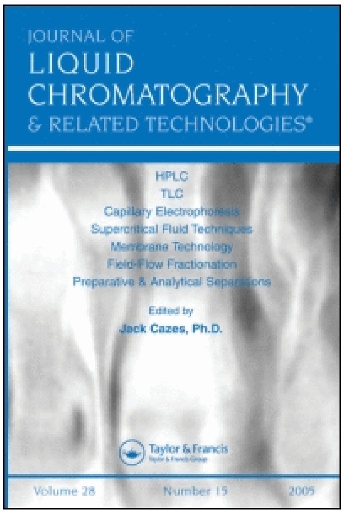

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RETENTION BEHAVIOUR OF SOME PHENOLS AND ANILINES ON CN-, DIOL-, AND SILICA PRECOATED HPTLC PLATES

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ABSTRACT

The retention behaviour of some phenols and aromatic amines on CN and Diol precoated high-performance thin-layer chromatographic plates was examined using normal-phase eluent systems: polar modifier (2-propanol, ethyl acetate, ethyl methyl ketone, dioxane, tetrahydrofuran or diisopropyl ether) in n-heptane. The results were compared with the retention parameters of investigated compounds obtained in the same eluent systems on bare silica. The results are presented by the comparison of ΔR_M values for pairs of positional isomers and by the $R_{M\ I}$ vs. $R_{M\ II}$ relationships of phenols and anilines for CN-silica - silica, diol-silica - silica and CN - diol stationary phases.

INTRODUCTION

Systems with various properties have been studied because of the need of chromatographic systems with different selectivity to use in difficult separations of closely related compounds and to separate natural mixtures from complex matrices including trace and ballast substances. An important problem is also the choice of suitable systems for chromatographic identification with high probability levels.[1]

Surface-modified sorbents, especially the polar bonded stationary phases, increase in importance as stationary phases in both TLC and HPLC. This can often be attributed to the extended range of selectivity possible when such phases are used in combination with simple eluents.

Surface-modified sorbents have a moderate polarity and can be used both in normal phase and reversed-phase chromatography.

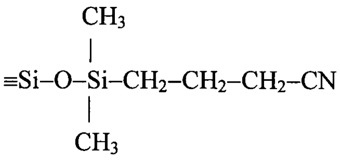
In the last ten years, the CN-bonded stationary phases were used in NP systems in phytochemical analysis by HPTLC for the separation of furocoumarins,[2] anthraquinone aglycones,[3] flavonoids,[4] taxol and related compounds,[5] alkaloids,[6,7] dyestuffs and plant pigments.[8-10] CN-plates were also used in biochemical analysis for the separation of amino acids,[7,8,11,12] nucleosides,[13] nucleotides and bases,[14] steroid hormones,[6,7,10,15-17] and androgens,[18] in pharmaceutical analysis for the separation of vitamins,[10] sulphonamides,[19] benzodiazepine derivatives,[20,21] nitrosamines and amines[22] and in environmental analysis to separate herbicides[23] and pesticides.[10,24]

Diol-bonded phases were also widely used in phytochemical analysis to separate flavonol aglycones[25] and glycosides,[25,26] flavonoids and related compounds,[4,27] sesquiterpenoids,[28] flavour compounds,[29] antifungal compounds from higher plants,[30] phenolic constituents[31,32] and also in biochemical analysis for the separation of aminoacids,[10,24] nucleotides and bases,[14] nucleosides,[13] in pharmaceutical analysis of vitamins,[10] estrogens[33] steroids,[10,34] antifungal tetracyclic compounds,[35] and lipophilic dyestuffs.[8] They were also used in the environmental analysis of pesticides,[10,24] nitrosamines and amines,[22] and preservatives in cosmetics.[10,36]

NP-bonded layers are also suitable for employing ion pair reagents[7,12] and chiral ion interaction agents.[37,38]

The polar bonded stationary phases consist of a silica matrix covered with chemically bonded ligands of different types[39] such as:

NP-CN



$$\equiv Si{-}O{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}{-}CH_2{-}CH_2{-}CH_2{-}CN$$

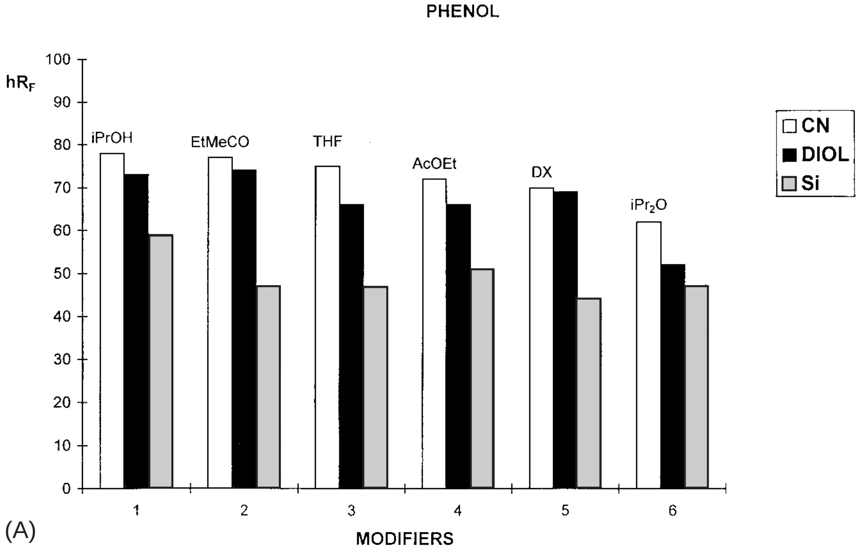
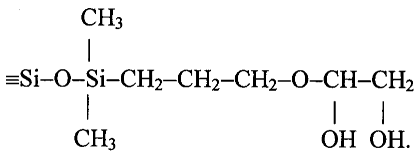


Figure 1A. Values of retention parameter hR$_F$ for phenol obtained on CN-, Diol-, and silica in investigated eluent systems: 1 - 2-propanol - n-heptane, 2 - ethyl methyl ketone - n-heptane, 3 - tetrahydrofuran - n-heptane, 4 - ethyl acetate - n-heptane, 5 - dioxane - n-heptane, 6 - diisopropyl ether - n-heptane in concentration of 30% modifier in each case.

NP-Diol



$$\equiv Si-O-\underset{CH_3}{\overset{CH_3}{Si}}-CH_2-CH_2-CH_2-O-\underset{OH}{CH}-\underset{OH.}{CH_2}$$

These sorbents have the density coverage $\Theta_1 = 3.5$ μmol/m^2 and $\Theta_2 = 3.0$ μmol/m^2 for cyanopropyl and diol phases, respectively.

Kowalska et al.[39] have studied the mechanism of solute retention in polar bonded phase systems and concluded that mixed adsorption-partition mechanisms of retention in such systems occurs. The partition mechanism on NP-CN and NP-Diol stationary phases in most investigated eluent systems (alcohol - n-aliphatic hydrocarbon) predominates. The diol phase generally behaved like deactivated silica.[32]

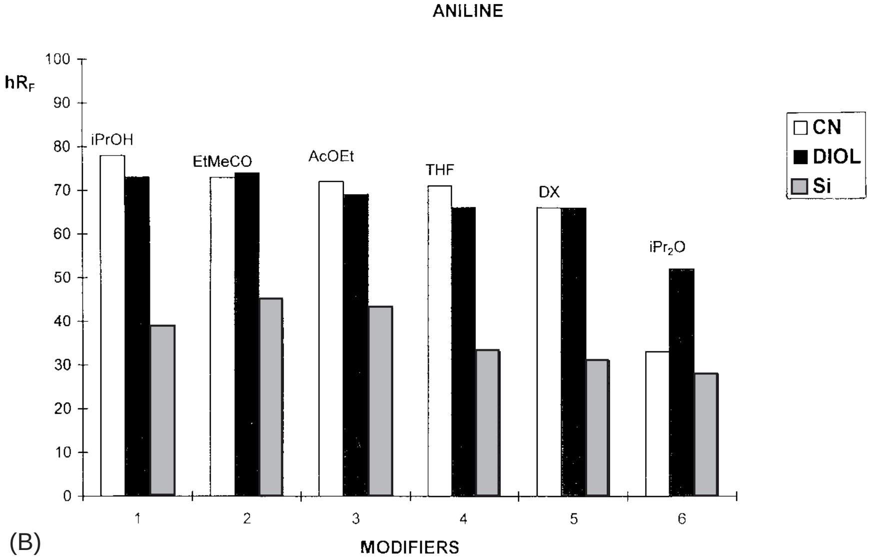


Figure 1B. Values of retention parameter hR_F for aniline obtained on CN-, Diol-, and silica in investigated eluent systems: 1 - 2-propanol - n-heptane, 2 - ethyl methyl ketone - n-heptane, 3 - ethyl acetate - n-heptane, 4 - tetrahydrofuran - n-heptane, 5 - dioxane - n-heptane, 6 - diisopropyl ether - n-heptane in concentration of 30% modifier in each case.

Linear relationships showing the effect of organic modifier on the retention of active compounds (R_M vs. log C) were obtained[27,40] according to Snyder-Soczewiński's displacement theory for normal phase systems.[41,42] The aim of this work is to compare the retention behaviour of *ortho*- and *para*- substituted phenols and aromatic amines in NP systems using bare silica and CN- and Diol-bonded silica in eluent systems containing such modifiers as: 2-propanol, ethyl acetate, ethylmethyl ketone, diisopropyl ether, dioxane, and tetrahydrofuran diluted with n-heptane in order to confirm the selectivity of separation of various compound groups and to compare their surface site-eluent-solute interactions.

EXPERIMENTAL

Thin layer chromatography was performed on 10x10 cm glass Diol F_{254}, CN F_{254}, and Si 60 HF_{254} HPTLC precoated plates (E. Merck, Darmstadt, Germany) in horizontal Teflon chambers with an eluent distributor (DS, Chromdes, Lublin, Poland). Samples (2 μL) of 2.5%w/v solution from the solutes in methanol were spotted and developed face-down to a distance of 8cm from the origin at ambient temperature.

Table 1

List of Compounds Investigated

No.	Compound	Abbrev.	No.	Compound	Abbrev.
	Phenols:			Aromatic Amines:	
1	Phenol	Ph	1	Aniline	An
2	4-Aminophenol	4APh	2	4-Chloroaniline	4CAn
3	2-Aminophnol	2APh	3	2-Chloroaniline	2CAn
4	Hydroquinone	4HPh	4	1,4-Phenylenediamine	4AAn
5	Resorcinol	2HPh	5	1,2-Phenylenediamine	2AAn
6	3,5-Xylenol	35MePh	6	p-Anisidine	4MeOAn
7	2,3-Xylenol	23MePh	7	o-Anisidine	2MeOAn
8	2,7-Dihydroxynaphthalene	27HN	8	p-Phenetidine	4EtOAn
9	2,3-Dihydroxynaphthalene	23HN	9	o-Phenetidine	2EtOAn
10	4-Hydroxybenzaldehyde	4HBa	10	4-Nitroaniline	4NtAn
11	2-Hydroxybenzaldehyde	2HBa	11	2-Nitroaniline	2NtAn
12	4-Nitrophenol	4NtPh	12	2-Aminonaphthalene	2AN
13	2-Nitrophenol	2NtPh	13	1-Aminonaphthalene	1AN
			14	4-Chloro-3-nitroaniline	4C3NtAn
			15	2-Chloro-4-nitroaniline	2C4NtAn
			16	4-Iodoaniline	4IAn
			17	2-Iodoaniline	2IAn
			18	4-Ethylaniline	4EtAn
			19	2-Ethylaniline	2EtAn

Binary mixtures of polar modifier: 2-propanol (iPrOH), ethyl acetate (AcOEt), ethyl methyl ketone (EtMeCO), diisopropyl ether (iPr_2O), dioxane (DX), or tetrahydrofuran (THF) and n-heptane were used as eluents. Solvents were analytical grade from Polish Reagents (POCh, Gliwice, Poland). The location of the spots was determined under UV light (λ=254 nm). The investigated compounds are listed in Table 1.

RESULTS AND DISCUSSION

The experiments were performed using binary eluents of the same concentration of polar solvents from different selectivity groups,[42] diluted in n-heptane. The eluent strengths of the modifiers can be estimated by comparing the hR_F values of phenol and aniline obtained on CN-silica, diol-silica, and on bare silica in investigated eluent systems (Figure 1 A, B).

The eluent strength of investigated modifiers depends on the sorbent active sites and the solute molecule.[43] On CN-silica, the eluotropic series for phenol is as follows (increasing eluent strength): diisopropyl ether and dioxane, ethyl acetate, tetrahydrofuran, ethylmethyl ketone, and 2-propanol, for aniline: diisopropyl ether, dioxane, tetrahydrofuran, ethyl acetate, ethyl methyl ketone,

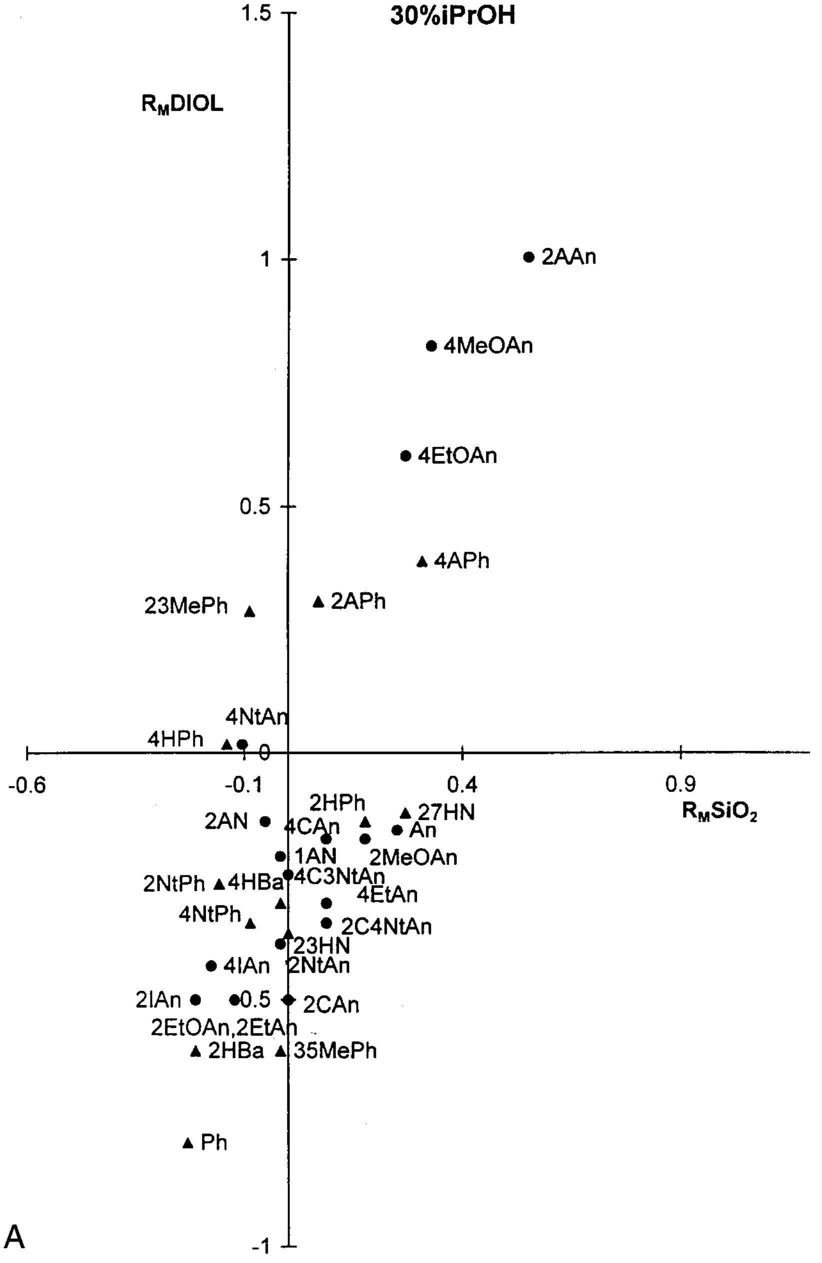


Figure 2A. Correlation between R_M values of phenols (solid triangles) and anilines (solid circles) on Diol- and silica; mobile phase: 2-propanol - n-heptane (3:7). For identification of solutes see Table 1.

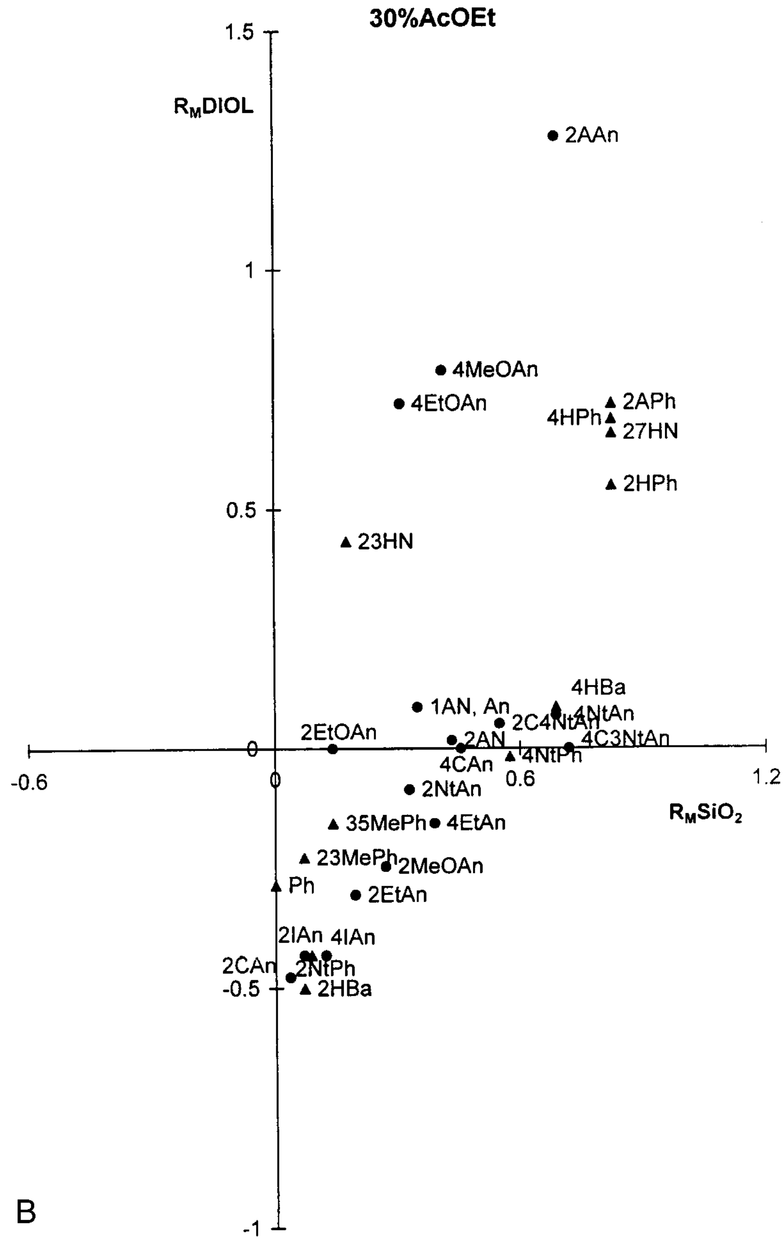


Figure 2B. Correlation between R_M values of phenols (solid triangles) and anilines (solid circles) on diol- and silica; mobile phase: ethyl acetate-n-heptane (3:7). For identification of solutes see Table 1.

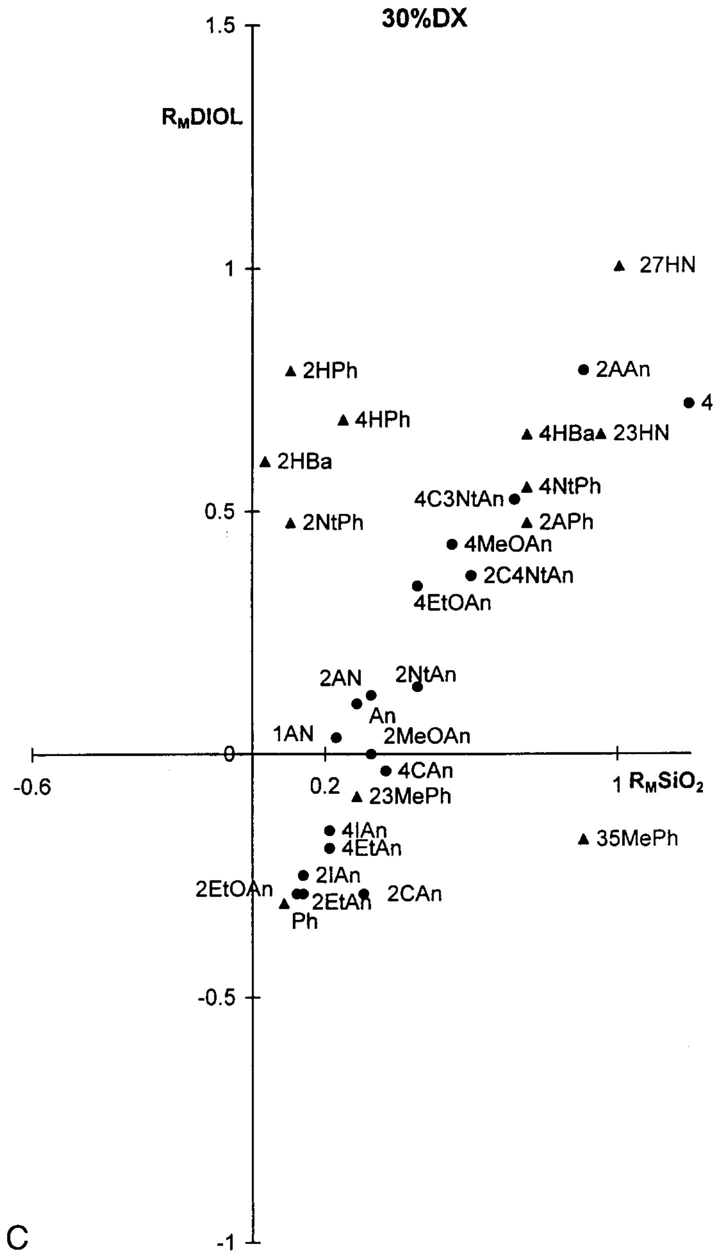


Figure 2C. Correlation between R_M values of phenols (solid triangles) and anilines (solid circles) on diol- and silica; mobile phase: dioxane - n-heptane (3:7). For identification of solutes see Table 1.

and 2-propanol. On diol-silica the eluotropic series for phenol is as follows: diisopropyl ether, tetrahydrofuran and ethyl acetate, dioxane, 2-propanol, and ethyl methyl ketone, for aniline: diisopropyl ether, dioxane and tetrahydrofuran, ethyl acetate, 2-propanol, and ethyl methyl ketone. From the diagrams (Figure 1) the differences in strength of interactions of phenol molecule (A) and aniline molecule (B) with surface active groups of diol-silica and bare silica can be estimated. The lower hR_F values obtained for phenol and aniline on the silica surface indicate their relatively strong interactions with surface hydroxyl groups of silica. The hydrogen atoms on the silica surface OH groups are strongly protonated as a result of the presence of vacant d-orbitals on the silicon atom.[44] The hydroxyl groups present on the diol ligand are weaker proton-donor centres because the hydroxyl groups are bonded to carbon atoms which do not cause displacement of their electron density.

The diol hydroxyl groups bonded to two neighbouring carbon atoms can also behave similarly as “bonded” hydroxyl groups on the silica surface[44] which are bound to neighbouring silicon atoms at a distance of 0.25-0.26 nm and interact via H-bonding. They, therefore, behave as B type centres[45] and are relatively weak adsorption centres on the silica surface among other proton donor OH groups - free (isolated) and active OH groups.[44] Thus, diol OH groups approximately 0.154 nm[46] apart, interacting via H-bonds, can behave like B centres. As a result, the interactions of solute molecules with the diol- surface are relatively weak.

The selectivity of separation is compared by ΔR_M values for pairs of investigated positional isomers in the examined NP-systems (see Table 2). Because of strongly specific interactions of polar substituents and surface active centres the differences of retention parameters for molecules with two polar substituents in the *ortho*- and *para* positions are, in most cases, the greatest for silica. The ΔR_M values for such solutes as pairs of hydroquinone-resorcinol (4HPh-2HPh) *ortho*- and *para*-phenylenediamine (4AAn, 2AAn), dihydroxy-naphthalenes (27HN, 23HN), predominantly, are the highest for silica layers. However, when the second substituent of phenol or aniline has moderate polarity - for example methoxy, ethoxy, or aldehyde group, the highest ΔR_M values are obtained for NP-bonded stationary phases (see Table 2), especially for diol-silica. The selectivity of separation of these solutes on bare silica is rather poor.

Nonpolar substituents like methyl- and ethyl- groups or halogen atoms cause nonspecific interactions with nonpolar fragments of cyanopropyl or diol ligands. This produces the high ΔR_M values are obtained especially on CN-silica and also on diol-silica for such pairs of isomers as xylenols (35MePh, 23MePh), ethyl anilines (4EtAn, 2EtAn) and in most cases chloroanilines (4CAn, 2CAn).

Table 2

ΔR_M Values for Pairs of Isomers in Investigated Chromatographic Systems

	iPrOH	AcOEt	EtMeCO	iPr_2O	DX	THF
			SiO_2			
4APh 2APh	0.54	---	---	---	---	---
4HPh 2HPh	-0.32	0.00	0.48	-1.38	0.14	0.10
35MePh 23MePh	0.07	0.07	0.11	0.76	0.62	0.10
27HN 23HN	0.29	0.68	-0.16	0.31	0.10	0.46
4HBa 2HBa	0.19	0.62	0.48	0.19	0.72	0.46
4NtPh 2NtPh	0.07	0.49	0.41	0.11	0.65	0.47
4CAn 2CAn	0.09	0.42	0.25	0.14	0.06	0.27
4AAN 2AAN	0.73	0.69	0.95	0.00	0.60	0.23
4MeOAn 2MeOAn	0.33	0.14	0.47	0.75	0.22	0.25
4EtOAn 2EtOAn	0.39	0.17	0.03	0.78	0.31	0.45
4NtAn 2NtAn	0.01	0.22	0.57	1.19	0.54	0.25
2AN 1AN	0.01	0.15	0.04	0.82	0.07	0.11
4C3NtAn 2C4NtAn	0.55	0.27	1.19	0.60	0.50	---
4IAN 2IAN	0.21	0.07	0.03	0.37	0.14	0.09
4EtAn 2ERtAn	0.12	0.19	0.02	0.60	0.12	0.07

Table 2 (continued)

	iPrOH	**AcOEt**	**EtMeCO**	**iPr_2O**	**DX**	**THF**
			Diol			
4APh 2APh	0.08	---	---	---	---	---
4HPh 2HPh	0.16	0.14	0.07	-0.13	-0.10	0.15
35MePh 23MePh	0.06	0.07	-0.06	0.12	-0.09	-0.10
27HN 23HN	0.25	0.23	0.25	0.29	0.35	0.33
4HBa 2HBa	0.29	0.59	0.55	-0.13	0.06	0.54
4NtPh 2NtPh	-0.62	-0.45	-0.39	0.98	1.03	0.54
4CAn 2CAn	0.32	0.48	0.16	0.74	0.25	0.32
4AAN 2AAN	---	---	---	---	---	---
4MeOAn 2MeOAn	1.07	1.00	0.38	1.19	0.43	---
4EtOAn 2EtOAn	0.72	0.96	0.39	0.63	0.52	---
4NtAn 2NtAn	0.41	0.16	0.30	0.65	0.58	0.31
2AN 1AN	0.07	-0.07	0.03	0.10	0.09	-0.06
4C3NtAn 2C4NtAn	0.17	-0.05	0.09	0.18	0.16	0.00
4IAN 2IAN	0.07	0.00	0.06	0.16	0.09	0.07
4EtAn 2ERtAn	0.19	0.15	0.25	0.51	0.09	0.30

(continued)

Table 2 (continued)

ΔR_M Values for Pairs of Isomers in Investigated Chromatographic Systems

	iPrOH	**AcOEt**	**EtMeCO CN**	**iPr_2O**	**DX**	**THF**
4APh 2APh	0.81	---	---	---	---	---
4HPh 2HPh	0.10	0.12	0.20	-0.12	0.07	0.06
35MePh 23MePh	-0.39	-0.08	-0.17	-0.28	-0.60	-0.11
27HN 23HN	0.18	0.29	0.27	0.35	0.27	0.32
4HBa 2HBa	---	---	---	---	---	---
4NtPh 2NtPh	---	---	0.12	---	---	---
4CAn 2CAn	0.11	0.21	0.13	0.65	0.24	0.20
4AAN 2AAN	0.43	---	---	---	---	---
4MeOAn 2MeOAn	0.86	0.76	0.80	0.76	0.44	0.28
4EtOAn 2EtOAn	1.07	0.84	0.92	0.46	0.63	0.41
4NtAn 2NtAn	0.09	0.25	0.25	0.60	0.58	0.36
2AN 1AN	0.10	-0.07	0.07	-0.09	0.05	-0.07
4C3NtAn 2C4NtAn	0.03	0.09	0.19	0.04	-0.05	---
4IAN 2IAN	-0.14	0.04	0.00	0.10	0.04	0.06
4EtAn 2ERtAn	0.28	0.21	0.33	0.48	0.04	0.28

Table 3

Parameters of Correlation $R_{M\,I}$ vs $R_{M\,II}$ Relationships for Investigated Solutes in Various Chromatographic Systems: Polar Adsorbent/Nonpolar Adsorbent

	Eluent System					
	iPrOH + H			**AcOEt + H**		
	Slope	**Intercept**	**r**	**Slope**	**Intercept**	**r**
$R_{M\,Diol}$ vs $R_{M\,Silica}$						
Amines	1.938	-0.227	0.834	1.238	-0.393	0.564
Phenols	1.191	-0.184	0.559	1.077	-0.333	0.841
$R_{M\,CN}$ vs $R_{M\,Silica}$						
Amines	1.366	-0.107	0.896	1.222	-0.440	0.632
Phenols	1.513	-0.196	0.728	0.866	-0.400	0.930
$R_{M\,CN}$ vs $R_{M\,Diol}$						
Amines	0.863	0.087	0.943	0.848	-0.045	0.963
Phenols	0.732	-0.051	0.792	0.735	-0.151	0.905

	Eluent System					
	EtMeCO + H			**$(iPr)_2O$ + H**		
	Slope	**Intercept**	**r**	**Slope**	**Intercept**	**r**
$R_{M\,Diol}$ vs $R_{M\,Silica}$						
Amines	0.396	-0.133	0.346	0.928	-0.300	0.865
Phenols	0.689	-0.188	0.455	0.987	-0.344	0.823
$R_{M\,CN}$ vs $R_{M\,Silica}$						
Amines	0.494	-0.247	0.430	0.578	-0.449	0.869
Phenols	0.151	-0.075	0.149	0.902	-0.0429	0.766

(continued)

Table 3 (continued)

Parameters of Correlation $R_{M\ I}$ vs $R_{M\ II}$ Relationships for Investigated Solutes in Various Chromatographic Systems: Polar Adsorbent/Nonpolar Adsorbent

	Eluent System					
	DX + H			THF + H		
	Slope	**Intercept**	**r**	**Slope**	**Intercept**	**r**
$R_{M\ CN}$ vs $R_{M\ Diol}$						
Amines	0.970	-0.093	0.975	1.004	-0.105	0.958
Phenols	0.598	-0.078	0.917	0.835	-0.090	0.975
$R_{M\ Diol}$ vs $R_{M\ Silica}$						
Amines	1.110	-0.351	0.919	1.033	-0.187	0.937
Phenols	0.219	0.335	0.205	0.363	-0.018	0.318
$R_{M\ CN}$ vs $R_{M\ Silica}$						
Amines	1.131	-0.473	0.912	0.998	-0.435	0.954
Phenols	0.190	0.147	0.197	0.147	-0.024	0.165
$R_{M\ CN}$ vs $R_{M\ Diol}$						
Amines	0.998	-0.114	0.971	0.906	-0.241	0.957
Phenols	0.578	0.012	0.746	0.701	-0.100	0.892

The selectivity of separation can be compared using $R_{M\ I}$ vs. $R_{M\ II}$ correlations. The retention parameters for amines and phenols obtained in all investigated systems are correlated for Diol- and silica, for CN- and silica and for CN- Diol-, respectively.

The parameters of correlation lines for phenols and amines are presented in Table 3 for all systems examined. The regression coefficients are rather low, especially for the bare silica and NP-bonded phases. It seems that the retention mechanisms on silica and modified silica are quite different in investigated eluent systems, especially for phenols (very low regression coefficients 0.201

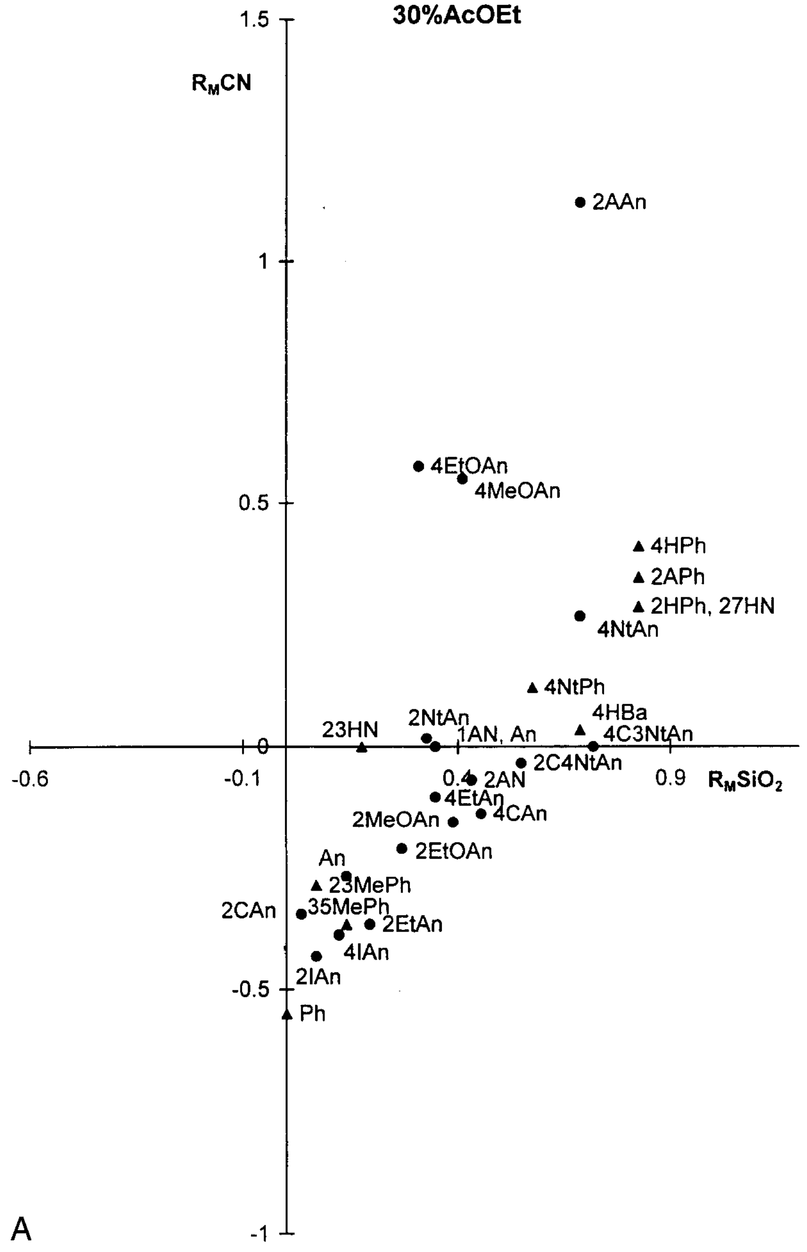


Figure 3A. Correlation between R_M values of phenols (solid triangles) and anilines (solid circles) on CN- and silica; mobile phase: ethyl acetate-n-heptane (3:7). For identification of solutes see Table 1.

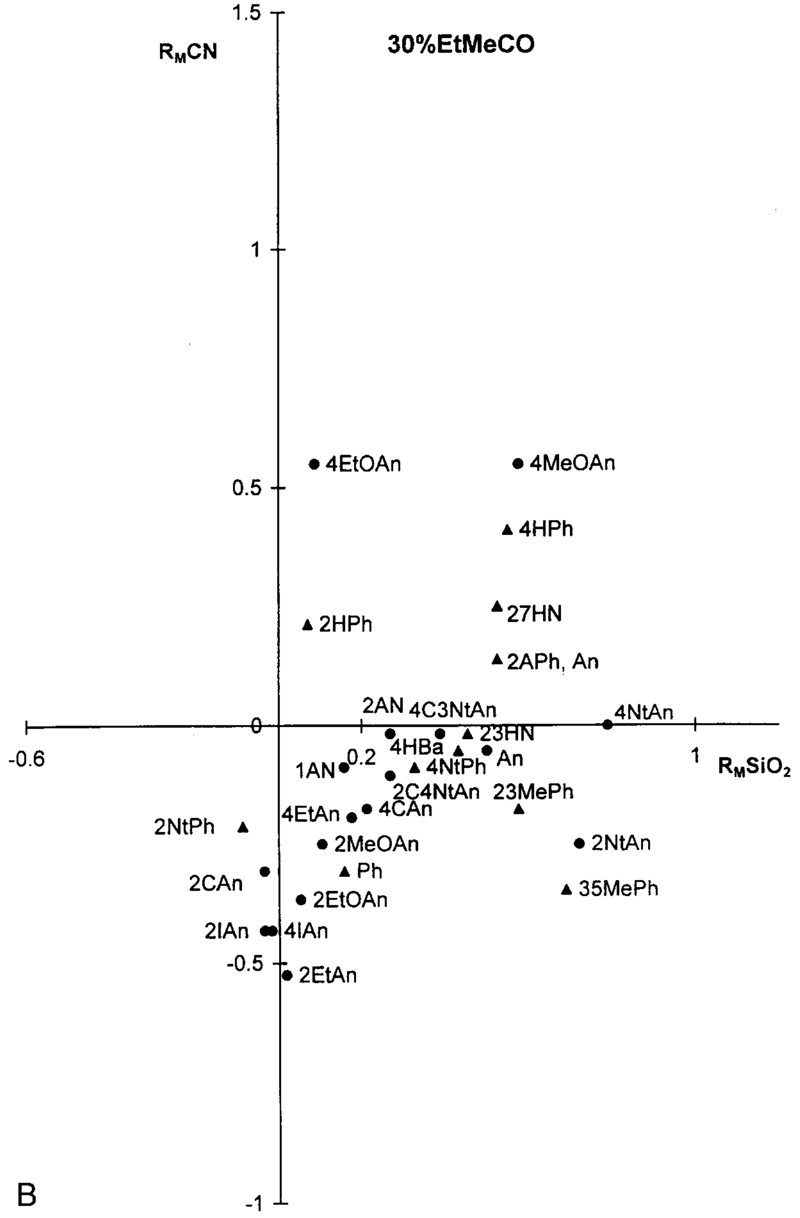


Figure 3B. Correlation between R_M values of phenols (solid triangles) and anilines (solid circles) on CN- and silica; mobile phase: ethyl methyl ketone-n-heptane (3:7). For identification of solutes see Table 1.

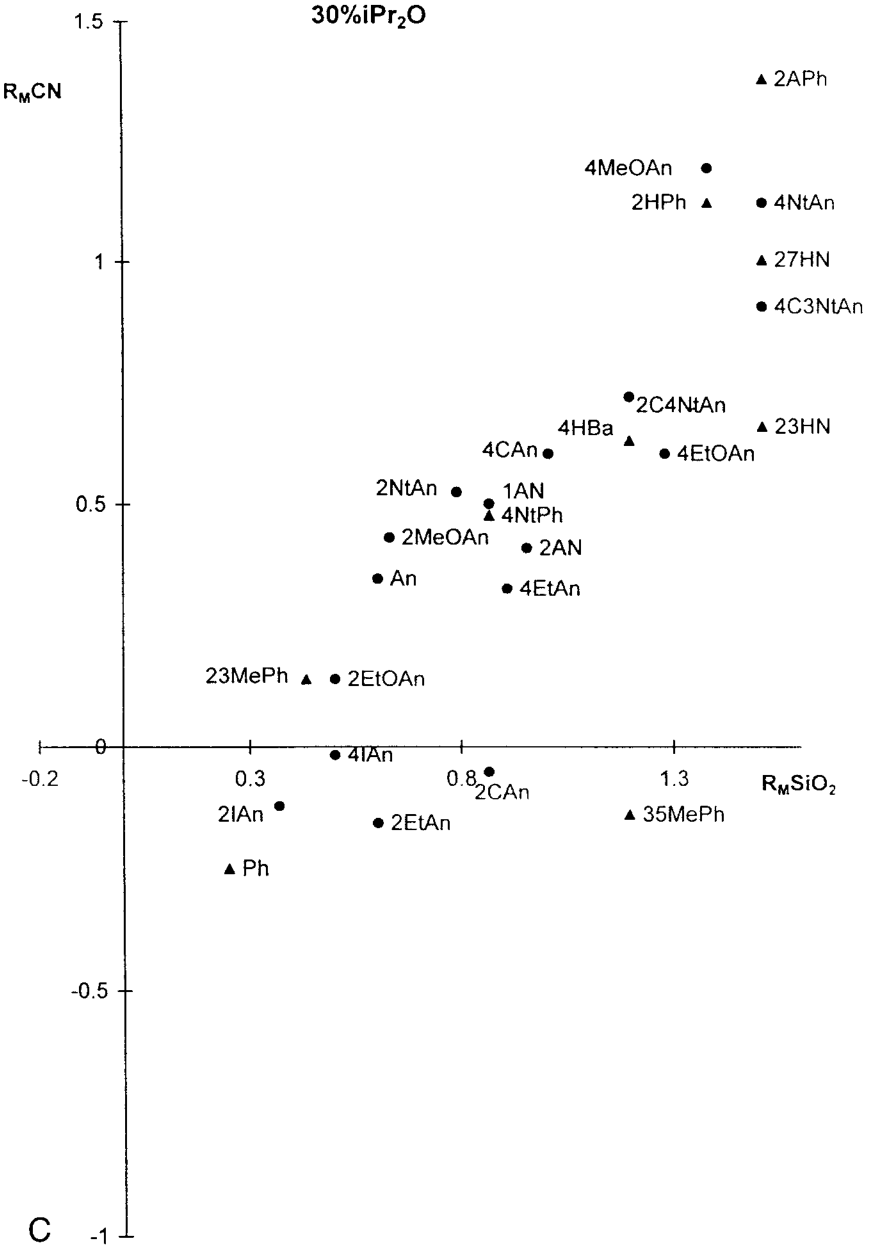


Figure 3C. Correlation between R_M values of phenols (solid triangles) and anilines (solid circles) on CN- and silica; mobile phase: diisopropyl ether - n-heptane (3:7). For identification of solutes see Table 1.

$\leq r \leq 0.841$). However, when NP-bonded phases are compared by the $R_{M\ CN}$ vs. $R_{M\ DIOL}$ relationship the regression coefficients are higher ($0.792 \leq r \leq 0.975$, in most cases higher than 0.9). It seems that the retention mechanisms on NP-bonded phases are similar.

The analysis of the slope values of $R_{M\ I}$ vs. $R_{M\ II}$ relationships gives some information about the choice of the best separation in the particular systems. For example, aromatic amines separate better on diol- than on silica, especially when 2-propanol, ethyl acetate, dioxane or tetrahydrofuran are used as modifiers (slope > 1.0). However, phenols are much better separated on silica layers when ethyl methyl ketone, dioxane, tetrahydrofuran are used as modifiers (slope < 1.0). When CN- and bare silica are compared, anilines are better separated on CN-silica than on silica when 2-propanol, ethyl acetate, dioxane are used as modifiers (slope > 1.0), but phenols are better separated on silica in the five eluent systems investigated (except system with 2-propanol).

Although the linear regression coefficients of $R_{M\ DIOL}$ vs. $R_{M\ CN}$ correlations are high, the slope values indicate better separation of phenols and anilines in CN-silica in almost all eluent systems (slope < 1.0) (see Table 3).

Detailed analysis of the selectivity of separation of investigated chromatographic systems is possible using $R_{M\ I}$ vs. $R_{M\ II}$ correlation diagrams. Figures 2 (A,B,C), 3 (A,B,C), and 4 (A,B) present $R_{M\ I}$ vs. $R_{M\ II}$ relationships in chosen eluent systems and compare diol- bare silica, CN-silica - bare silica and Diol - CN-, respectively. Figure 2 A shows $R_{M\ DIOL}$ vs. $R_{M\ silica}$ relationships in 2-propanol - n-heptane eluent system. Points are widely dispersed, which confirms differences in selectivity of separation on two compared surfaces of adsorbents. For instance, amines (solid circles) separated on silica in the range of 0.8 R_M units are eluted on diol- in a range of 1.5 units and phenols (solid triangles) in the range of 0.5 R_M unit on silica, and in 1.0 R_M unit on diol-phase. Some groups of phenols and anilines can be eluted together on silica systems and also separated on diol- phases. For example, 2CAn, 2NtAn, 4C3NtAn, 2AN or 4MeOAn, 4EtOAn, An, elute virtually identically on silica and can be separated using diol- phases. However, there are also some groups of solutes which preferentially separated on silica rather than on the diol-bonded phase. For example, 2IAn, 2ClAn, 2EtAn can be better separated on silica.

Figure 2B presents a $R_{M\ DIOL}$ vs. $R_{M\ Si}$ diagram using an ethyl acetate - n-heptane (3:7) mixture as the eluent. Similarly, amines eluted in a narrow range on silica of about 0.8 R_M units are separated in the range of about 1.7 R_M units on Diol-silica. For example, anilines such as 4EtOAn, 1AN, 2NtAn, 4EtAn, and phenols such as 2APh, 27HN, 2HPh, 4HBa which eluted in a narrow range on silica are well separated on a diol layer.

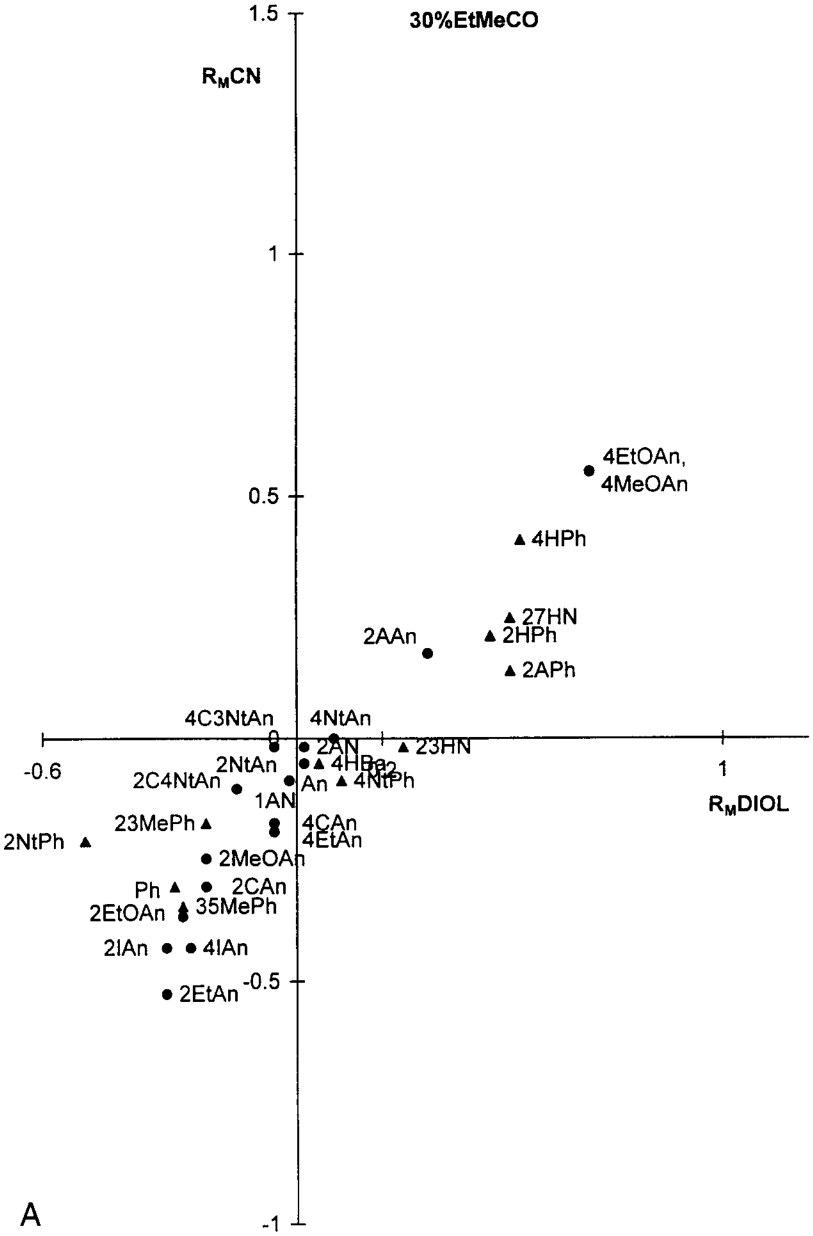


Figure 4A. Correlation between R_M values of phenols (solid triangles) and anilines (solid circles) on CN- and Diol-; mobile phase: ethyl methyl ketone - n-heptane (3:7). For identification of solutes see Table 1.

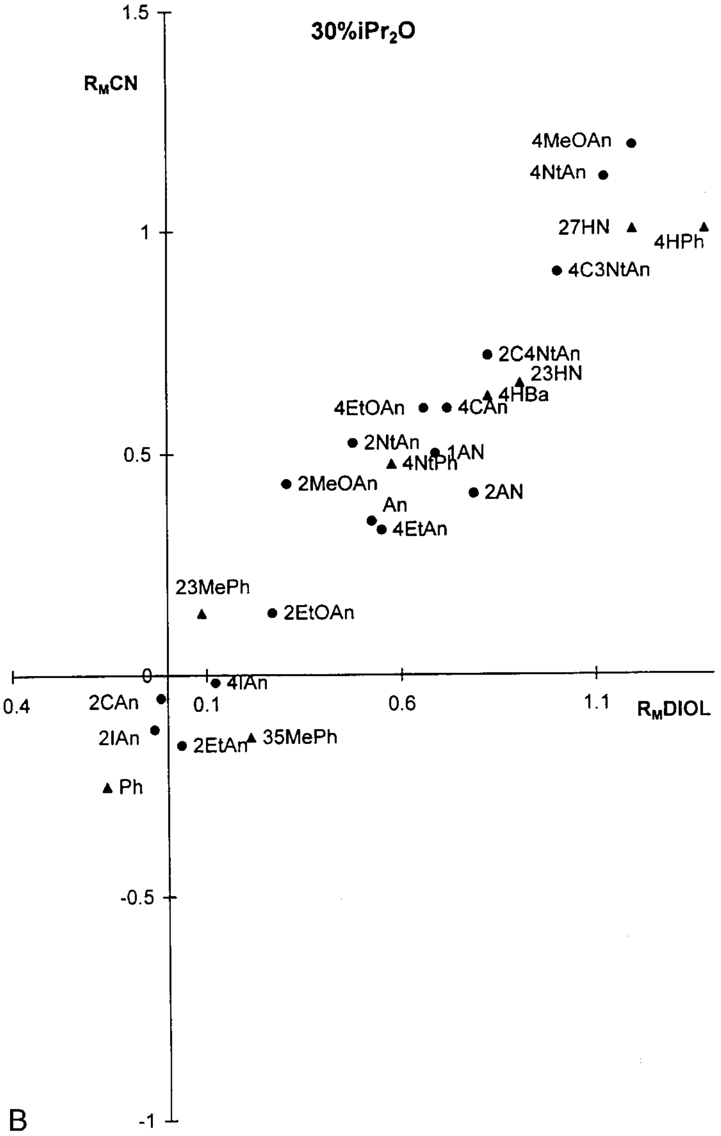


Figure 4B. Correlation between R_M values of phenols (solid triangles) and anilines (solid circles) on CN- and Diol-; mobile phasediisopropyl ether - n-heptane (3:7). For identification of solutes see Table 1.

Figure 2C presents a correlation diagram when dioxane is used as the modifier. Aniline points (solid circles) accumulate near a single correlation line with a relatively high regression coefficient (see Table 3). However, there are several examples of differences in selectivity of separation on the examined adsorbents (see pairs of 2CAn - 4CAn, 2MeOAn - 4MeOAn). The points of phenols (solid triangles) are strongly dispersed. Phenols such as 2HPh, 2HBa, 2NtPh, Ph or 27HN - 23HN and 4HBa, 4NtPh, 2APh eluted in a narrow ranges on silica and are better separated on diol-silica.

A similar situation is observed when the CN-silica and silica stationary phases are compared. The points of the $R_{M\ CN}$ vs. $R_{M\ Si}$ correlations are widely spread. Figures 3 (A,B,C) show the comparison of retention parameters obtained on CN-silica and bare silica using ethyl acetate (A), ethyl methyl ketone (B) or diisopropyl ether (C) as the more polar components of eluents. The points are strongly dispersed, which confirms different mechanisms of retention on CN- and silica. The R_M values of amines (solid circles) obtained on CN-silica are in the range of 1.6 R_M units and in the range of 0.7 R_M units on silica when ethyl acetate is used as the modifier (Figure 3A). R_M units on CN silica are in the range of 1.4 R_M units and in the range of about 1.0 R_M unit on silica when diisopropyl ether is used as modifier (Figure 3C). Individual differences in selectivity of separation using the two examined adsorbents have been observed. Phenols substituted with a second polar group (4HPh, 2APh, 27HN, 4HBa) separate better using CN-silica (Figure 3A). Similar results are obtained on diol-silica using ethyl acetate and ethyl methyl ketone as modifiers (see Figure 3B). Amines such as 2NtAn, 2MeOAn, 2EtAn eluted in a narrow range on silica in systems using ethyl acetate - n-heptane (Figure 3A) and diisopropyl ether - n-heptane (Figure 3C). These amines generally separate more effectively on CN-silica.

Figures 4A, B present diagrams correlating R_M parameters obtained for phenols and anilines on CN-silica and Diol-silica in ethyl methyl ketone - n-heptane (A) and diisopropyl ether-n-heptane (B) eluent systems. Points are accumulated near a single correlation line which confirms a similar retention mechanism on NP-bonded phases. This also suggests the similar character of diol- and CN-silica active sites, specifically centres of B type. However, there are some individual differences in the selectivity of separation on NP bonded phases.

CONCLUSIONS

1. Diol hydroxyl groups distanced about 0.154 nm, interacting with each other via H-bonds can behave like silica “bonded” hydroxyl groups - centres of B type. Chromatographic properties of diol-silca and CN-silca are similar.

2. The selectivity of the separation of pairs of *ortho* - *para* positional isomers, pairs of phenols and anilines substituted with the second group of moderate polarity (methoxy, ethoxy, aldehyde) is better on Diol- and also on CN- than on bare silica in investigated eluent systems.

3. The best separation of pairs of positional isomers substituted with the nonpolar groups - xylenols, ethylanilines, chloroanilines is obtained on CN-silica in most investigated eluent systems.

4. The type of polar group substituted on the molecule causes differences in interactions with diol as well as with CN ligands. Large differences in chromatographic parameters of phenols and anilines substituted with the second polar group ($-NH_2$, -OH, MeO-, EtO-, -CHO, $-NO_2$ and others) also result.

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