHYL ACETATE MOBILE PHASES

Compound No.	Mole fraction ethyl acetate									
	0.030	0.059	0.087	0.115	0.143	0.170	0.196	0.222	0.248	0.273
	n-Heptane–ethyl acetate (v/v)									
	98:2	96:4	94:6	92:8	90:10	88:12	86:14	84:16	82:18	80:20
1	1.096	0.721	0.498	0.350	0.220	0.107	0.025	-0.06	-0.14	-0.21
2	0.833	0.496	0.286	0.152	0.017	-0.06	-0.16	-0.24	-0.28	-0.39
3	1.367	1.046	0.855	0.721	0.582	0.473	0.393	0.307	0.233	0.187
4	0.733	0.382	0.167	-0.03	-0.10	-0.23	-0.28	-0.41	-0.48	-0.57
5	–	1.278	1.081	0.938	0.802	0.682	0.606	0.514	0.449	0.367
6	–	1.461	1.272	1.128	0.990	0.878	0.797	0.708	0.621	0.557
7	–	1.390	1.195	1.048	0.912	0.800	0.716	0.624	0.536	0.479
8	–	1.480	1.290	1.150	1.017	0.900	0.827	0.739	0.655	0.593
$\log X_s$	-1.523	-1.229	-1.060	-0.939	-0.845	-0.770	-0.708	-0.654	-0.605	-0.564
ε_{AB}	0.205	0.233	0.262	0.278	0.293	0.307	0.317	0.323	0.330	0.337

TABLE IV

SLOPE, INTERCEPT AND CORRELATION COEFFICIENT VALUES FOR LOG k' vs. SOLVENT STRENGTH FOR (a) 2-PROPANOL AND (b) ETHYL ACETATE BINARY MOBILE PHASES ON SILICA

Compound No.	Slope	Intercept	Correlation coefficient
(a) 1	−18.28	5.89	−1.00
2	−20.65	6.77	−1.00
3	−16.92	5.68	−1.00
4	−16.43	5.17	−1.00
5	−15.42	5.44	−1.00
6	−15.89	5.65	−0.994
7	−15.99	5.71	−1.00
8	−15.44	5.53	−1.00
(b) 1	−8.69	2.57	−1.00
2	−9.38	2.97	−1.00
3	−8.70	3.13	−1.00
4	−9.30	2.60	−1.00
5	−8.80	3.37	−1.00
6	−8.80	3.55	−1.00
7	−8.89	3.50	−1.00
8	−8.62	3.53	−1.00

n-heptane–2-propanol system. However, this is still a very good correlation. Fig. 1 shows a plot of log k' vs. solvent strength of 2-propanol for 1,2,3,4-tetrahydro-1-naphthol with n-heptane–2-propanol mobile phases. Fig. 2 shows similar results for the n-heptane–ethyl acetate mobile phases using 1,2,3,4-tetrahydro-1-naphthol.

Plots of log k' vs. log mole fraction of the strong solvent
        The standard solutes investigated herein appear in Table I. For polar mobile phases eqn. 5 shows that plots of log k' vs. log mole fraction of the strong solvent should be linear[30]. Table V lists the slope, intercept, and correlation coefficient values for the results of log k' vs. log mole fraction of the strong solvent. The high values of the correlation coefficient indicates that the plots are very linear. Figs. 3 and 4 are plots of log k' vs. log mole fraction of the strong solvent for 1,2,3,4-tetrahydro-1-naphthol in n-heptane–2-propanol and n-heptane–ethyl acetate mobile phases, respectively. Unlike the results discussed for Table IV, the results for n-heptane–2-propanol mobile phases in Fig. 3 remained linear when plotted over the entire mobile phase composition range.

Theoretical interpretations
        According to eqn. 4 the slope values in Table IV are equal to $\alpha' A_s$, and according to eqn. 5 the slope values in Table V are equal to A_s/n_b. The interpretation of the results for the slopes are given in the following two sections. Snyder and Glajch[32] have stated that α' for high-performance chromatographic silica is equal to 0.57. The n_b values for 2-propanol and ethyl acetate on silica have been determined by Snyder[11] to be equal to

TABLE V

SLOPE, INTERCEPT AND CORRELATION COEFFICIENT VALUES FOR LOG k' vs. LOG MOLE FRACTION OF THE STRONG SOLVENT FOR (a) 2-PROPANOL AND (b) ETHYL ACETATE BINARY MOBILE PHASES ON SILICA

Compound No.	Slope	Intercept	Correlation coefficient
(a) 1	−1.06	−1.57	−1.00
2	−1.18	−1.61	−1.00
3	−0.99	−1.23	−1.00
4	−0.97	−1.55	−1.00
5	−1.00	−1.02	−1.00
6	−1.03	−1.01	−1.00
7	−1.04	−1.00	−1.00
8	−1.00	−0.94	−1.00
(b) 1	−1.25	−1.05	−1.00
2	−1.35	−0.94	−1.00
3	−1.25	−0.49	−1.00
4	−1.34	−1.27	−1.00
5	−1.37	−0.38	−1.00
6	−1.37	−0.19	−1.00
7	−1.39	−0.28	−1.00
8	−1.35	−0.14	−1.00

4.4 and 5.2, respectively. Using this information, the slopes in Tables IV and V, and eqn. 6, the experimental and calculated A_s values can be determined. Table VI contains a list of calculated A_s, experimental A_s, and ΔA_s(calculated A_s − experimental A_s) from the log k' vs. solvent strength data for both n-heptane–2-propanol and n-heptane–ethyl acetate mobile phases. Table VII has similar information but from log k' vs. log mole fraction of the strong solvent data.

Log k' vs. solvent strength. Hydrogen bonding and localization of the solutes to the stationary phase is expected due to the polar nature of the functional groups. If localization or hydrogen bonding occurs, experimental A_s values should be larger than the calculated A_s values[3,4,24]. In all cases, this can be seen in Table VI with the n-heptane–2-propanol mobile phases. In Table VI for n-heptane–2-propanol, the largest absolute ΔA_s values occurred for compounds with the lowest pK_a values (see Table I). This would seem to follow since the smaller the pK_a value the more readily the compound would donate a proton and therefore more strongly localize or take part in hydrogen bonding with the stationary phase. Compound 4 has a pK_a of about 10.3 and the absolute ΔA_s value is smaller than for compounds 1 or 2 but larger than for compounds 5, 6, 7, and 8 which have pK_a values of around 15.2. Compounds 5, 6, 7, and 8 have the smallest absolute ΔA_s values suggesting they are not as strongly localized and are not as polar as the other compounds. The results for compound 3 do not correlate well, when comparing it's pK_a value to it's ΔA_s value. The pK_a values only give a very rough indication of the factors involved in obtaining experimental A_s values larger than calculated A_s values. Nevertheless, it is instructive to correlate the pK_a values with experimental A_s values because the pK_a values give a qualitative measure of the ability of the model compounds to donate protons.
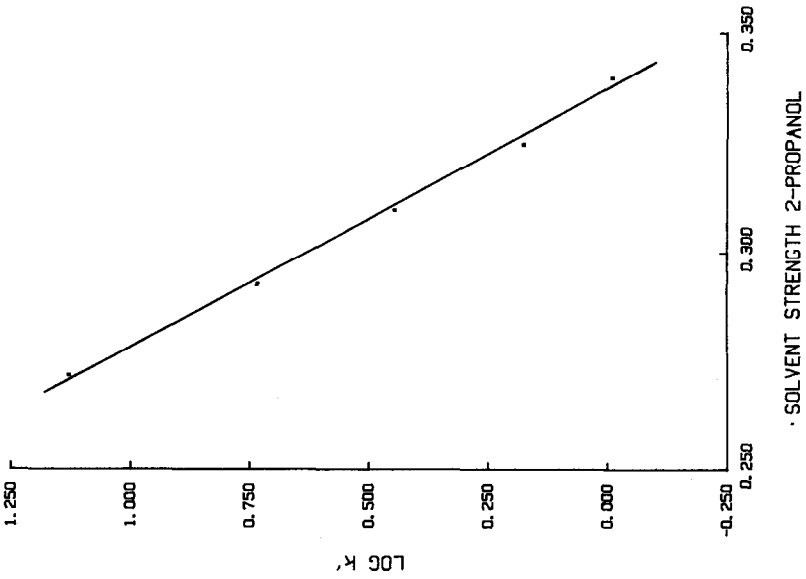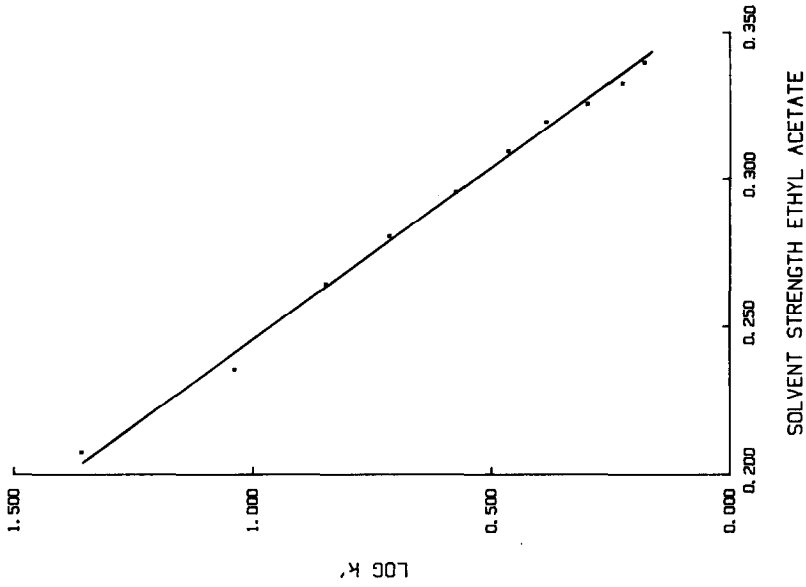
Fig. 1. Plot of log k' vs. solvent strength (ε) for 1,2,3,4-tetrahydro-1-naphthol using n-heptane–2-propanol mobile phases.

Fig. 2. Plot of log k' vs. solvent strength (ε) for 1,2,3,4-tetrahydro-1-naphthol using n-heptane–ethyl acetate mobile phases.
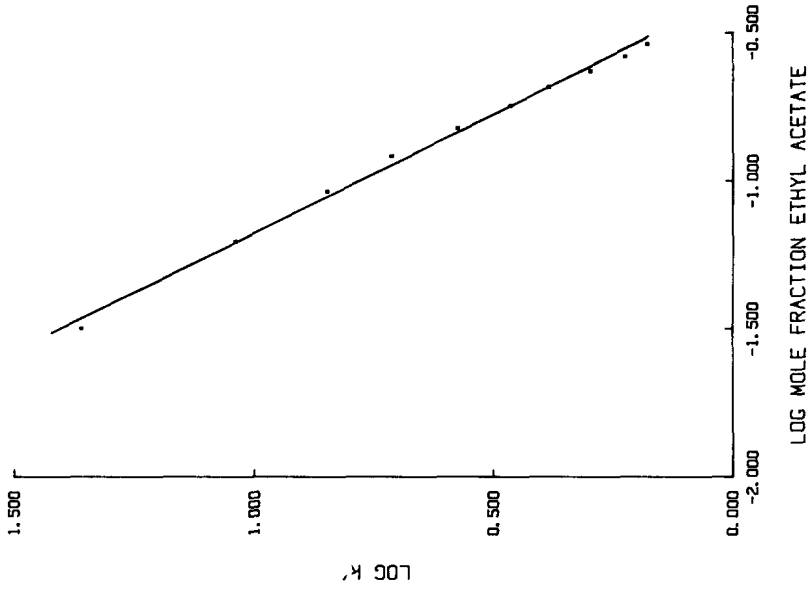
Fig. 3. Plot of log k' vs. log mole fraction 2-propanol for 1,2,3,4-tetrahydro-1-naphthol using n-heptane–2-propanol mobile phases.
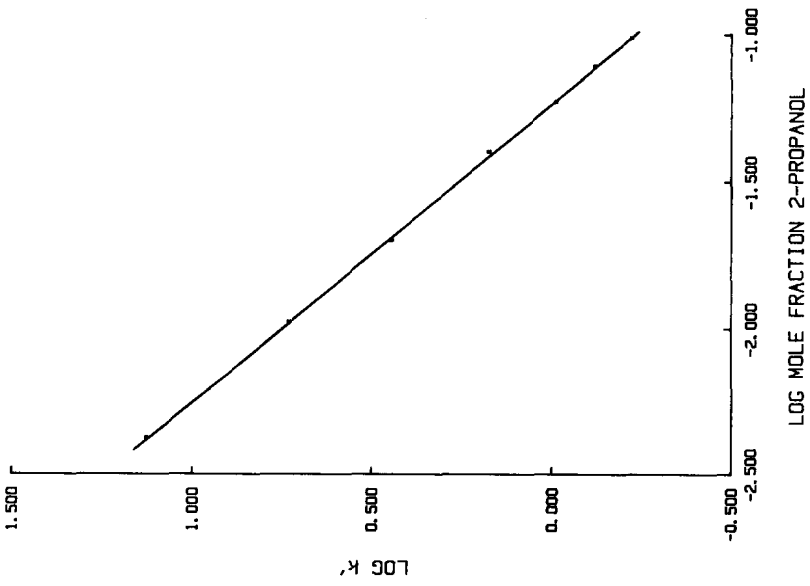
Fig. 4. Plot of log k' vs. log mole fraction ethyl acetate for 1,2,3,4-tetrahydro-1-naphthol using n-heptane–ethyl acetate mobile phases.

TABLE VI

CALCULATED AND EXPERIMENTAL A_s VALUES USING LOG k' vs. SOLVENT STRENGTH FOR (a) 2-PROPANOL AND (b) ETHYL ACETATE BINARY MOBILE PHASES ON SILICA

Compound No.	$A_s(calc)$	$A_s(exp)$	ΔA_s
(a) 1	15.7	32.1	−16.4
2	15.7	36.2	−20.5
3	18.1	29.7	−11.6
4	17.2	28.8	−11.6
5	17.5	27.0	−9.5
6	18.4	27.9	−9.5
7	17.5	28.1	−10.6
8	18.4	27.1	−8.7
(b) 1	15.7	15.3	0.4
2	15.7	16.5	−0.8
3	18.1	15.3	2.8
4	17.2	16.3	0.9
5	17.5	15.4	2.1
6	18.4	15.4	3.0
7	17.5	15.6	1.9
8	18.4	15.1	3.3

TABLE VII

RELATIVE MOLECULAR AREAS OF THE SOLUTES FROM LOG k' vs. LOG MOLE FRACTION OF THE STRONG SOLVENT FOR (a) 2-PROPANOL AND (b) ETHYL ACETATE BINARY MOBILE PHASES ON SILICA

Compound No.	$A_s(calc)$	$A_s(exp)$	ΔA_s	$A_s(exp)^a$	$\Delta A_s{}^a$
(a) 1	15.7	4.68	11.0	23.8	−8.1
2	15.7	5.17	10.5	26.5	−10.8
3	18.1	4.34	13.8	22.3	−4.2
4	17.2	4.25	13.0	21.8	−4.6
5	17.5	4.38	13.1	22.5	−5.0
6	18.4	4.52	13.9	23.2	−4.8
7	17.5	4.56	12.9	23.4	−5.9
8	18.4	4.40	14.0	22.5	−4.1
(b) 1	15.7	6.50	9.20	17.1	−1.4
2	15.7	7.02	8.68	18.5	−2.8
3	18.1	6.49	11.6	17.1	1.0
4	17.2	6.96	10.2	18.4	−1.2
5	17.5	7.13	10.4	18.7	−1.2
6	18.4	7.13	11.3	18.8	−0.4
7	17.5	7.21	10.3	19.0	−1.5
8	18.4	6.99	11.4	18.5	−0.1

[a] These A_s(exp) and ΔA_s values are based on the corrected n_b values which account for localization.

The experimental A_s values from the ethyl acetate binary mobile phases in Table VI, in most cases, are relatively smaller and much closer to the calculated A_s values compared to similar data from the 2-propanol binary mobile phases. The compounds with the smallest pK_a values (compounds 1, 2, and 4) have A_s experimental values relatively close to their calculated A_s values. For the remaining compounds, with the larger pK_a values, the experimental A_s values are relatively smaller compared to the calculated A_s values. The primary reason the experimental A_s values with the 2-propanol binary mobile phases are larger than the corresponding experimental A_s values with n-heptane–ethyl acetate mobile phases is due to the polarity of the 2-propanol binary mobile phases. The n-heptane–2-propanol mobile phases can localize and hydrogen bond to a greater extent than the n-heptane–ethyl acetate mobile phases[3,32]. Also, eqn. 4 recognizes the localization of the solute and solvent. However, eqn. 4 does not take into consideration the "interaction" of these two effects. Snyder *et al.*[3] have considered this and for the case of localizing solutes and solvents the term Δ_1 must be added to eqn. 4. The term Δ_1 corrects eqn. 4 for the "interaction" of solute and solvent localization, and its effect on k'. The term Δ_1 would become larger for increasing localization of the solute and solvent. The larger A_s(exp) values in Table VI for the 2-propanol binary mobile phases compared to the ethyl acetate binary mobile phases are due to 2-propanol localizing more strongly than ethyl acetate and the "interaction" effect being greater for 2-propanol compared to ethyl acetate.

Log k' vs. log mole fraction of the strong solvent. The method used to obtain experimental A_s values, as in Table VII, has been used in discussing solute configuration on the adsorbent[24,30]. A calculated A_s value assumes flatwise adsorption[33]. Snyder[30] has stated that experimental A_s values will be smaller than calculated if vertical adsorption occurs on the stationary phase. Vertical adsorption is often favored for strong solvents and silica[30]. Since the experimental A_s values in Table VII are considerably smaller than the calculated values, vertical adsorption is more likely than flatwise adsorption. The experimental A_s values in Table VII are smaller for the compounds in n-heptane–2-propanol mobile phases compared to the corresponding compounds in n-heptane–ethyl acetate mobile phases. This would seem to follow since 2-propanol is a stronger solvent than ethyl acetate.

However, another way to interpret the data is to consider the n_b values for the polar solvents. In using the n_b values to calculate the experimental A_s values, it was assumed that the solvents did not localize[32]. However, the solvents do localize and thus the n_b values would be larger than those used here due to localization. Snyder and Glajch[36] have commented on this earlier. Also, in the derivation of eqn. 5, it is assumed that solvent strength does not change with increasing percentage of strong solvent[11]. However, it has been shown that solvent strength does vary with percentage of strong solvent[32], and eqn. 5 may not be applicable to the data in this work. However, eqn. 5, or a slightly modified form of the equation, is widely used in chromatography; thus it is appropriate to comment on the use of eqn. 5 in the interpretation of chromatographic data. Snyder and Glajch[32] have reported localization functions for 2-propanol and ethyl acetate of 18.1 and 8.5, respectively. The appropriate localization function was added to the n_b values for 2-propanol and ethyl acetate to obtain corrected n_b values of 22.5 and 13.7, respectively. If these corrected n_b values are used to calculate the experimental A_s values, the new experimental A_s values for the n-heptane–2-propanol mobile phases are generally closer to the calculated A_s values compared to the

experimental A_s values calculated with uncorrected n_b values (see Table VII). Also, the experimental A_s values for the n-heptane–ethyl acetate mobile phases are much closer to the calculated A_s values in Table VII compared to the n-heptane–2-propanol mobile phases. Thus, by correcting the n_b values for the polar mobile phases, a better correlation is obtained between A_s(calc) and A_s(exp) for both 2-propanol and ethyl acetate binary mobile phases. The ΔA_s values for the 2-propanol binary mobile phases are still somewhat high. This is most likely due to the polar nature of 2-propanol.

Ideally, the A_s(exp) values in Table VI and Table VII should be very close to one another for a given compound. By comparing A_s(exp) values in Table VI for the ethyl acetate binary mobile phases with the corresponding A_s(exp) values in Table VII based on the larger n_b values, it can be seen that the A_s values are roughly the same for a given compound. By making the same comparison for the 2-propanol binary mobile phases in Tables VI and VII, the A_s(exp) values are considerably larger in Table VI compared to the A_s(exp) values in Table VII. However, the larger differences observed for the A_s(exp) values for the 2-propanol binary mobile phases is most likely related to the very polar nature of 2-propanol. In addition, eqn. 4 is considered to be more broadly based and the theoretical treatment of eqn. 4 has been discussed much more extensively in the literature than eqn. 5[11]. Thus, the data analysis using eqn. 4 is considered to be more valid. More work would have to be done to explain the differences observed in the A_s(exp) values for both binary mobile phases.

CONCLUSIONS

Linear relationships obtained for log k' vs. solvent strength and log k' vs. log mole fraction of the strong solvent showed that these relationships would be useful for predicting the retention characteristics of aromatic hydroxyl compounds. The interpretation of the retention data with equations from the Snyder model showed the importance of considering localization effects for both polar solutes and polar solvents. Comparison of A_s values for the aromatic hydroxyl compounds from graphs of log k' vs. solvent strength and log k' vs. log mole fraction of the strong solvent showed that the A_s values were roughly the same for ethyl acetate binary mobile phases. However, much larger differences in A_s values were obtained for the A_s values from the graphs with 2-propanol binary mobile phases. It was concluded that eqn. 4 was more valid in the interpretation of the retention data than eqn. 5.

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