BASIS OF RETENTION IN NORMAL-PHASE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY WITH CYANO-PROPYL COLUMNS

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SUMMARY

The retention of various less polar solutes on a cyano-propyl-silica column has been studied as a function of mobile phase composition. These data can be correlated quantitatively in terms of a general model for all liquid–solid chromatographic separations, based on displacement of adsorbed solvent molecules by adsorbing solute molecules. It appears that fully-bonded cyano-silica columns function as deactivated silica, when moderately polar or non-polar mobile phases are used; *i.e.*, the adsorption sites are hindered silanol groups, rather than cyano groups. Thus our experience with silica as column packing can be used to predict many of the separation characteristics of cyano-silica columns. With more polar mobile phases, on the other hand, significant retention differences are observed between analogous high-performance liquid chromatographic systems based on silica *vs.* cyano-silica columns. This suggests that more polar solvents mask the effects of residual silanols on the cyano-silica surface, leaving the cyano groups to function as the principal adsorption sites.

INTRODUCTION

High-performance liquid chromatography (HPLC) is today the most widely used technique for the separation and analysis of complex mixtures of organic compounds. Roughly 70% of these separations are carried out with hydrophobic column packings and water–organic mobile phases; *i.e.*, by means of reversed-phase systems. The remaining applications of HPLC are largely accounted for by either size-exclusion chromatography or by preparative separations that use silica columns. There is increasing interest however in the use of various polar bonded-phase columns (diol-silica, cyano-silica, amino-silica) as an alternative to these reversed-phase separations. These normal-phase separations offer differing selectivity and employ mobile phases

that more readily dissolve many organic compounds. Many of the problems of silica are also avoided: more variable day-to-day retention, irreversible retention of some polar samples, and the difficulty of controlling mobile-phase water content[1].

One practical hindrance to the use of polar bonded-phase columns in the normal-phase mode is our relative lack of knowledge concerning these separations. For related separations on silica and alumina packings, there is an enormous literature describing both practical applications and theoretical models of the retention process. This in turn allows a rational basis for the interpretation and use of separations based on silica or alumina[1-4]. A similar understanding of separations on amino-silica packings is now beginning to emerge[5], and it appears that retention on polar bonded-phase packings is essentially similar to retention on alumina or silica[3,4].

Cyano-silica columns are becoming increasingly popular for normal-phase separation[6-11], yet little is known concerning the basis of sample retention in these systems. Several workers[7,10,11] have reported data which show that cyano-silica is a relatively weak adsorbent, providing smaller retention times *vs.* silica or amino-silica columns for the same samples and mobile phases. Selectivity on cyano-silica is in some cases markedly different *vs.* that on silica, as illustrated by the preferential retention of carbonyl-containing solutes *vs.* hydroxy-substituted solutes, on cyano-silica *vs.* silica[10]. Hussain *et al.*[12] have studied retention on a cyano-silica column as a function of solute structure and mobile phase composition, for a series of phenolic solutes. They conclude that the data are fit approximately by a model involving one-to-one displacement of an adsorbed solvent molecule by an adsorbing solute molecule, as is the case for similar systems with silica as adsorbent[13]. In the present paper we extend these earlier studies of retention on cyano-silica by examining the retention of less polar solutes eluted by rather weak mobile phases. The latter systems are less encumbered by solute–solvent interaction effects and therefore are better suited to an understanding of the essential features of retention on this column packing (see Discussion of ref. 3).

EXPERIMENTAL

Equipment

A Varian Model 5000 liquid chromatograph (Varian, Palo Alto, CA, U.S.A.) was used with a Model CV-6-UHPa-N60 manual injection valve (Valco, Houston, TX, U.S.A.) and 254 nm fixed-wavelength photometric detector.

Materials

The column (15 × 0.46 cm I.D. Supelcosil-CN; Supelco, Bellefonte, PA, U.S.A.) is a maximally bonded (3.5 μmoles/m^2, 170 m^2/g) and end-capped dimethylcyano-propyl silica.

Mobile phases were formulated from solvents purchased variously from Fisher Scientific (Fair Lawn, NJ, U.S.A.), J. T. Baker (Phillipsburg, NJ, U.S.A.) and 3M (Minneapolis, MN, U.S.A.).

Procedures

All separations were carried out at ambient temperature (23 ± 3°C). Sample volumes were 10 μl with 0.2% concentration of solute in either hexane or the mobile

phase. Flow-rate was constant at 2.0 ml/min. Column deadtime t_0 was determined by injections of hexane and/or dichloromethane; t_0 ranged from 0.80–0.97 min depending on the mobile phase used. The compound m-nitroacetophenone was used to verify retention reproducibility (k' values with hexane as mobile phase). This was determined as ±5% day-to-day over a period of one year. Within-day precision was much better.

RESULTS AND DISCUSSION

It will be seen that the present data can be interpreted in terms of the displacement model for solute retention in liquid–solid chromatography, as reviewed[2-4]. Retention data for unsubstituted aromatic hydrocarbons are needed in order to apply this model, but these solutes are very weakly retained from mobile phases as strong as hexane ($\varepsilon^0 = 0.00$) or stronger. In the present study we have observed that k' values less than 0.3 are unreliable. Therefore it was necessary to use mobile phases weaker than hexane for these hydrocarbon solutes. Table I summarizes data for several aromatic hydrocarbons eluted by mixtures of 3M F7-22 perfluorocyclic ether and hexane. These data can be interpreted in terms of a fundamental relationship[3]

$$\log k' = \log k_p - \alpha' A_s \varepsilon^0 \tag{1}$$

Here k_p refers to the k' value for pentane as mobile phase (equivalent to k_h for hexane as mobile phase), α' is an adsorbent activity function for this column (assumed equal to 1.00), A_s is the molecular area of the solute and ε^0 is the solvent strength value of the mobile phase. Eqn. 1 can be used to calculate values of ε^0 for the mobile phases of Table I from these k' values. Since the experimental $\log k'$ values for the first three

TABLE I

RETENTION DATA FOR POLYCYCLIC AROMATIC HYDROCARBONS

Cyano-silica column, FC-72–hexane mobile phases.

Solute	A_s*	Log k' values (log k_h) FC-72 (%, v/v)				Average log k_h
		0	10	15	20	
Acenaphthylene	8.6	−0.96 −**	−0.46 (−0.62)	−0.40 (−0.60)	−0.33 (−0.62)	−0.61
Phenanthrene	10.2	−0.71 −**	−0.34 (−0.53)	−0.29 (−0.53)	−0.23 (−0.52)	−0.53
Fluoranthene	10.7	−0.60 −**	−0.25 (−0.44)	−0.18 (−0.43)	−0.13 (−0.45)	−0.44
Chrysene	12.3	−0.41 (−0.41)	−0.17 (−0.37)	−0.10 (−0.38)	−0.01 (−0.35)	−0.38
Perylene	12.8	−0.26 (−0.26)	−0.05 (−0.29)	0.02 (−0.29)	0.08 (−0.28)	−0.28
ε^0****		(0.000)	−0.018	−0.023	−0.029	

* Values from ref. 2.

** $\log k'$ less than −0.5 (inaccurate).

*** Calculated from eqn. 1 and data for chrysene and perylene.

solutes of Table I are too small to be accurate for the reference mobile phase hexane, average ε^0 values were calculated from the data for chrysene and perylene (eqn. 1). These ε^0 values are shown in Table I. Values of log k_h (hexane mobile phase) can now be calculated from eqn. 1 ($k_p \equiv k_h$), using the k' values of Table I and values of A_s from ref. 2. These values are shown in parentheses in Table I, and their average value is given in the last column. The agreement of these calculated log k_h values for a given solute is ± 0.02 units (one standard deviation). Note that *measured* log k_h values in hexane for the first three solutes appear to be considerably in error, due to the small values of k' involved.

We desire the log k_h values of benzene and naphthalene, in order to measure the increase in log k_h as a result of substituting these molecules with various polar substituent groups. These log k_h values can be obtained from the k_h values of other hydrocarbons of carbon number n via

$$\log k_h = A + Bn \tag{2}$$

which holds for the aromatic hydrocarbons as solutes and different polar adsorbents[2]. Here, A and B are constants for a given column packing. Average values of log k_h are plotted in Fig. 1 *vs.* aromatic carbon number for the solutes of Table I. A straight-line relationship is obtained as predicted by eqn. 2, allowing extrapolation for log k_h values for benzene ($n = 6$) and naphthalene ($n = 10$): -0.86 and -0.69, respectively.

Retention vs. mobile phase composition

Table II summarizes retention data for a number of polar and nonpolar solutes as a function of the composition of dichloromethane–hexane mobile phases. Also listed in Table II are values of A_s corresponding to localized or delocalized* solute molecules[2–4]. The larger "localized" A_s values are those for silica as adsorbent, while the smaller "delocalized" values correspond to actual solute molecular areas; the latter are close to experimental values found for alumina as adsorbent. The question of which A_s values apply for cyano-silica as adsorbent is important both in understanding the basis of retention on this adsorbent and for predicting the magnitude of changes in retention as a function of mobile phase composition. Eqn. 1 can be used to calculate mobile phase ε^0 values on either basis —localized or delocalized A_s values— for the various solutes of Table II. The bottom of Table II summarizes these calculations. Here the "nonpolar" solutes chrysene and perylene are differentiated from the remaining twelve polar solutes of Table II. For the latter polar solutes, ε^0 values are shown in Table II for the case of localized *vs.* delocalized A_s values. Comparison of these values with ε^0 values for the non-polar solutes (where localized and delocalized A_s values are the same), shows good agreement between data based on localized A_s values (± 0.001 unit in ε^0), but much poorer agreement for data based

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* "Delocalized" A_s values refer to an absence of *site-competition delocalization* as discussed in ref. 3, but not necessarily to delocalized solute molecules (solutes adsorbed on alumina can localize, but give "delocalized" A_s values because of an absence of site-competition delocalization). These delocalized A_s values are therefore proportional to the molecular areas required by each solute when adsorbed onto the surface of an adsorbent. The "localized" A_s values of Table II are experimental values for silica, reflecting site-competition delocalization effects (which involve localized solute molecules).
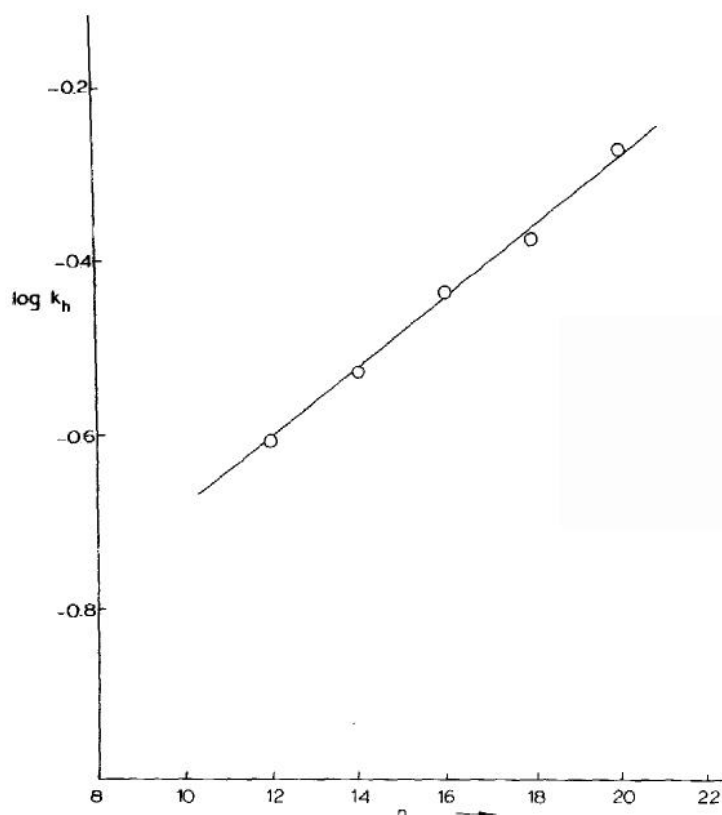
Fig. 1. Plot of retention in hexane mobile phase (log k_h) vs. solute carbon number (n) for aromatic hydrocarbon solutes of Table I.

on delocalized A_s values. We therefore conclude that solute localization in this system leads to A_s values similar to those found for silica as adsorbent (localized A_s values). The overall agreement of experimental log k' values with values calculated from eqn. 1 for the data of Tables I and II is ±0.03 units (one standard deviation).

The variation of mobile phase ε^0 values with the mole fraction N_B of the stronger solvent B in a binary mixture A–B is given as[2,3]

$$\varepsilon^0_{AB} = \varepsilon^0_B + \frac{\log (N_B 10 \qquad + 1 - N_B)}{\alpha' n_b} \tag{3}$$

Here ε^0_{AB} refers to the solvent strength value of the binary solvent mixture A–B, ε^0_A and ε^0_B are the ε^0 values of pure solvents A and B for this adsorbent, and n_b is the A_s value of solvent B (its molecular area). The experimental ε^0 values of Table II (ignore "delocalized" A_s data) are well fit by eqn. 3 with an assumed value of $\varepsilon^0_B = 0.067$ for dichloromethane. The standard deviation of the fit is only ±0.001 unit in ε^0. Thus the mobile phase effect on retention for cyano-silica as packing is quite similar to what has previously been observed for silica as adsorbent.

TABLE II

RETENTION DATA FOR SUBSTITUTED AND UNSUBSTITUTED AROMATIC HYDROCARBONS

Cyano-silica column, dichloromethane–hexane mobile phase.

Solute	A_s^*		Log k' values (log k_h)					Average** log k_h
			Dichloromethane (%, v/v)					
	loc.	deloc.	0	5	10	15	20	
Chrysene	12.3	12.3	−0.41 (−0.41)	−0.52 (−0.41)	−0.59 (−0.40)			−0.41 ± 0.00
Perylene	12.8	12.8	−0.26 (−0.26)	−0.39 (−0.27)	−0.47 (−0.26)	−0.53 (−0.25)		−0.26 ± 0.01
Benzyl alcohol	15.4	8.2	0.51 (0.51)	0.34 (0.48)	0.25 (0.59)	0.17 (0.51)	0.00 (0.42)	0.50 ± 0.07
m-Nitroacetophenone	22.7	8.8	0.36 (0.36)	0.14 (0.34)	0.01 (0.38)	−0.04 (0.46)	−0.20 (0.42)	0.40 ± 0.05
1-Naphthyl acetate	16.2	10.4	0.10 (0.10)	−0.19 (−0.04)	−0.31 (−0.05)	−0.37 (−0.01)	−0.50 (−0.06)	−0.01 ± 0.04
2-Napthyl acetate	16.2	10.4	−0.10 (−0.10)	−0.26 (−0.04)	−0.37 (−0.11)	−0.40 (−0.05)	−0.57 (−0.13)	−0.10 ± 0.03
1-Nitronaphthalene	15.6	9.4	−0.09 (−0.09)	−0.21 (−0.07)	−0.30 (−0.05)	−0.33 (0.01)	−0.48 (−0.13)	−0.05 ± 0.04
1-Cyanonaphthalene	16.5	8.7	0.00 (0.00)	−0.16 (−0.01)	−0.28 (−0.01)	−0.34 (0.02)	−0.48 (−0.03)	−0.01 ± 0.02

2-Naphthaldehyde	16.4	9.2	−0.07 (−0.07)	−0.20 (−0.05)	−0.27 (−0.01)	−0.34 (0.02)	−0.43 (0.01)	−0.02 ± 0.03
1-Acetonaphthalene	17.3	9.6	0.00 (0.00)	−0.16 (−0.01)	−0.27 (0.00)	−0.36 (0.01)	−0.46 (0.01)	0.00 ± 0.01
2-Acetonaphthalene	17.3	9.6	0.13 (0.13)	−0.13 (0.03)	−0.22 (0.06)	−0.29 (0.09)	−0.41 (0.05)	0.07 ± 0.04
1-Naphthyl nitrile	17.6	10.5	0.39 (0.39)	0.15 (0.31)	0.04 (0.32)		−0.22 (0.26)	0.32 ± 0.05
1,5-Dinitronaphthalene	23.1	10.7	0.32 (0.32)	0.11 (0.32)		−0.06 (0.45)	−0.23 (0.38)	0.37 ± 0.05
Dimethyl-2,6-naphthalene dicarboxylate	24.3	12.7	0.12 (0.12)	−0.10 (0.12)	−0.26 (0.13)	−0.27 (0.27)	−0.45 (0.21)	0.17 ± 0.06

ε^0 values

From deloc. A_s[***]	0.000	0.019	0.028	0.037	0.045
From loc. A_s[***]	0.000	0.010	0.017	0.020	0.028
Non-polar solutes[§]	0.000	0.009	0.015	0.020	–
Calculated (eqn. 3)[§§]	0.000	0.009	0.016	0.022	0.027

* Values from ref. 2, loc. values are for silica, deloc. values are area ratios.

** Calculated from eqn. 1 and ε^0 values from eqn. 3.

*** Calculated from eqn. 3 for polar solutes (all but chrysene and perylene).

§ Calculated from eqn. 3 for chrysene and perylene (average).

§§ Assumes ε^0 for pure dichloromethane equals 0.067, $\alpha' = 1.00$ and $n_b = 4.1$.

Group retention selectivity on cyano-silica

A preceding study[5] of retention on amino-silica has shown that less-basic substituent groups such as cyano and nitro are preferentially held on this adsorbent in comparison with retention on silica. Likewise acidic groups such as hydroxy are also preferentially held on amino-silica, because the latter is a more basic adsorbent. These observations can be rationalized in terms of the solvent selectivity triangle[14], which allows classification of different solvents in terms of their functionality and selective interactions with various solutes. Thus silica appears to function as a group VIII phase, being acidic but only weakly basic and/or dipolar. Amino-silica behaves as a group I phase, being basic but only weakly acidic or dipolar (see Discussion of ref. 4).

On the basis of the latter discussion for silica *vs.* amino-silica, we expected cyano-silica to exhibit quite different group retention selectivity. If the cyano groups in this adsorbent function as primary adsorption sites, then cyano-silica should behave as a dipolar group VI adsorbent; similar to the behavior of various nitriles as solvents. Comparison of such an adsorbent *vs.* silica should then show preferential retention of non-basic solutes with large dipole moments (*e.g.*, nitriles and nitro compounds).

Table III summarizes group retention values $\Delta R_M = (\log k_{hx} - \log k_h)$ as determined from the retention data for a substituted aromatic (k_{hx}) and the parent unsubstituted compound (k_h). Corresponding values of $\Delta R_M = Q_i^0$ for a silica of unit activity $(\alpha' = 1.00)$ are also listed in Table III. Fig. 2 compares these two sets of values, and a rather good correlation is observed. That is, retention on cyano-silica is quite similar to that found for silica, except that ΔR_M values or group retention energies are reduced on cyano-silica by a factor of about 5 (actually 3.5-fold *vs.* the usual chromatographic silicas with $\alpha' = 0.70$). Specifically, no tendency toward generally larger ΔR_M values for cyano or nitro groups (*vs.* other groups) is noted.

TABLE III

COMPARISON OF FUNCTIONAL-GROUP RETENTION FOR CYANO-SILICA *vs.* SILICA

Data of Table II and ref. 2.

Solute	*Group X*[*]	*log k_{hx} − log k_h*[**]	*Q_i^0 (silica)*[***]
Benzyl alcohol	OH (al)	1.36	5.6
1-Naphthyl acetate	–OOC–CH₃	0.68	3.45
2-Naphthyl acetate		0.59	
1-Nitro naphthalene	–NO₂	0.64	2.77
1-Cyanonaphthalene	–CN	0.68	3.33
2-Naphthaldehyde	–CHO	0.67	3.5
1-Acetonaphthalene	–COCH₃	0.69	4.56
2-Acetonaphthalene		0.76	
1-Naphthyl nitrile	–CN (al)	1.01	5.3
Polyaromatic hydrocarbons[§]	–CH =	0.04	0.1–0.25[§]

     * (al) indicates an aliphatic group; other groups are aromatic substituents.

    ** k_{hx} Refers to k_h for substituted aromatic; k_h refers to k_h value for parent unsubstituted aromatic.

  *** Group retention energy from ref. 2.

    § Data of Fig. 1 and Table I.

The correlation of Fig. 2 and the earlier noted similarity of solvent effects for silica and cyano-silica suggest that cyano groups are not the primary adsorption sites for cyano-silica. Rather it appears that residual silanols are providing retention that is closely similar to that on silica. The much weaker retention on cyano-silica *vs.* silica is then the result of the shielding of these silanol groups by the adjacent cyano-propyl bonded phase. If this is in fact true, then we can predict that separation on cyano-silica will closely parallel that on silica, except that the normal value of $\alpha' = 0.7-1.0$ for silica will be replaced by $\alpha' = 0.2$ for cyano-silica. This would then yield Q_i^0 values for cyano-silica close to those found earlier for silica[2]. We would also predict that the apparent solvent-strength value for dichloromethane would be equal to 0.2 times the value ($\varepsilon^0 = 0.32$) for silica. This is indeed the case, the value found (0.067) being close to the latter prediction (0.064). It is also interesting to compare the present cyano-silica with a partly-bonded C_{18}-silica (1.6 μmoles/m^2) operated in the normal-phase mode[14]. The latter shows an activity α' equal to 0.48, which is intermediate between values for cyano-silica (0.2) and non-bonded silica (0.7–1.0).

As the polarity of solute molecules and mobile phases required for their elution increases, there is some evidence that the similarities between silica and cyano-silica become less pronounced. Thus using similar alcohol–hexane mobile phases, one
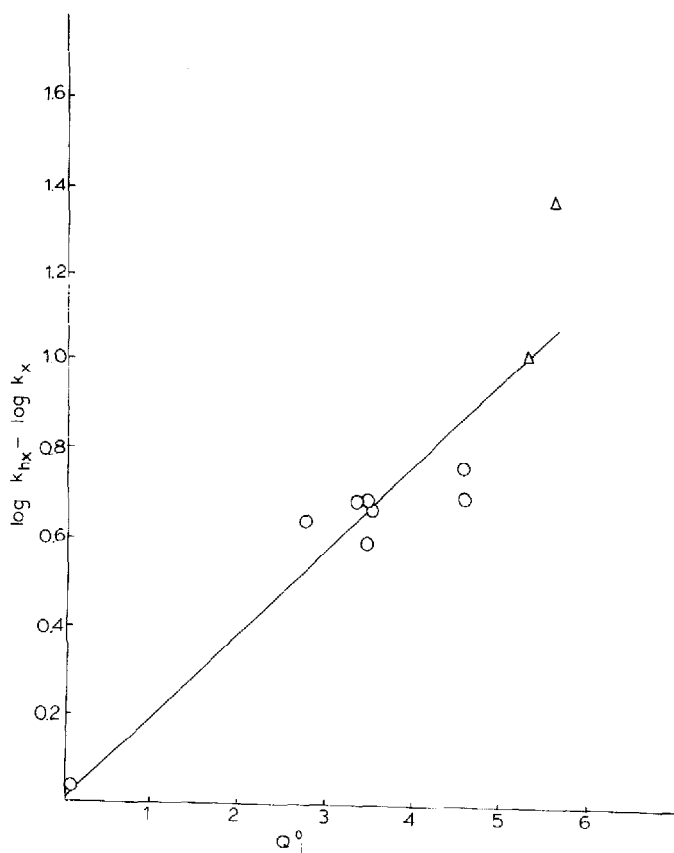

Fig. 2. Comparison of group retention selectivity on cyano-silica *vs.* silica (see text). O, Aromatic substituent groups; △, aliphatic substituent groups. Data of Table III.

study[10] showed preferential retention on cyano-silica *vs.* silica of carbonyl-containing solutes (ketones, lactones). Another study[15] of retention on cyano-silica *vs.* silica showed preferential retention of more hindered phenols and of multi-ring phenols on cyano-silica. On the other hand, still another study of retention in cyano-silica *vs.* various poly-cyano liquid phases (liquid–liquid chromatography)[16] shows similar retention of various phenols among these different columns. All of these observations suggest that more polar sample–mobile phase systems may lead to suppression of the effect of surface silanols in retention on cyano-silica, leaving the cyano-groups as the major adsorption sites. However it is also possible that these apparent differences between the two adsorbent types are due to other effects: solute–solvent interactions, differences in the silicas involved, etc. Further experimental work is required if firm conclusions are to be drawn.

Practical consequences of separation on cyano-silica

Less polar solutes will be weakly retained on cyano-silica and therefore not well separated with the common solvents as mobile phase (hexane or stronger). Solutes of intermediate polarity should be conveniently separated on cyano-silica using non-polar or moderately polar mobile phases. We have found for such solutes that retention times are reasonably constant within-day and over many months, without having to add water to the mobile phase as in the case for silica as adsorbent[1]. Basic compounds such as quinoline and its benz-derivatives were found to tail markedly with dichloromethane–hexane as mobile phase, and this may reflect a heterogeneous population of residual silanol sites. Other workers[6] have obtained good results from separations of basic drugs on cyano-silica when 0.1–0.5% (v/v) of propyl amine is added to the mobile phase. A recent study[17] has shown that addition of small amounts of water to the mobile phase increased the column plate number for the case of a poly-hydroxy-substituted prostaglandin separated on cyano-silica, while having no effect on the separation of other compounds. Thus mobile phase additives such as amines and water may occasionally prove beneficial in the case of cyano-silica, but are not generally required.

Reported separations on cyano-silica have generally employed more polar mobile phases, often those containing alcohols as components. For such separations retention on cyano-silica seems only moderately reduced *vs.* that on silica. This would be expected as a result of the strong adsorption of alcohols onto surface silanol groups, which in turn attenuates their *net* adsorption strength with respect to solute molecules.

Certain other consequences of the weaker adsorbent surface for cyano-silica can be predicted. Localization effects due to attachment of solute and/or solvent molecules to strong sites will be diminished, leading to generally poorer separations of isomeric solutes. Likewise the smaller effective value of α' for this adsorbent will lead to a diminished *range* of k' values for all solutes. On the one hand this means that isocratic elution should more often be possible with cyano-silica *vs.* silica, but that peak capacity in gradient elution will be generally larger for silica.

Method development for separations on cyano-silica should proceed essentially as for silica[18]. The appropriate solvent strength (value of ε^0) can first be determined by trial-and-error, *e.g.*, using mixtures of dichloromethane–hexane (or FC-113 $=$ 1,1,2-trifluorotrichloroethane). Mobile phases of the same strength, but

TABLE IV

EQUI-ELUOTROPIC SERIES FOR RETENTION OPTIMIZATION ON CYANO-SILICA

Calculated from data for silica[3], assuming $\alpha' = 0.2$. Compare the similar approach for separation on silica[3,4,18].

$\alpha'\varepsilon^{0}$*	Polar solvent B (%, v/v)			
	B (dichloromethane)– A (hexane)**	B (acetonitrile)– A (hexane)**	B (MTBE)***– A (hexane)**	B (methanol)– A (dichloromethane)
0.00	0	0	0	–
0.02	17	6	12	–
0.04	42	15	29	–
0.06	100	27	48	0
0.08		48	73	12
0.10		84	100	31
0.12				57
0.14				100

   * An increase in $\alpha'\varepsilon^{0}$ by 0.02 units should decrease k' by about two-fold.
  ** FC-113 (1,1,2-trifluorotrichloroethane) can be substituted for hexane[20].
 *** Methyl tert.-butyl ether.

containing localizing basic or non-basic solvents (methyl tert.-butyl ether, acetonitrile) in place of dichloromethane, are then used in order to change band spacing. This approach has been used successfully by Massart et al.[19]. Table IV provides a tabulation of ε^{0} values for use in this way (cf. ref. 4 for silica as column packing).

CONCLUSIONS

The retention of various non-polar or moderately polar solutes from less polar mobile phases on cyano-silica has been studied. These data suggest that cyano-silica behaves as a deactived (weak) silica when less polar mobile phases are used; i.e., with little participation of cyano groups as adsorption sites. When more polar mobile phases are used, literature data suggest this may no longer be the case. Nevertheless it is useful to regard cyano-silica as a weak silica, and method development (retention optimization) for cyano-silica can proceed in the same way as for silica.

Cyano-silica does not appear useful for the separation of less polar samples, because of the weak retention of these samples from mobile phases as weak as hexane. For the separation of more polar solutes cyano-silica offers certain advantages as an alternative to silica: greater convenience due to the absence of a need for adding water to the mobile phase (as for silica), more reproducible retention of sample components from day to day, and less frequent irreversible adsorption of polar samples. A given sample may require the use of gradient elution in the case of silica, but this will be less often the case for cyano-silica. Cyano-silica is prone to band-tailing in the case of basic solutes, but this can be alleviated by adding 0.1–0.5% (v/v) of an alkyl amine to the mobile phase.

GLOSSARY OF TERMS

A, B	constants in eqn. 2 for the retention of polyaromatic hydrocarbon solutes with a given adsorbent and mobile phase
A_s	the relative molecular area required by an adsorbing solute molecule on the adsorbent surface ("delocalized"); also, the A_s value in eqn. 1, which can be larger for localized solute molecules
k'	solute capacity factor (see ref. 1)
k_h, k_p	value of k' for a given solute with hexane (h) or pentane (p) as mobile phase; $k_h = k_p$
n_b	relative molecular area required by an adsorbing solvent molecule B from a binary solvent mixture A–B; B is the stronger solvent
N_B	mole fraction of solvent B in a binary solvent mixture A–B
Q_i^0	adsorption energy of a substituent group i substituted into some solute molecule
R_M	log k'
ΔR_M	change in R_M for a solute as a result of introducing some substituent group i into the solute molecule; $\alpha' Q_i^0 = \Delta R_M$
X	a substituent group (Table III)
α'	adsorbent activity function, assumed equal to one for cyano-silica; alternatively, if cyano-silica is regarded as a weak silica, α' would equal about 0.20.
ε^0	solvent strength parameter, equal to adsorption energy of solvent molecule per unit adsorbent surface
ε_A^0, ε_B^0, ε_{AB}^0	ε^0 values of solvents A, B or mixture A–B

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