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RELATIVE RETENTION AND COLUMN SELECTIVITY FOR THE COMMON POLAR BONDED-PHASE COLUMNS

THE DIOL-SILICA COLUMN IN NORMAL-PHASE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

Retention data for several solutes and mobile phases composed of methylene chloride–hexane and isopropanol–hexane are reported for a diol column. These data are in agreement with a previous model of retention in normal-phase systems. These and other data from the literature have been used to characterize the selectivity of diol, cyano and amino columns for various sample types. The diol and amino columns each preferentially retain basic solutes (*e.g.*, esters, ketones) *vs.* dipolar solutes (nitro and nitrile derivatives), when compared to a cyano column. The amino column strongly retains acidic solutes.

INTRODUCTION

Although most separations using high-performance liquid chromatography (HPLC) are presently carried out under reversed-phase conditions, there is a continuing interest in the use of normal-phase chromatography[1], particularly with polar bonded-phase columns. The separation by reversed-phase HPLC of some samples may be poor, even after conditions have been optimized. Normal-phase HPLC, being based on a different retention process, often provides a greater resolution for such samples, particularly in the case of isomers[1]. In addition, many organic compounds have limited solubility in aqueous–organic mobile phases, but dissolve well in normal-phase solvents. Finally, many of the problems associated with silica[2] (*e.g.*, irreversible retention of highly polar compounds and difficulty in maintaining a constant mobile phase water content) are avoided through the use of polar bonded-phase columns.

Polar bonded-phase columns are commercially available in three common forms: cyano, diol and amino. Separation on these columns is similar in many respects

to that on silica and alumina; *i.e.*, retention involves a competition between solute and solvent molecules for sites on the adsorbent surface. Previously published studies have shown that the well-documented displacement model for alumina and silica[3] is applicable to separations on cyano[4–6], amino[6–8], diol[6] and other polar bonded-phase packings[9,10]. In this paper we will further examine the retention on a diol column of various solutes. This in turn allows us to make a comparison of column selectivity and column strength among the cyano, diol and amino columns. Some apparent anomalies for isopropanol as a polar solvent are also reported for the cyano column.

EXPERIMENTAL

A Varian 5000 programmable liquid chromatograph was used with a Rheodyne automatic injector, a 10-μl sample loop and a photometric detector. Automatic proportioning was employed for strong solvent concentrations at or above 1%.

Diol columns (25 × 0.46 cm I.D., 5-μm packing, supplied in pH 7 buffered aqueous mobile phase) were the gift of DuPont (Wilmington, DE, U.S.A.). Amino columns [25 × 0.46 cm I.D., 5-μm packing, supplied in either acetonitrile–water (75:25) or 100% hexane mobile phase] were supplied by Supelco (Bellefonte, PA, U.S.A.). Cyano columns were obtained from both Supelco [15 × 0.46 cm I.D., 5-μm packing and supplied in either acetonitrile–water (25:75) or 100% hexane mobile phase] and DuPont [15 × 0.46 cm I.D., 6-μm packing, supplied in hexane–isopropanol (96:4)]. Both the amino and cyano columns were endcapped by the manufacturers. The solvents were HPLC grade from Fisher Scientific (Pittsburgh, PA, U.S.A.) and J. T. Baker (Phillipsburg, NJ, U.S.A.). Solutes were from Aldrich (Milwaukee, WI, U.S.A.), Baker and Sigma (St. Louis, MO, U.S.A.).

The temperature of the column was maintained constant at 30°C by means of a contact heater. System pressure ranged from 20 to 140 atm depending on the solvent system used. Solvent flow was 2.00 ml/min. Sample weights were always less than 20 μg to avoid overloading of the column. Column deadtime (t_0) ranged from 1.5 to 1.7 min and *m*-nitroacetophenone was injected daily to verify reproducibility (capacity factor, k' range = $\pm 10\%$ over a one-year period).

RESULTS AND DISCUSSION

Diol column

Our interpretation of the retention data reported in this study is based upon the displacement model of retention for liquid–solid chromatography[3]. As this model is treated extensively elsewhere, only an outline of relevant aspects is discussed here. The displacement model assumes the formation of an adsorbed monolayer of solute plus solvent molecules on the surface of the stationary phase. During the course of the separation, solute and solvent molecules compete for a limited number of adsorption sites. For a homogeneous surface and the situation where solute and solvent interactions with the mobile phase essentially cancel, a fundamental relationship can be derived[3] between solute retention (k') and mobile phase strength (ε^0):

$$\log(k_2/k_1) = \alpha' A_s(\varepsilon_1^0 - \varepsilon_2^0) \tag{1}$$

Here k_1 and k_2 are k' values for the solute in mobile phases 1 and 2, α' is the adsorbent activity function for the column (assumed equal to 1.0), A_s is the molecular area of the solute, and ε_1^0 and ε_2^0 are solvent strength values (ε^0) for mobile phases 1 and 2.

Table I summarizes retention data on the diol column for fourteen solutes: twelve substituted aromatics and two polycyclic aromatics. Log k' values are given for each solute and five different mobile phase compositions [ranging from pure hexane to dichloromethane–hexane (35:65)]. Solvent strength values for these five mobile phases were determined from retention data for chrysene and perylene by means of eqn. 1 (A_s values for these non-localizing hydrocarbon solutes can be calculated from their molecular areas). Using the calculated solvent strength values for the non-polar hydrocarbons, eqn. 1 was then used to determine "experimental" A_s values for the various non-hydrocarbons of Table I. Listed in Table I are three sets of A_s values: localized, delocalized and experimental. Delocalized values of A_s correspond to actual solute molecular areas (similar to those found for adsorption on alumina[11]). The larger "localized areas" of Table I are values determined for silica as adsorbent; these A_s values reflect "site-competition delocalization"[3,10] among solute and solvent molecules as they compete for a place on the adsorbent surface. The experimental A_s values for the non-hydrocarbons of Table I fall between the localized and delocalized values for adsorption on silica and alumina, respectively. Thus, site-competition delocalization appears to be occurring on the diol column, but to a lesser extent than on silica.

The degree of site-competition delocalization occurring on the diol column can be defined in terms of an empirical parameter c, where

$$A_s = A_s(\text{alumina}) + c[A_s(\text{silica}) - A_s(\text{alumina})] \tag{2}$$

The experimental data of Table I suggest that $c = 0.7 \pm 0.1$ for the diol column. That is, site-competition delocalization effects are about 70% as important on the diol column as on unbonded silica. Eqn. 2 reflects the fact that site-competition delocalization is possible on silica but not alumina[3].

The capacity factor k_h in pure hexane as mobile phase can be determined for each of the solutes of Table I (eqn. 1), assuming that ε^0 is zero for hexane. Log k_h values are given in parentheses in Table I; the last column shows the average of these calculated values for each solute. Individual values of log k_h agree with the average within ± 0.04 units (one standard deviation).

For a mobile phase that is a binary mixture of a weaker solvent A and a stronger solvent B, solvent strength ε_{AB}^0 is given by[10]

$$\varepsilon_{AB}^0 = \varepsilon_A^0 + \{\log[N_b\, 10^{\alpha' n_b(\varepsilon_B^0 - \varepsilon_A^0)} + 1 - N_b]\}/\alpha' n_b \tag{3}$$

ε_A^0 and ε_B^0 are the solvent strengths of the pure solvents A and B respectively, N_b is the mole fraction of the stronger solvent B and n_b is the molecular area of the B solvent. Eqn. 3 can be rearranged to solve for the solvent strength of pure solvent B.

$$\varepsilon_B^0 = (1/\alpha' n_b)\log\{10^{\alpha' n_b \varepsilon_A^0}[10^{\alpha' n_b(\varepsilon_{AB}^0 - \varepsilon_A^0)} - 1 + N_b]/n_b\} \tag{4}$$

TABLE I

RETENTION DATA FOR POLYCYCLIC AROMATIC HYDROCARBONS AND SUBSTITUTED AROMATIC HYDROCARBONS

Diol-silica column, methylene chloride–hexane mobile phase.

Solute	A_s[a]			*log k' (log k_h)*					*Average log k_h*[b]
	loc	*del*	*exp*	*Methylene chloride (%, v/v)*					
				0	*5*	*10*	*20*	*35*	
Chrysene	12.3	12.3		−0.20)	−0.41	−0.521	−0.764	−1.02	
				(−0.20)	(−0.236)	(−0.186)	(−0.210)	(−0.162)	−0.218 ± 0.025
Perylene	12.8	12.8		−0.041	−0.28	−0.391	−0.682	−0.914	
				(−0.041)	(−0.099)	(−0.043)	(−0.105)	(−0.021)	−0.061 ± 0.033
1-Nitronaphthalene	15.6	9.4	13.7	−0.080	−0.24	−0.391	−0.613	−0.936	
				(−0.080)	(−0.046)	(−0.018)	(0.004)	(0.002)	−0.048 ± 0.031
1-Cyanonaphthalene	16.5	8.7	14.2	0.017	−0.16	−0.315	−0.532	−0.851	
				(0.017)	(0.041)	(0.072)	(0.108)	(0.014)	0.043 ± 0.027
2-Naphthylacetate	16.2	10.4	14.5	0.068	−0.13	−0.373	−0.544	−0.936	
				(0.068)	(0.076)	(0.087)	(0.109)	(0.075)	0.077 ± 0.009
2-Naphthaldehyde	16.4	9.2	14.2	0.076	−0.11	−0.256	−0.476	−0.799	
				(0.076)	(0.091)	(0.131)	(0.164)	(0.019)	0.099 ± 0.022
1-Naphthylacetate	16.2	10.4	14.5	0.11	−0.097	−0.284	−0.544	−0.903	
				(0.11)	(0.109)	(0.111)	(0.109)	(0.108)	0.110 ± 0.001
1-Acetonaphthalene	17.3	9.6	15.0	0.11	−0.064	−0.241	−0.476	−0.821	
				(0.11)	(0.149)	(0.167)	(0.200)	(0.225)	0.136 ± 0.036
2-Acetonaphthalene	17.3	9.6	15.0	0.21	0.017	−0.162	−0.415	−0.745	
				(0.21)	(0.230)	(0.246)	(0.260)	(0.301)	0.237 ± 0.022
1,5-Dinitronaphthalene	23.1	10.7	19.4	0.31	0.086	−0.099	−0.355	−0.712	
				(0.31)	(0.361)	(0.429)	(0.519)	(0.641)	0.405 ± 0.091
2,6-Dimethyl naphthylene dicarboxylate	24.3	12.7	20.8	0.38	0.13	−0.076	−0.360	−0.750	
				(0.38)	(0.425)	(0.490)	(0.577)	(0.704)	0.468 ± 0.086
1-Naphthyl nitrile	17.6	10.5	15.5	0.480	0.222	0.0086	−0.274	−0.750	
				(0.480)	(0.442)	(0.431)	(0.424)	(0.331)	0.444 ± 0.025
m-Nitroacetophenone	22.7	8.8	18.5	0.48	0.24	0.0086	−0.268	−0.631	
				(0.48)	(0.502)	(0.512)	(0.566)	(0.659)	0.515 ± 0.036
Benzyl alcohol	15.4	8.2	13.2	1.146	0.96	0.727	0.413	0.136	
				(1.146)	(1.147)	(1.086)	(1.008)	(1.056)	1.089 ± 0.060
ε^0_{AB}[c]				(0.000)	0.014	0.027	0.045	0.070	
ε^0_B[d]					0.096	0.100	0.100	0.109	

[a] Localized (loc) and delocalized (del) values of A_s from ref. 3; exp = experimental.
[b] Data from k' values less than −0.5 excluded.
[c] Calculated from eqn. 1, assuming $\varepsilon^0 = 0.00$ for hexane (chrysene and perylene solutes).
[d] Calculated from eqn. 4.

TABLE II

RETENTION DATA FOR STEROIDS

Diol-silica column, methylene chloride–hexane mobile phase.

Solute	*Methylene chloride (%, v/v)*	*log k'*	ε°	A_s *(exp)*	A_s *(calc)*[a]
4-Androstene-17-β-ol-3-one	18	1.00	0.042	27.3	25
	26	0.77	0.053		
	36	0.41	0.064		
	50	0.09	0.076		
4-Androstene-17-α-ol-3-one	18	1.21	0.042	29.9	25
	21	1.07	0.046		
	31	0.70	0.059		
	60	0.02	0.081		
Adrenosterone	13	1.22	0.033	34.0	31
	18	0.89	0.042		
	23	0.60	0.048		
	40	0.03	0.068		
Corticosterone	40	1.06	0.068	40.6	38
	47	0.81	0.073		
	57	0.54	0.080		
	81	0.05	0.092		
Prednisone	59	1.17	0.081	48.1	43
	70	0.85	0.087		
	80	0.65	0.092		
	100	0.29	0.099		

[a] According to ref. 3, assuming $c = 0.7$ (eqn. 2).

The value of n_b for dichloromethane is 4.1, from which we calculate that ε_B^0 for this solvent is equal to 0.101 ± 0.005 (one standard deviation).

Steroid solutes. In order to further verify eqn. 1 for stronger mobile phases, more highly retained solutes were necessary. Five steroids were studied at four different dichloromethane concentrations (giving k' values ranging from 1 to 20 for these solutes). Table II summarizes resulting experimental values of k', calculated values of ε_{AB}^0 (eqn. 3), experimental values of A_s (eqn. 1, slope of the log k' *versus* ε_{AB}^0 line, determined by linear regression), and calculated values of A_s (eqn. 2, $c = 0.7$). These latter values of A_s are in reasonable agreement, further verifying the applicability of eqns. 1 and 2.

The preceding analysis of experimental data for the diol column (Tables I and II) plus previously published work on the amino and cyano columns confirm the overall applicability of the displacement model (with localization effects) for polar bonded-phase systems. Separation on these polar bonded-phase columns should therefore be predictable as a function of mobile phase composition.

Column selectivity and strength

The selectivity of the cyano, diol and amino columns might be expected to parallel the acidity, basicity and dipolarity of the individual functional groups (–CN, –O–CH[OH]–CH_2OH, and –NH_2)[1], as measured by the "solvent-selectivity" tri-

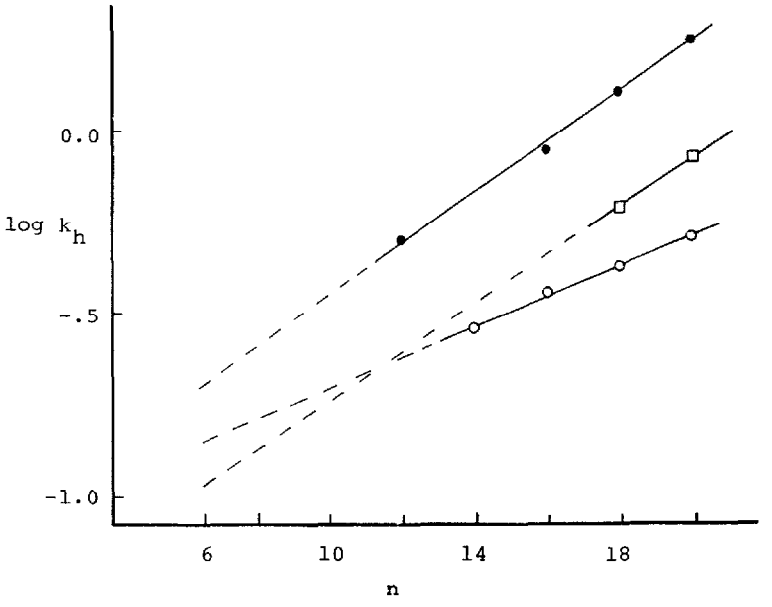

Fig. 1. Retention (log k_h) *vs.* carbon number (n) for unsubstituted aromatic hydrocarbons. Data of Table I and ref. 4. ● = amino column; ○ = cyano column; □ = diol column.

TABLE III

COMPARISONS OF FUNCTIONAL-GROUP RETENTION (ΔR_m) AND ADSORBENT ACTIVITY FUNCTIONS FOR SILICA *VS.* AMINO, DIOL AND CYANO COLUMNS

Solute	*Group X*[a]	$Q_{i(silica)}$[b]	*log* k_{hX} − *log* k_h[c]			$Q_i/\Delta R_m$[d]		
			$\Delta R_{m(amino)}$	$\Delta R_{m(diol)}$	$\Delta R_{m(cyano)}$	*Amino*	*Diol*	*Cyano*
Basic solutes								
1-Acetonaphthone	$-COCH_3$	4.69	1.06	0.87	0.69	4.42	5.39	6.80
2-Acetonaphthone		4.69	1.14	0.97	0.76	4.11	4.84	6.17
1-Naphthylacetate	$-OOCCH_3$	3.45	1.11	0.84	0.68	3.10	4.11	5.07
2-Naphthylacetate		3.45	1.10	0.81	0.59	3.14	4.26	5.85
2,6-Dimethylnaphthalene dicarboxylate	$-COOCH_3$	2.09	1.36	1.198	0.86	1.53	1.74	2.43
Acidic and dipolar								
1-Nitronaphthalene	$-NO_2$	2.77	0.81	0.68	0.64	3.44	4.07	4.33
1,5-Dinitronaphthalene		1.39	1.28	1.135	1.06	1.09	1.22	1.31
1-Cyanonaphthalene	–CN	3.33	0.90	0.77	0.68	3.69	4.32	4.90
1-Naphthylnitrile	$-CH_2CN$ (al)	5.27	1.48	1.17	1.01	3.56	4.50	5.22
Average						3.12	3.83	4.68
Benzyl alcohol	–OH (al)	5.6		2.08	1.36			

[a] (al) indicates aliphatic group; other groups are aromatic substituents.
[b] Group retention energy on standard silica surface (ref. 3).
[c] k_{hX} refers to k_h for substituted aromatic, k_h refers to parent unsubstituted compound.
[d] Q_i (silica)/ΔR_m (column).

angle[12]. Thus a cyano column would be expected to be more dipolar, so as to selectively retain dipolar solutes. Similarly, an amino column should be basic, and retain acidic solutes more strongly, and *vice versa* for a diol column. Previous studies suggest that these predictions are correct for the amino and cyano columns. More recently, Smith and Cooper[13] have reported that the amino and diol columns are each relatively basic, and the cyano column is essentially dipolar.

We were interested in further characterizing the selectivity of these columns toward various classes of solute molecules. For determination of column selectivity, it is necessary to compare functional-group retentions as $\log k_{hX} - \log k_h$, where k_{hX} is the capacity factor for the substituted aromatic solute and k_h is that for the parent aromatic hydrocarbon. Fig. 1 plots average values of $\log k_h$ for aromatic hydrocarbons *vs.* carbon number for the three bonded-phase columns (amino, diol and cyano). In order to determine $\log k_h$ for the parent naphthalene and benzene molecules (substituted aromatic solutes of this study and refs. 4 and 7), the lines in Fig. 1 were extrapolated to carbon numbers 10 and 6 respectively.

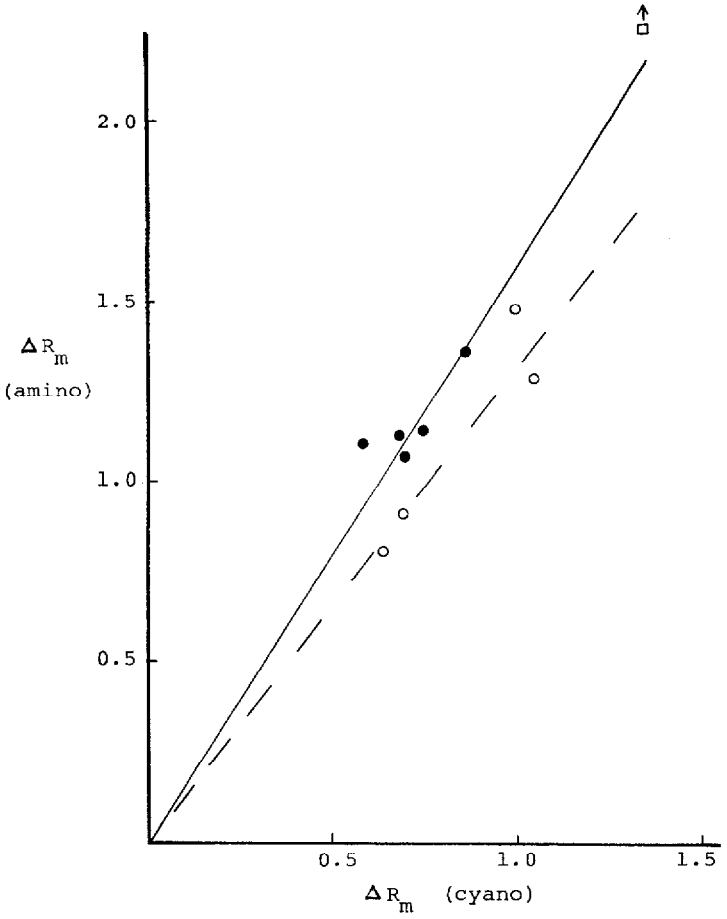

Fig. 2. Group retention values (ΔR_m) for amino *vs.* cyano columns. Regression data summarized in Table III; ——— = correlation curve for basic solutes (esters, ketones); – – – = correlation curve for dipolar solutes (nitriles and nitro compounds). ● = basic solutes; ○ = dipolar solutes; □ = benzyl alcohol.

TABLE IV

ANALYSIS OF REGRESSION LINES FROM ΔR_m DATA COMPARING AMINO, DIOL AND CYANO COLUMNS

	Slope (all solutes)	*2 × S.D.*[a]	*Slope*	
			Basic solutes[b]	*Dipolar solutes*[c]
Amino *vs.* cyano	1.4	0.127	1.60	1.32
Amino *vs.* diol	1.20	0.053	1.22	1.19
Cyano *vs.* diol	0.8	0.056	0.76	0.90

[a] Approximate 90% confidence.
[b] Esters and ketones.
[c] Nitro and nitrile compounds.

Experimental data for the cyano column are taken from our previous work[4]; data for the amino column are from the present study plus values from an earlier publication[7]; data for the diol column are from the present study. Table III summarizes group retention values, $\Delta R_m = (\log k_{hX} - \log k_h)$, for the three polar bonded-phase columns. In Figs. 2, 3 and 4, group retention values are plotted for the amino *vs.* cyano, amino *vs.* diol, and cyano *vs.* diol columns, respectively.

Linear regressions were performed on the data for all of the substituted aromatics on each column. In addition, the best straight line was obtained for the more basic compounds alone (esters and ketones), as well as for the more dipolar

TABLE V

RETENTION DATA FOR SUBSTITUTED AND UNSUBSTITUTED AROMATICS

Cyano column, 2-propanol–hexane mobile phase.

Solute	A_s	*log k'*					
		2-Propanol (%, v/v)					
		0	*0.1*	*0.2*	*0.4*	*0.8*	*1.4*
Chrysene	12.3	−0.268	−0.268	−0.276	−0.260	−0.301	−0.292
Perylene	12.8	−0.114	−0.149	−0.155	−0.167	−0.187	−0.229
Acetophenone	15.2	−0.155	−0.208	−0.215	−0.244	−0.244	−0.260
1-Cyanonaphthalene	16.5	0.000	0.000	−0.018	0.000	−0.027	0.000
Benzyl cyanide	15.5	0.230	0.204	0.204	0.204	0.176	0.176
m-Nitroacetophenone	22.7	0.342	0.301	0.279	0.279	0.255	0.230
1,3-Dinitronaphthalene	30.2	0.431	0.415	0.415	0.398	0.362	0.362
Benzyl alcohol	15.4	0.519	0.398	0.380	0.380	0.279	0.230
ε^{0}_{AB} [a]		(0.000)	0.002	0.002	0.002	0.004	0.004
ε^{0}_{B} [b]			0.25	0.21	0.16	0.14	0.11

[a] Calculated from eqn. 1 (benzyl alcohol data omitted).
[b] Calculated from eqn. 4.

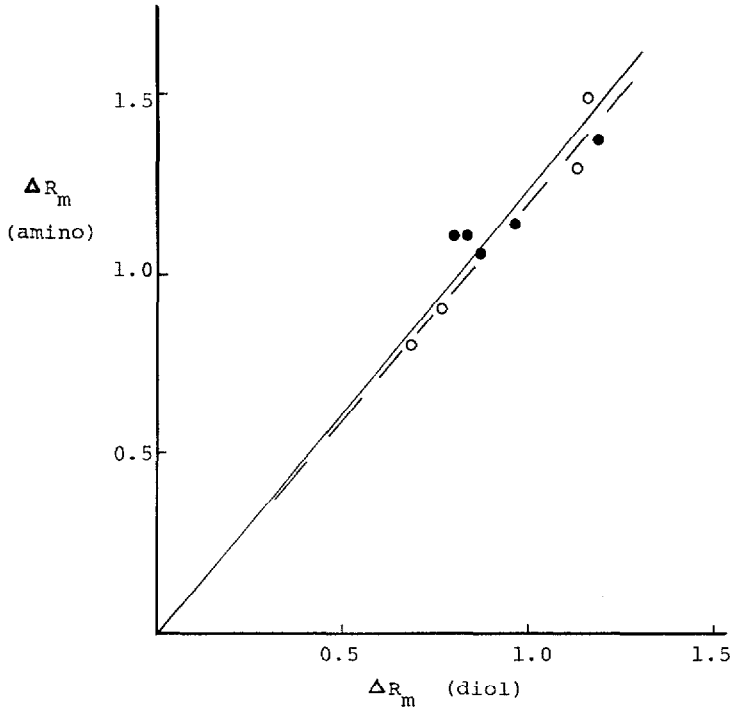

Fig. 3. Group retention values (ΔR_m) for amino *vs.* diol columns. See Fig. 2 for details.

1.8	*2.0*	*4.0*	*7.0*	*10*	*15*	*20*	*27*	*35*
−0.328	−0.357	−0.420	−0.441	−0.446	−0.509	−0.519	−0.54	−0.54
−0.260	−0.260	−0.319	−0.339	−0.370	−0.215	−0.429	−0.46	−0.47
−0.252	−0.208	−0.252	−0.362	−0.426	−0.449	−0.480	−0.52	−0.62
−0.027	−0.041	−0.076	−0.165	−0.223	−0.263	−0.308	−0.36	−0.45
0.114	0.127	0.083	0.021	−0.039	−0.104	−0.144	−0.24	−0.32
0.230	0.207	0.182	0.124	0.069	0.073	−0.034	−0.12	−0.18
0.301	0.310	0.250	0.201	0.148	0.077	0.031	−0.05	−0.10
0.079	0.030	−0.041	−0.253	−0.364	−0.427	−0.553	−0.60	−0.74
0.006	0.006	0.009	0.012	0.015	0.018	0.020	0.023	0.026
0.12	0.11	0.09	0.08	0.07	0.06	0.06	0.05	0.05

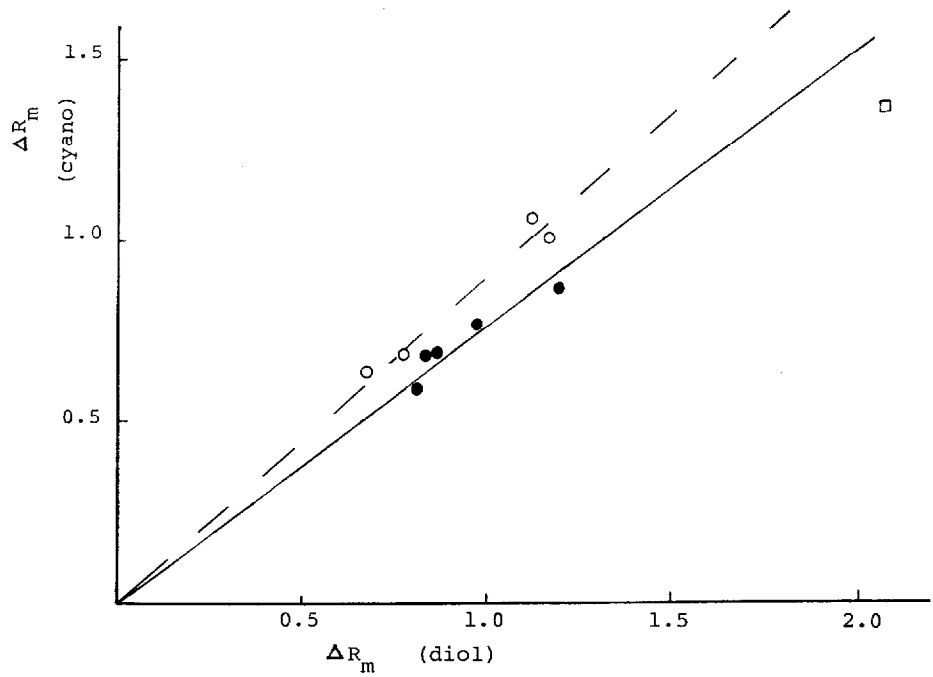

Fig. 4. Group retention values (ΔR_m) for cyano *vs.* diol columns. See Fig. 2 for details.

compounds alone (nitro and nitrile compounds)[a]. For the amino column *vs.* the cyano column (Fig. 2), there is increased retention of the more basic compounds compared with dipolar compounds (regression analysis indicates that these lines in Fig. 2 are independent, with greater than 90% confidence as summarized in Table IV).

The cyano column relative to the diol column shows increased retention of the more dipolar compounds compared with the more basic compounds (again regression analysis indicates the differences are significant to greater than 90% confidence). Finally, the amino column relative to the diol column shows greater retention of the more basic esters and ketones in comparison to the more dipolar nitro and nitrile compounds. However, these differences are less than noted above for the other columns and do not fall outside the 90% confidence limits.

On the basis of the comparisons of Table IV (summaries of Figs. 2–4), it appears that basic solutes are preferentially retained by the amino column, and dipolar solutes are preferentially retained by the cyano column, with the diol column exhibiting an intermediate behavior. However, the retention of proton donors, such as phenols and alcohols, was found by us to be strongest on the amino column. Thus the amino column gives generally stronger retention for *both* acidic and basic solutes. Our conclusions are hence in general agreement with those of Cooper and Smith[5,6,13].

Comparisons with silica. It has been noted previously (for less polar solutes and solvents) that retention on a cyano column shows similarities to retention on bare

[a] Solute basicity is best represented by the ratio β/π of ref. 14, equal to 0.5 for aromatic esters and ketones, and 0.3–0.4 for aromatic nitriles and nitrocompounds.

silica. Since the other polar bonded-phase columns correlate with retention on the cyano column, they also show similarities with silica. It is expected, however, that as the residual silanols on the bonded-phase columns are deactivated by stronger solvents, these similarities with silica will decrease.

The "strength" of a polar bonded-phase column strength *vs.* silica can be obtained by comparing the average value of $\Delta R_m = (\log k_{hX} - \log k_h)$ for that column *vs.* the average value of the group adsorption energy (Q_i) for silica (Table III). Based upon these average values, the strengths of the amino, diol and cyano columns are respectively, about 3.0-, 3.8- and 4.7-fold less than that of silica ($\alpha' = 0.7$). However, we have found significant variations in column strength from different manufacturers, and also batch-to-batch from the same supplier. In addition, we have found that column strength is critically dependent upon the solvents used in preparing the column. For example, cyano columns prepared in hexane were found to be significantly stronger than those prepared (by the manufacturer) in reversed-phase solvents. The same phenomenon has been noted with amino columns.

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