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Journal of Chromatography A, 919 (2001) 39–50

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Comparison of chromatographic properties of cyanopropyl-, diol- and aminopropyl- polar-bonded stationary phases by the retention of model compounds in normal-phase liquid chromatography systems

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Received 6 March 2001; accepted 29 March 2001

Abstract

Polar-bonded stationary phases, such as CN-, diol- and NH_2-silica, have been characterised by the retention of model solutes (phenols, aromatic amines and quinoline bases) in normal-phase systems using *n*-heptane — polar modifier (2-propanol, tetrahydrofuran or dioxane) mixtures as eluents. The selectivity of separation for the particular groups of substances has been analysed by the $\log k_I$ versus $\log k_{II}$ relationships for CN- and diol, CN- and NH_2- and NH_2- and diol phases in examined eluent systems by the plotting of correlation lines. The values of regression coefficient *r* indicate either the similarity of the retention mechanisms of model solutes in some examined systems where $r>0.9$, or differences among various systems where $r \ll 0.9$. The values of slopes of correlation lines show the selectivity of separation for particular group of compounds. The selectivity of separation has also been characterised by $\Delta\log k$ values. The effect of modifier (2-propanol, tetrahydrofuran and dioxane) on selectivity of model solutes on these phases has also been discussed.

Keywords: Stationary phases, LC; Selectivity; Normal phase systems; Retention behaviour; Phenols; Amines, aromatic; Quinolines

1. Introduction

Systems with various properties are necessary for the separation, identification and quantitation of complex mixtures including closely related compounds and various biological matrices. The chromatographic determination of biologically active compounds with the high probability level often requires the use of several chromatographic systems with different selectivities of separation [1].

Surface-modified sorbents (especially polar stationary phases bonded to silica matrix) having moderate polarity, can be used both in normal and reversed-phase chromatography, which causes the possibility of various separation selectivities.

Recently polar-bonded stationary phases have been used in normal-phase (NP) high-performance thin-layer chromatography systems for phytochemical analysis [2–13], for biochemical analysis

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0021-9673/01/$ – see front matter
PII: S0021-9673(01)00796-8

[6,7,9,14–16] for pharmaceutical analysis [9,17–20], and for environmental analysis [9,21–24]. Stationary phases with CN-ligands have been used in RP HPLC systems [25–27] and in NP HPLC systems [28,29]. Similarly, diol-silica [30–32] and aminopropyl phases [33–36] have been used in various difficult separations. Polar-bonded stationary phases have been also applied as sorbents for cleanup preconcentration of different solutes from matrix substances [37–40]. For example, in the comparison of different SPE-bonded phases, the best recoveries of oxytetracycline and sulphadimidine have been obtained using CN-bonded silica as the sorbent [38].

It is known that chromatographic retention provides some information about combined nature of the mobile and stationary phases [41]. In RP liquid chromatography the dominant solute properties which influence a retention are cavity formation and a solvent (as donor) to solute (as acceptor) hydrogen bond interactions, whereas normal-phase processes are sensitive to dipole–dipole interactions and to hydrogen bond formation to the solvent (hydrogen bond donor or acceptor) [42].

Stationary phases can be characterized by specific retention properties and should manifest themselves in QSRR equations [43], for example linear solvation energy relationships (LSERs) derived from the Abraham equation [44,45]:

$$\log k = c + rR_2 + vV_x + s\pi_2^{\mathrm{H}} + a\sum\alpha_2^{\mathrm{H}} + b\sum\beta_2^{\mathrm{H}} \quad (1)$$

where R_2, π_2^{H}, α_2^{H}, β_2^{H}, V_x are solute descriptors as follows: R_2, excess molar refraction; π_2^{H}, solute dipolarity-polarizability; α_2^{H}, solute hydrogen bond acidity; β_2^{H}, solute hydrogen bond basicity; and V_x, solute molar volume. The constants c, r, s, a, b and v refer to the corresponding properties of chromatographic system considered.

In RP systems the solute volume and the refractivity (V_x, R_2) contribute to the retention, whereas solute dipolarity–polarizability and hydrogen bond basicity (π_2^{H}, β_2^{H}) favour elution [46]. In normal-phase systems solute refractivity contributes to elution and solute dipolarity–polarizability and hydrogen bonding abilities increase the retention. However, polarity of the mobile phase is affected to a different degree by the mobile phase composition. Thus, polar solvent molecules can preferentially solvate adsorbent surface and change solute–adsorbent interactions. It is mentioned [47] that all types of interactions are important regarding affecting retention in NPLC with polar-bonded stationary phases. As it is reported, [47] solutes basicity contributes greatly to retention, particularly for diol and amino columns (b coefficient is the least for cyano phases), whereas solute acidity and dipolarity/polarizability also make significant contribution to retention. The solute size has a negative effect on retention (coefficient v is still greatest for cyano phases). These results are similar to those obtained for silica [48]. However, the results published by Park et al. indicate that the HB (hydrogen bonding) interactions between solute as HB donor and the stationary phase as HB acceptor predominate over HB interactions between the solute as HB acceptor and the stationary phase as HB donor interactions for all polar-bonded stationary phases and silica [49].

On the basis of the analysis of the retention–modifier concentrations' relationships for various model substances ($k = f(\phi)$), Kowalska and co-workers have studied retention mechanism on different polar-bonded stationary phases such as CN-, diol- and NH_2- in normal-phase systems of type n-aliphatic hydrocarbon–alcohol and concluded mixed adsorption–partition mechanism of solute retention in the systems with predomination of partition mechanism [50]. The results of experiments on cyano-, C_8 and C_{18} phases in RP systems point out dual nature of retention process: dispersive forces of solute molecules with organic ligands of stationary phases (the partition mode) and specific interactions with active sites of matrix (silica) surface with the displacement of solute molecules (the adsorption mode) [51].

For the characteristics of the stationary phases k–k plots (defined as plots of logarithmic retention factors measured on columns'/plates' pairs with different model solutes in the same eluents) can be used to study stationary phase effects in liquid chromatography [52]. Plots of logarithmic retention factors determined in different chromatographic systems (k_{I} versus k_{II} plots) were used for the characterisation of RP systems [52–55]. Formerly, similar correlations for static partition coefficients were analysed by Collander [56]. Plots of logarithmic

retention factors were also used in NP-systems for the characterisation of such adsorbents like silica, magnesium silicate (Florisil), alumina and mixed silica–magnesia adsorbents [57–60].

Since the chemical nature of the stationary phase can have a major effect on selectivity, the aim of this work was the examination of commercially available polar stationary phases: diol, cyanopropyl and aminopropyl bonded to the silica matrix. To study stationary phase effects retention behaviour of three groups of model solutes with different electron donor–electron acceptor properties (phenols, aromatic amines and heterocyclic bases) in NP systems of the type: polar-bonded stationary phase/nonaqueous eluent was examined to assert solute–solvent–surface active sites interactions. Analysis of the $\log k_I$ versus $\log k_{II}$ correlation diagrams and creating the correlation lines allows to compare the selectivity of separation in studied chromatographic systems.

2. Experimental

The chromatographic experiments were performed at 19±1°C using Shimadzu liquid chromatograph equipped with a gradient pump of type LC 10 AT at a flow-rate 1 ml/min and UV–Vis detector SPD–10 AV (at $\lambda = 254$ nm). Solutions of single solutes were injected in the eluent with the help of a Rheodyne injector.

Stainless steel column (250×4 mm I.D.) was packed with 10-μm LiChrosorb Diol (Merck, Darmstadt, Germany) by the slurry method. Another column (100×4 mm I.D.) was packed with 10-μm LiChrosorb CN (Merck). A column manufactured by Alltech–Econosphere NH_2 5-μm (150×4.6 mm I.D.) was also used in the experiments. Some properties of these columns are listed in Table 1.

As mobile phases, *n*-heptane solutions of 2-propanol (iPrOH), tetrahydrofuran (THF) or 1,4-dioxane (DX) were used. All solvents were for HPLC (Merck).

Model solutes investigated in the paper (aromatic amines, phenols and quinoline bases) are listed in Table 2.

3. Results and discussions

Selectivity of the chromatographic system is the main parameter, which decides about the success of separation in chromatography, both on analytical and preparative scale. For a pair of substances the selectivity is quantitatively characterised by the separation coefficient ($\alpha = k_I/k_{II}$ for compounds I and II); for the larger group of substances the $\log k_I$ versus $\log k_{II}$ ($R_{M\,I}$ *v*ersus $R_{M\,II}$) correlations provide with the selectivity characteristics [61]. For such correlations the following characteristic cases can be distinguished (see Fig. 1) [62]:

(A) identical selectivity of systems I and II, slope ≈1, correlation coefficient $r \approx 1$;

(B) similar selectivity of both systems, but the system I generally more selective (larger values of $\Delta \log k$ for the extreme substances), slope <1, $r \approx 1$;

(C) system I selective, system II nonselective, slope →0;

(D) system I nonselective, system II selective, slope →∞;

(E) selectivity of the both systems differentiated, $r \ll 0.9$;

(F) lack of correlation, retention strongly differentiated, $r \to 0$.

Systems I and II can differ from each other by modifier, by sorbent or by both components of chromatographic systems. More profitable is the correlation from Fig. 1F. Such a diagram can be

Table 1
Properties of the stationary phases as supplied by the manufacturers

No.	Stationary phase	Particle size (μm)	Ligand	Surface area BET ($m^2\ g^{-1}$)	Carbon loading (%)	Surface coverage (μmol m^{-2})	Pore size (Å)
1	LiChrosorb CN	10	~$CH_2CH_2CH_2CN$	300	6.1	3.82	60
2	LiChrosorb Diol	10	~$(CH_2)_3OCH(OH)CH_2OH$	300	7.1	3.91	60
3	Econosphere NH_2	5	~$CH_2CH_2CH_2NH_2$	200	2.0	2.75	80

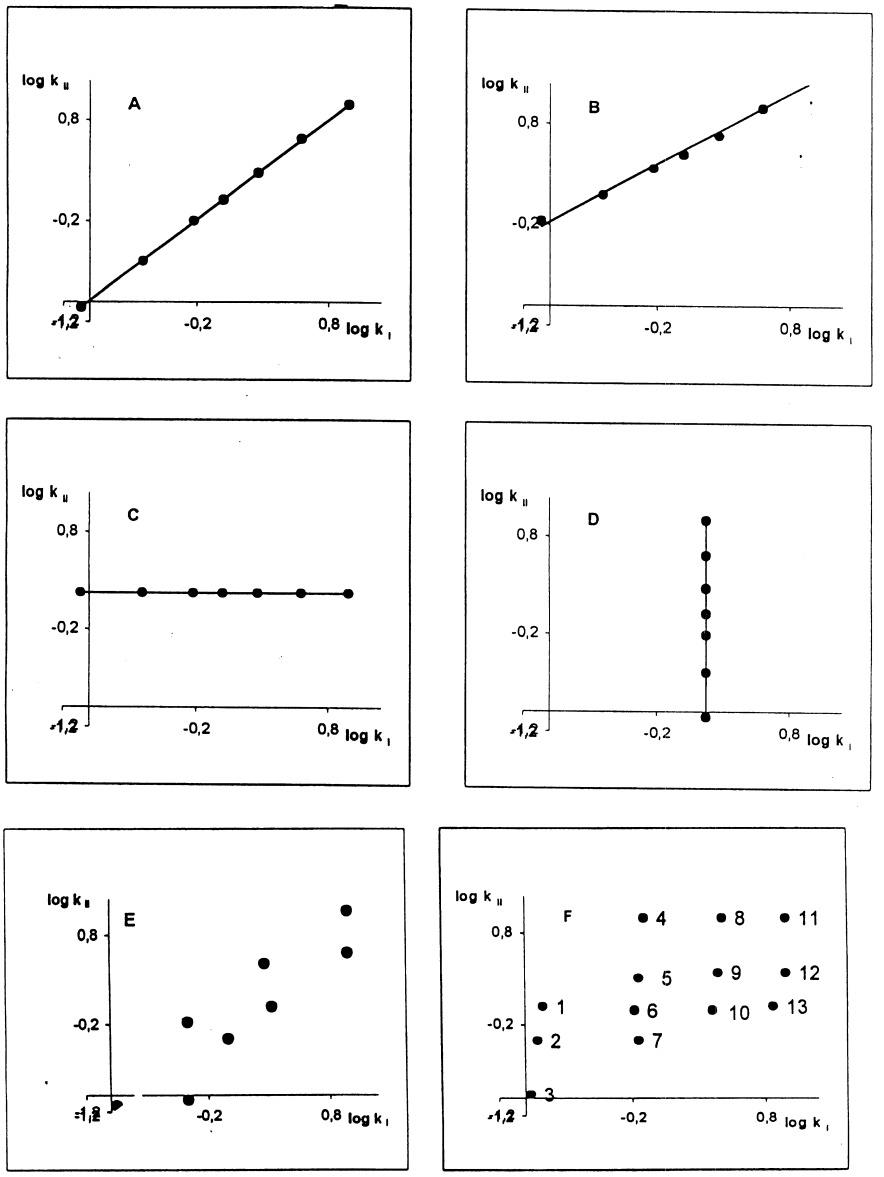

Fig. 1. Schematic representation of types of $\log k_{I}$ versus $\log k_{II}$ correlations.

applied to the rational planning of the separation of multicomponent mixtures [58]. In the first stage the system I can be applied, which makes group separation possible: (1+2+3), (4+5+6+7), (8+9+10), (11+12+13). Then, the individual groups of components can be separated using system II.

Moreover, the analysis of $\log k_{I}$ versus $\log k_{II}$ correlation diagrams can give some information about adsorbent surface active sites and about solute–modifier–adsorbent surface interactions [57–60]. It is possible when systems I and II differ from each other only in one element (for example the same eluent, two different adsorbents) and the chromatographed compounds are model solutes with defined structures and properties.

The experimental results obtained for the mono-,

bi- and trifunctional model solutes listed in Table 2 are given as the relationships of retention factors: $\log k$ values of the solutes in different chromatographic systems as $\log k_I$ versus $\log k_{II}$ correlations. The analysis of the $\log k_I$ versus $\log k_{II}$ correlation diagrams allows to compare selectivities of separation in the studied chromatographic systems.

Table 3 presents the parameters of correlation lines for all investigated systems — sorbents and modifiers. The values of the regression coefficients are in most cases relatively low ($r<0.9$), which indicates the lack of linearity and which results from different selectivities and mechanism of separation of the groups of substances in the investigated systems. Only in few cases the correlation coefficient values are about 0.90 ($0.95\geq r\geq 0.90$), which proves fair goodness of fit [63] and demonstrates similar mechanism of retention. Such a situation has occurred in the case of retention of aromatic amines on CN- and diol-silica phases when dioxane as modifier has been used, and in the case of retention of quinoline bases on aminopropyl- and CN-silica when tetrahydrofuran or dioxane as modifier was used (see Table 3). In one case the value of correlation coefficient is even higher $r>0.95$ which proves good goodness of fit [63] for the retention of anilines on CN and diol phases when tetrahydrofuran as modifier has been used. It seems that retention mechanism of amines on CN and diol phases is similar when dioxane or tetrahydrofuran as modifier have been used. It simultaneously seems that retention mechanism of quinoline bases on CN and aminopropyl phases is similar when the same eluent modifiers (dioxane or tetrahydrofuran) have been used. As it has been formerly reported dioxane (basic solvent with $\beta=0.64$ [64]) form a strongly adsorbed layer on silica and magnesium silicate surface and often co-adsorption of solute molecules on dioxane film occurs [58,59,65,66]. It has also been reported that tetrahydrofuran molecules on magnesium silicate surface behave similarly [58]. In the case of polar-bonded stationary phases, such a situation can also be explained by formation of solvent film on the surface of sorbents, especially for diol and aminopropyl phases, for which solvents (solutes) basicity contributes greatly to retention [47]. When 2-propanol as modifier was used, low correlation coefficients ($r<0.9$) for all groups of substances on stationary phases

Table 2
List of compounds investigated

Symbol	Compound	Polar group type [67]
Anilines		
An	Aniline	AB
3MeAn	3-Methylaniline	AB
4MeAn	4-Methylaniline	AB
4EtAn	4-Ethylaniline	AB
2IAn	2-Iodoaniline	AB
4IAn	4-Iodoaniline	AB
4BrAn	4-Bromoaniline	AB
2ClAn	2-Chloroaniline	AB
1NA	1-Naphthylamine	AB
2MeOAn	2-Methoxyaniline	B-AB
2EtOAn	2-Ethoxyaniline	B-AB
4EtOAn	4-Ethoxyaniline	B-AB
$2NO_2An$	2-Nitroaniline	B-AB
$3NO_2An$	3-Nitroaniline	B-AB
$4NO_2An$	4-Nitroaniline	B-AB
$4C13NO_2An$	4-Chloro-3-nitroaniline	B-AB
$24NO_2An$	2,4-Dinitroaniline	B-B-AB
$26NO_2An$	2,6-Dinitroaniline	B-B-AB
12AB	1,2-Phenylenediamine	AB-AB
14AB	1,4-Phenylenediamine	AB-AB
15AN	Naphthalene-1,5-diamine	AB-AB
Phenols		
Ph	Phenol	AB
3ClPh	3-Chlorophenol	AB
4BrPh	4-Bromophenol	AB
34MePh	3,4-Xylenol	AB
23MePh	2,3-Xylenol	AB
34ClPh	3,4-Dichlorophenol	AB
35ClPh	3,5-Dichlorophenol	AB
246ClPh	2.4.6-Trichlorophenol	AB
27HN	2,7-Dihydroxynaphthalene	AB
3Me4ClPh	3-Methyl-4-chlorophenol	AB-AB
$2NH_2Ph$	2-Aminophenol	AB-AB
$3NH_2Ph$	3-Aminophenol	AB-AB
3HPh	Resorcinol	AB-AB
35HPh	Phloroglucinol	AB-AB-AB
23HPh	Pyrogallol	AB-AB-AB
4Al2MeOPh	Eugenol	B-AB
$2NO_2Ph$	2-Nitrophenol	B-AB
$24NO_2Ph$	1,2-Dinitrophenol	B-B-AB
$26NO_2Ph$	2,6-Dinitrophenol	B-B-AB
Quinolines		
Q	Quinoline	B
8MeQ	8-Methylquinoline	B
26MeQ	2,6-Dimethylquinoline	B
2ClQ	2-Chloroquinoline	B
2HQ	2-Hydroxyquinoline	AB-B
4HQ	4-Hydroxyquinoline	AB-B
5HQ	5-Hydroxyquinoline	AB-B
8HQ	8-Hydroxyquinoline	AB-B
$5NH_2Q$	5-Aminoquinoline	AB-B
57Cl6HQ	5,7-Dichloro-6-hydroxyquinoline	AB-B
$5NO_26NH_2Q$	5-Nitro-6-aminoquinoline	AB-B-B
$6NO_2Q$	6-Nitroquinoline	B-B
$8NO_2Q$	8-Nitroquinoline	B-B

Table 3
Parameters of correlation lines $\log k_I$ versus $\log k_{II}$ obtained for amines, phenols and quinoline bases on polar-bonded stationary phases in different eluent systems[a]

Solutes	Eluent system																	
	iPrOH+H						THF+H						DX+H					
	Intercept, *a*	Slope, *b*	Correlation coefficient, *r*	*F*[b]	SD[c]	*n*[d]	Intercept, *a*	Slope, *b*	Correlation coefficient, *r*	*F*	SD	*n*	Intercept, *a*	Slope, *b*	Correlation coefficient, *r*	*F*	SD	*n*
$\log k_{CN} = a + b \log k_{Diol}$																		
Amines	0.19±0.21[e]	0.95±0.11	0.8726	0.95	0.28	21	0.54±0.11	1.05±0.05	0.9681	21.61	0.12	20	0.37±0.18	1.06±0.08	0.9213	4.59	0.19	20
Phenols	0.27±0.40	0.81±0.23	0.7429	0.91	0.52	17	0.38±0.41	0.18±0.23	0.2343	1.61	0.45	13	0.26±0.31	0.57±0.15	0.7216	1.79	0.28	12
Quinolines	0.31±0.29	0.76±0.15	0.8621	2.44	0.25	10	0.15±0.65	0.30±0.50	0.3126	0.92	0.70	9	0.34±0.53	0.15±0.38	0.1856	1.20	0.56	10
$\log k_{CN} = a + b \log k_{NH2}$																		
Amines	−0.24±1.37	2.83±0.40	0.6447	1.00	0.37	20	−0.24±1.37	2.83±0.40	0.6447	1.00	0.37	20	−0.19±1.22	2.21±0.46	0.5934	0.98	0.41	20
Phenols	−0.01±0.90	0.44±0.24	0.2139	0.94	0.57	17	0.22±1.41	0.11±0.45	0.0201	0.85	0.27	11	1.51±3.46	−3.19±1.24	0.4677	1.32	0.36	12
Quinolines	0.31±0.46	0.29±0.24	0.4110	1.62	0.38	9	0.03±0.66	1.93±0.22	0.9183	0.87	0.31	8	0.30±0.26	0.95±0.13	0.9231	2.83	0.22	10
$\log k_{Diol} = a + b \log k_{NH2}$																		
Amines	−0.15±0.30	0.96±0.11	0.7989	1.27	0.28	20	−0.78±1.09	2.79±0.33	0.7131	0.95	0.31	21	−0.51±1.07	1.92±0.39	0.6053	1.24	0.34	19
Phenols	−0.33±1.08	0.51±0.29	0.2444	0.93	0.68	17	1.35±3.14	−4.51±0.96	0.5350	0.83	0.69	13	0.82±2.74	−1.82±1.07	0.3227	1.06	0.44	14
Quinolines	−0.005±0.51	0.25±0.27	0.3346	0.88	0.42	9	0.43±1.44	0.70±0.47	0.3058	1.22	0.73	10	0.35±0.82	−0.07±0.41	0.0569	1.16	0.69	10

[a] Statistical characterization of the correlation $\log k_I = a + b \log k_{II}$ was performed at the 90% confidence level.
[b] *F*, value of the statistical significance *F*-test.
[c] SD, average residual of the fit.
[d] *n*, number of points.
[e] Standard deviation.

investigated are maintained. It has been formerly asserted that 2-propanol influences LSERs of polar-bonded stationary phases considerably [46,47], which changes their HB-donor/HB-acceptor properties. The addition of polar modifier in nonpolar diluent (e.g., *n*-hexane) does not vary appreciably sorbent dipolarity but sorbent acidity and/or basicity are significantly changed [49,64].

Low regression coefficients are obtained for phenols in all systems compared, which confirms different retention mechanisms of this group on various polar-bonded stationary phases.

When diol-silica and aminopropyl phases are compared in all investigated eluent systems, it should also be mentioned that there are low values of correlation coefficients for all groups of compounds investigated in spite of phases' similarities in LSER coefficients [47].

Slope values of $\log k_I$ versus $\log k_{II}$ plots give information about the selectivity of separation of the particular group. When the value of the slope is near 1, the selectivity of separation is similar. Such a situation appears in about six cases. However, the selectivity of separation of amines is higher on cyanopropyl phase than on aminopropyl-silica in tetrahydrofuran–*n*-heptane and dioxane–*n*-heptane mobile phases, and on diol-silica than on aminopropyl phases in the same eluent systems. The selectivity of separation of phenols is higher on diol-silica then on cyanopropyl and aminopropyl phases in all eluent systems investigated. Similarly, the selectivity of separation of quinoline group is better on diol phase than on cyanopropyl-silica in all eluent systems (see Table 3).

The results of experiments are also presented in the correlation diagrams. As examples, some correlation diagrams are shown in Figs. 2–4.

Fig. 2 presents the correlation points of retention parameters of amines obtained on CN and NH_2 phases in eluent containing dioxane and *n*-heptane. The points are strongly dispersed. There are some compounds eluted together on NH_2-silica (for example 2-phenylenediamine, 4-chloro-3-nitroaniline, 3-nitroaniline, 4-methylaniline, 2-methoxyaniline)

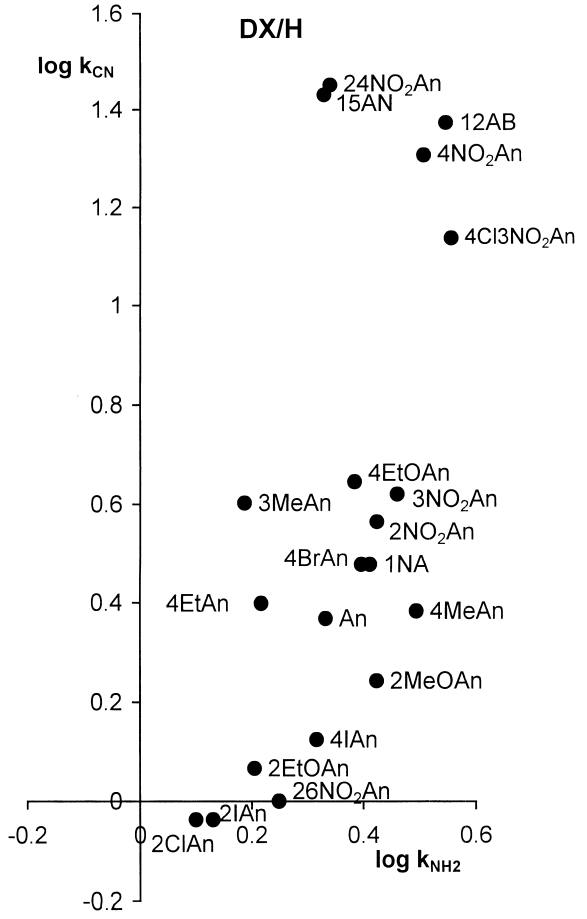

Fig. 2. Correlation between log k values of anilines on CN- and aminopropyl-silica. Mobile phase: dioxane–n-heptane (in concentrations of 5% DX for CN- and 10% DX for NH_2-silica). For symbols of solutes see Table 1.

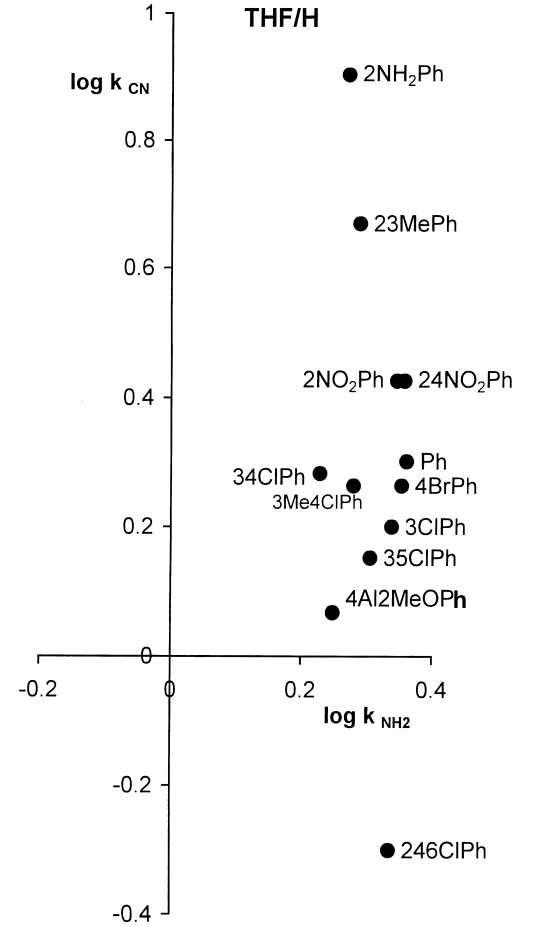

Fig. 3. Correlation between log k values of phenols on CN- and aminopropyl-silica. Mobile phase: tetrahydrofuran–n-heptane (in concentrations of 5% THF for CN- and 10% THF for NH_2-silica). For symbols of solutes see Table 1.

which are well separated on cyanopropyl phase. The group of amines eluted in a narrow range on NH_2-silica (about 0.45 log k units) is better separated on cyanopropyl phase in the range of about 1.5 log k units, when dioxane as mobile phase modifier is used (see Fig. 2). Similarly, the group of phenols eluted in a narrow range on NH_2 phase — (about 0.2 log k units) is separated in a range of about 1.2 log k units on cyanopropyl phase with tetrahydrofuran — n-heptane as eluent (see Fig. 3).

Similar conclusions can be drawn from the comparison of retention parameters correlated for diol-silica and the aminopropyl phase. For quinolines the correlation points are dispersed, so that satisfactory separation for particular pairs of compounds is obtained using one of the sorbents (diol-silica or aminopropyl-silica, see Fig. 4).

The slope values do not always indicate the best selectivity of separation in one of the systems, especially when correlation coefficient is low ($r<$ 0.9) and points are dispersed along the vertical to the x-axis line (compare slope values for log k_{CN} versus log k_{NH2} correlation line for phenols in system tetrahydrofuran–n-heptane in Table 3 and Fig. 3).

Retention parameters obtained for aromatic amines in all investigated systems are shown as log k

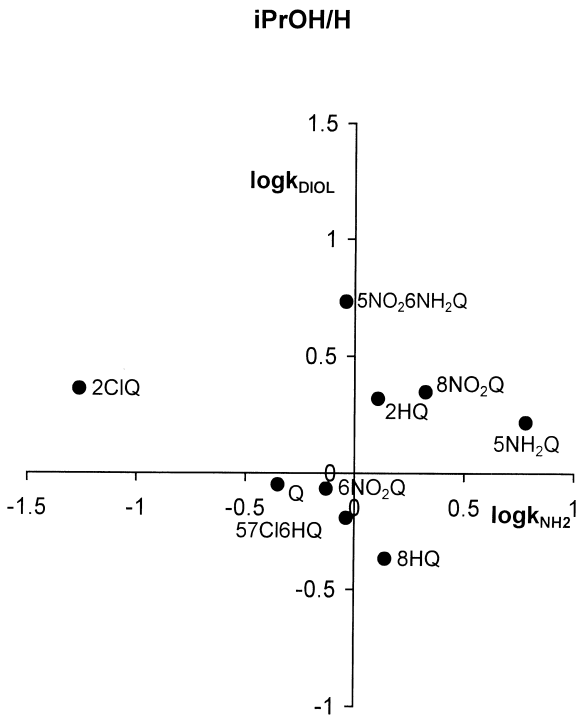

Fig. 4. Correlation between log k values of quinoline bases on diol- and. aminopropyl-silica. Mobile phase: 2-propanol–*n*-heptane (in concentrations of 15% iPrOH for diol- and 10% iPrOH for NH_2-silica). For symbols of solutes see Table 1.

spectrum in Fig. 5. It is distinctly perceptible that aminopropyl phase is not selective for the separation of this group (systems 4, 5 and 6). From the spectrum is also seen that diol-silica (systems 1, 2, 3) and especially CN-silica are more selective for the separation of aromatic amines. Especially wide rage of retention coefficients is obtained on CN-silica when 2-propanol as modifier was used (system 7). Generally, 2-propanol gives the best selectivity of the separation of amines on all polar-bonded phases examined (systems 1, 4 and 7).

Similar conclusions can be drawn from the spectrum shown in the Fig. 6 which presents log k values for phenols obtained in all systems investigated. Similarly the selectivity of separation is poor for phenols on aminopropyl phase (systems 4, 5, 6) and the highest on diol-silica (systems 1, 2, 3) and on CN phase (systems 7, 8, 9). The wide range of retention coefficients is obtained particularly on diol- and CN-silica when 2-propanol was used as modifier (systems 1 and 7).

For quinoline bases, the selectivity of separation in investigated chromatographic systems is shown as log k spectrum in Fig. 7. It is seen that all polar-bonded stationary phases can be used for the separation of quinoline derivatives, especially with 2-propanol or tetrahydrofuran as eluent modifier.

The selectivity of separation can be particularly characterised by $\Delta\log k$ values for aromatic amines ($\Delta\log k = \log k_{AnX} - \log k_{An}$), for phenols ($\Delta\log k = \log k_{PhX} - \log k_{Ph}$) and for quinoline bases ($\Delta\log k = \log k_{QX} - \log k_{Q}$) presented in Table 4. When all chromatographic systems are taken into consideration, the most selective systems can be chosen for particular compounds with the highest $\Delta\log k$ values. For aromatic amines, $\Delta\log k$ values are the highest on diol phase in 13, on CN phase in seven out of 20 cases examined in all eluent systems. For phenols, $\Delta\log k$ values are the highest on diol phase in seven, on NH_2 phase in one and on CN phase in 10 out of 18 cases. For quinolines, $\Delta\log k$ values are the highest on diol phase in seven, on NH_2 phase in two and on CN phase in three out of 12 cases (see Table 4) examined in all eluent systems. It follows from $\Delta\log k$ values that aromatic amines possessing a second substituent of electron-donor character (–NO_2, MeO–, EtO–) are better separated on diol-silica in most cases. Similarly quinolines possessing a second substituent of electron-donor–acceptor character (hydroxyquinolines and aminoquinolines), i.e., possessing B and AB centres [67] are better separated on diol-silica stationary phase in most eluent systems. However, anilines and phenols substituted with a halogen atom are in most eluent systems better separated on CN-silica.

4. Conclusions

Similar retention mechanism for amines is observed on CN-silica and diol phases especially when tetrahydrofuran or dioxane are used as eluent modifier. Similar retention mechanism for quinoline bases is observed for CN-silica and aminopropyl-silica phases when tetrahydrofuran or dioxane is used as eluent component.

Diol- and aminopropyl phases have different

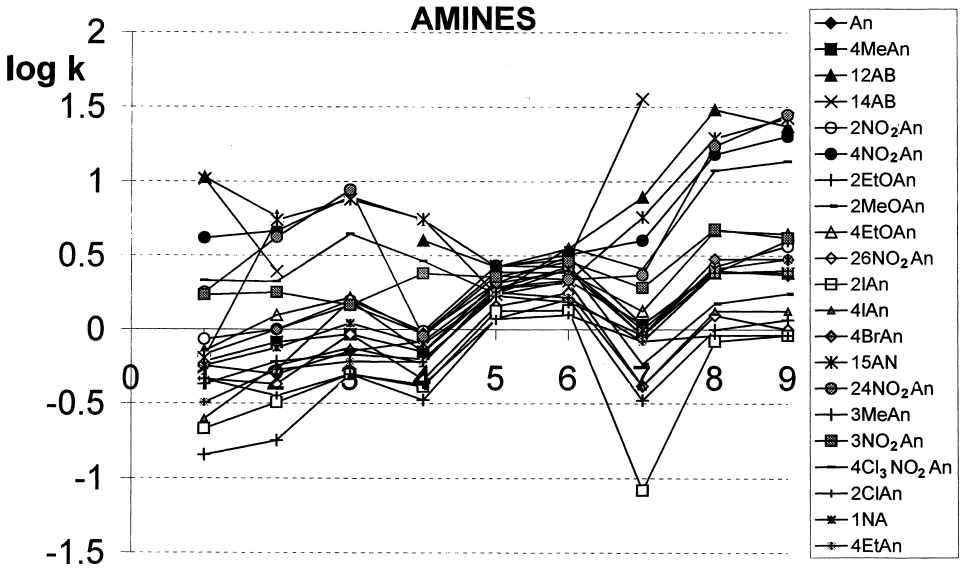

Fig. 5. Graphical comparison of log k values obtained for anilines in following chromatographic systems. Diol phase, 1.15% iPrOH, 2.20% THF, 3.20% DX; aminopropyl phase, 4.10% iPrOH, 5.10% THF, 6.10% DX; cyanopropyl phase, 7.10% iPrOH, 8.5% THF, 9.5% DX. All modifiers dissolved in *n*-heptane. For symbols of solutes see Table 1.

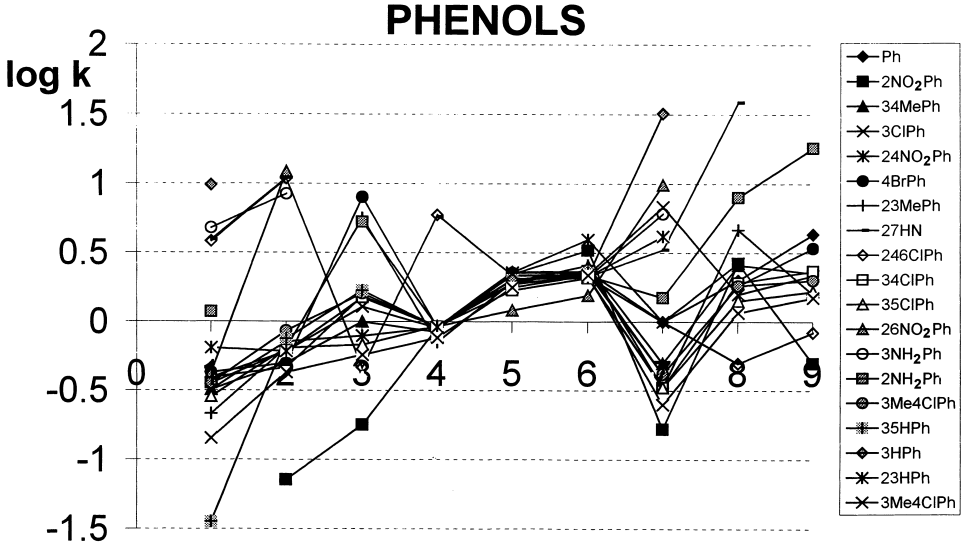

Fig. 6. Graphical comparison of log k values obtained for phenols in following chromatographic systems — diol phase: 1.15% iPrOH; 2.20% THF; 3.20% DX; aminopropyl phase: 4.10% iPrOH; 5.10% THF; 6.10% DX; cyanopropyl phase: 7.10% iPrOH; 8.5% THF; 9.5% DX. All modifiers dissolved in *n*-heptane. For symbols of solutes see Table 1.

selectivity of separation for all groups of model solutes in investigated eluent systems.

Low regression coefficients are obtained for phenols in all systems compared, which confirms different retention mechanisms of this group on various polar-bonded stationary phases.

Table 4
Δlog k values for investigated compounds in examined chromatographic systems

Symbol	DIOL			NH_2			CN		
	15% iPrOH	20% THF	20% DX	10% iPrOH	10% THF	10% DX	10% iPrOH	5% THF	5% DX
$\Delta\log k = \log k_{Anx} - \log k_{An}$									
An	0	0	0	0	0	0	0	0	0
3MeAn	−0.12	0.08	−0.02	−0.12	−0.06	−0.15	−0.07	−0.01	0.23
4MeAn	0.03	0.22	0.11	−0.07	0.03	0.16	0	−0.01	0.02
4EtAn	−0.25	0.03	−0.07	−0.14	−0.04	−0.12	−0.11	−0.01	0.03
2ClAn	−0.09	−0.15	−0.15	−0.30	−0.22	−0.23	−0.11	−0.44	−0.41
2lAn	−0.43	−0.19	−0.15	−0.31	−0.16	−0.20	−1.11	−0.48	−0.41
4lAn	−0.36	0.06	0.02	−0.15	−0.01	−0.01	−0.41	−0.27	−0.24
4BrAn	0.07	0.30	0.31	0.05	0.03	0.06	−0.07	0.08	0.11
1NA	0	0.18	0.19	−0.02	−0.04	0.07	−0.03	0.01	0.11
2MeOAn	−0.25	0.03	0.34	−0.07	−0.01	0.09	−0.27	−0.22	−0.12
2EtOAn	−0.60	−0.45	−0.15	−0.40	−0.22	−0.13	−0.51	−0.40	−0.30
4EtOAn	0.10	0.40	0.36	0.05	0.10	0.05	0.09	0.27	0.28
$2NO_2$An	0.18	0.30	0.34	0.07	0.14	0.10	−0.07	0.03	0.20
$3NO_2$An	0.48	0.55	0.31	0.46	0.07	0.13	0.25	0.28	0.25
$4NO_2$An	0.86	0.97	1.04	0.82	0.14	0.17	0.57	0.79	0.94
$4Cl3NO_2$An	0.57	0.62	0.79	0.54	−0.05	0.22	0.38	0.68	0.77
$24NO_2$An	0.49	0.93	1.09	0.03	0.08	0.01	0.33	0.84	1.08
$26NO_2$An	−0.09	−0.07	0.11	−0.26	−0.13	−0.08	−0.41	−0.30	−0.37
12AB	1.27	1.06	0.15	0.68	0.14	0.21	0.86	1.09	1.00
14AB	1.26	0.69	0.15	0.08	0.14	0.14	1.52	−0.40	−0.37
15 AN	0.05	1.04	1.03	0.82	−0.05	−0.01	0.72	0.90	1.06
$\Delta\log k = \log k_{Phx} - \log K_{Ph}$									
Ph	0	0	0	0	0	0	0	0	0
3ClPh	0	0.12	−0.08	−0.01	−0.02	−0.02	0.83	−0.10	−0.30
4BrPh	0.04	0.03	0.72	0	−0.01	−0.01	−0.38	−0.04	−0.10
4Al2MeOPh	0.21	0.12	−0.19	0.01	−0.36	−0.04	0.62	−0.30	−0.64
34MePh	−0.09	0.03	−0.19	−0.03	−0.36	0.04	−0.30	0.11	−0.28
23MePh	−0.28	0.14	0.57	−0.11	−0.07	0.04	−0.48	0.37	−0.44
34ClPh	−0.04	0.12	−0.01	0.01	−0.13	−0.05	−0.48	−0.02	−0.27
35ClPh	−0.14	0.14	−0.35	0.01	−0.06	−0.04	−0.48	−0.15	−0.41
246ClPh	0.99	1.37	−0.52	0.82	−0.03	−0.04	0	−0.60	−0.72
3Me4ClPh	0.48	0.33	0.54	0.01	−0.09	−0.03	0.18	0.60	0.62
$2NH_2$Ph	1.09	1.26	−0.19	0.01	−0.08	−0.04	0.78	−0.30	−0.64
$3NH_2$Ph	0.04	1.42	−0.19	0.01	−0.28	−0.17	0.99	−0.30	−0.64
3HPh	−1.04	0.21	0.04	0.01	−0.06	−0.01	0	−0.30	−0.64
$2NO_2$Ph	0	−0.81	−0.93	−0.01	−0.01	0.15	−0.78	0.12	−0.94
$24NO_2$Ph	−0.09	0.19	−0.29	0	−0.01	0.23	0	0.12	−0.64
27HN	1	1.37	−0.19	0.80	−0.36	−0.04	0.52	1.29	−0.64
$26NO_2$Ph	−0.34	−0.16	−0.40	−0.35	−0.32	−0.27	−0.38	−0.02	−0.46
35HPh	−0.04	0.27	0.02	0.01	−0.08	0.01	−0.38	−0.04	−0.34
23HPh	1.40	0.33	−0.19	0.04	−0.05	−0.03	1.51	−0.30	−0.64
$\Delta\log k = \log k_{QX} - \log k_{Q}$									
Q	0	0	0	0	0	0	0	0	0
8MeQ	−0.70	−0.58	−0.58	0.35	−0.38	−0.33	−0.52	−1.54	−0.75
2ClQ	0.53	1.04	1.23	−0.90	−0.68	−1.31	0.34	−1.24	−1.23
26MeQ	−0.40	−0.16	0.17	0.35	−0.10	−0.05	0.08	−0.46	−0.45
2HQ	0.52	1.50	1.19	0.46	0.20	0.34	0.34	−0.05	0.22
4HQ	1.33	0.17	0.17	0.35	0.13	0.33	0.08	−0.46	−0.45
5HQ	0.53	1.24	0.17	0.35	0.21	0.30	0.08	−0.46	−0.45
8HQ	0	−0.16	−0.13	0.49	0.17	0.26	−0.10	−0.01	0.02
$5NH_2$Q	1.21	1.20	1.20	1.13	0.20	0.35	1.15	−0.46	0.20
$6NO_2$Q	0.32	0.20	0.23	0.22	−0.10	0.25	0.04	0.20	0.09
$8NO_2$Q	0.51	1.24	0.43	0.68	0.23	0.29	0.32	0.25	0.18
57C16HQ	−0.05	0.39	0.38	0.31	0.19	0.33	0.60	0.25	−0.03
$5NO_26NH_2$Q	0.83	1.05	1.15	0.31	0.22	0.35	0.69	0.26	0.65

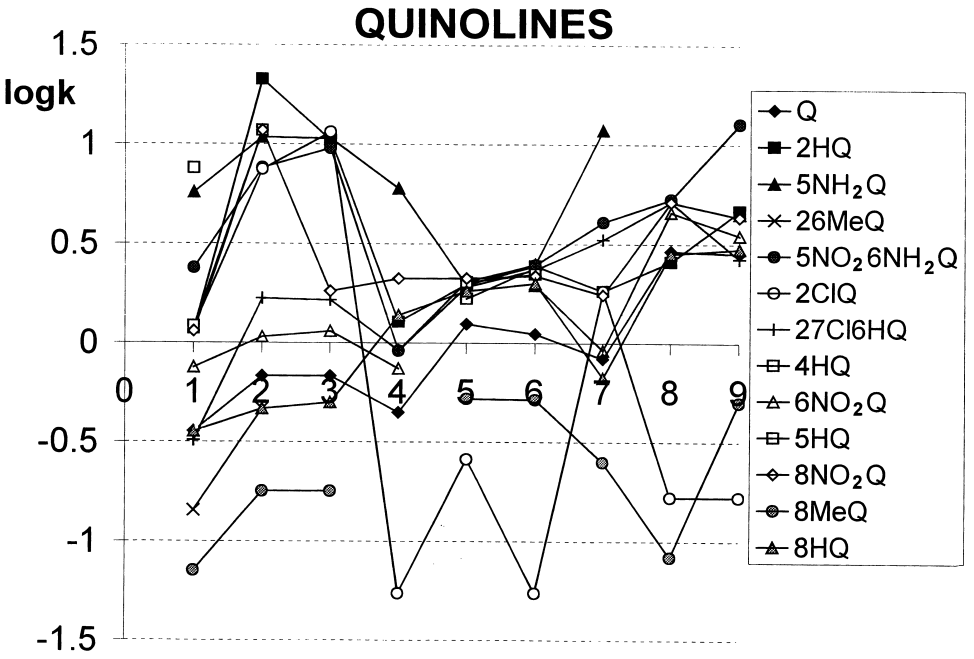

Fig. 7. Graphical comparison of log k values obtained for quinoline bases in following chromatographic systems. Diol phase, 1.15% iPrOH, 2.20% THF, 3.20% DX; aminopropyl phase, 4.10% iPrOH, 5.10% THF, 6.10% DX; cyanopropyl phase, 7.10% iPrOH, 8.5% THF, 9.5% DX. All modifiers dissolved in *n*-heptane. For symbols of solutes see Table 1.

The selectivity of separation demonstrated as slope values for k-plots and as $\Delta\log k$ values is the best for CN- or diol-silica for all investigated model solutes.

Aminopropyl phase is not selective especially for amines and phenols.

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