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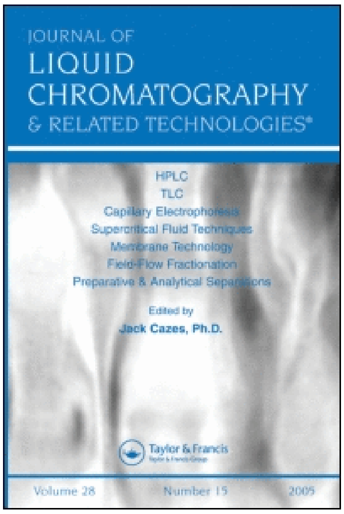

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ΔR_M as the Parameter Characterizing Chromatographic Properties of Polar Bonded Stationary Phases in Isoeluotropic Systems

Monika Waksmundzka-Hajnos[a]; Anna Hawrył[a]
[a] Department of Inorganic Chemistry, Faculty of Pharmacy, Medical University, Lublin, Poland

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ΔR_M as the Parameter Characterizing Chromatographic Properties of Polar Bonded Stationary Phases in Isoeluotropic Systems

Monika Waksmundzka-Hajnos* **and Anna Hawrył**

Department of Inorganic Chemistry, Faculty of Pharmacy,
Medical University, Lublin, Poland

ABSTRACT

Eluent strengths of binary eluents consisting of nonpolar diluent (*n*-heptane) and polar modifiers from various selectivity groups were used to obtain comparable eluent strengths in relation to monofunctional solutes: phenol, aniline, and quinoline on the layers of polar bonded stationary phases. In such optimised isoeluotropic eluents, retention factors of *para*-substitued phenols, aromatic amines, and some quinolines (with omitted 8- and 2-derivatives to eliminate effect *ortho*-) were measured chromatographically using plates precoated with NH_2-silica, diol-silica, and CN-silica. Differences in eluent strengths of polar modifiers (2-propanol, ethyl acetate, dioxane, tetrahydrofuran, acetone, methyl

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*Correspondence: Monika Waksmundzka-Hajnos, Department of Inorganic Chemistry, Faculty of Pharmacy, Medical University, Staszica 6, 20-081, Lublin, Poland; E-mail: mwaks@panaceum.am.lublin.pl.

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ethyl ketone, dichloromethane, and diisopropyl ether) depend on the electron-donor character of solute and type of stationary phase. Selectivity of separation was analysed by ΔR_M values and by R_M spectra. For the separation of phenols and aromatic amines, the most selective were aminopropyl phases for quinolines and cyanopropyl phases. Chromatographic properties of polar bonded stationary phases were analysed by means of $\Delta R_{M\,I}$ vs. $\Delta R_{M\,II}$ correlations.

Key Words: Polar bonded stationary phases; Phenols; Amines; Quinolines; HPTLC; Isoeluotropic eluents; ΔR_M.

INTRODUCTION

The retention factor in chromatography is the additive value, which results from the dependencies drawn by Martin et al.,[1] and Green and Marcinkiewicz,[2] who introduced term R_M relates also to $\log k$:

$$R_M = \log\left(\frac{1}{R_F} - 1\right) \tag{1}$$

where R_F is retardation factor.

However, the hypothesis of the additivity of R_M caused great discussion and, finally, it was Busch[3] who formulated additivity rules and indicated the following deviation reasons: complex character of chromatographic process (change of a composition and volume proportions of phases) and ionization of substances; constitutional effects in molecule, which is not a common sum of functional groups because of reciprocal interactions of these groups (internal hydrogen-bond effects, steric and electromeric effects).

Influence of all structural effects in partition chromatography was investigated, in a more detailed way, by Green and Marcinkiewicz.[4]

For the adsorption chromatography quantitative adsorption model, combining molecular structure and retention coefficient was worked out by Snyder[5,6] and derived as the relationship:

$$R_M = \log\left(\frac{V_a \cdot w}{v^0}\right) + \alpha(S^0 - A_s \cdot \varepsilon^0) + \Delta e_{as} \tag{2}$$

where V_a is the capacity of mono-layer on adsorbent surface; S^0, value of adsorption energy of molecule; w/v^0, ratio of the mass of adsorbent (g) to the solvent volume (mL); α, adsorbent activity; A_S, adsorbent surface occupied by molecule; ε^0, elution strength of solvent; Δe_{as} is the secondary effects of solvent, compound structure, and adsorbent surface.

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From Eq. (2), it is clearly seen that R_M value characterises the adsorption energy of molecule in a definite chromatographic system. ΔR_M defined as $R_{MAX} - R_{MA}$ characterises, also, the energy of adsorption and depends on the adsorbent and on the solute molecule.[5,7] The ΔR_M values for particular substituents can be taken into consideration as the energy parameter determining the adsorption of the functional group. ΔR_M parameters obtained in isoeluotropic eluents for *para*-substituted derivatives of compounds with the same properties (structural descriptors) to eliminate secondary effects of compounds' structure on the retention, define the adsorption energy of particular substituents. By comparison of ΔR_M obtained in isoeluotropic eluents with the unified elution strength of solvent, adsorbent properties, and activity can be anticipated.

Salotto et al.[7] have compared relative retention on polar bonded stationary phases with dichloromethane–*n*-heptane eluents for monofunctional solutes in comparison to suitable aromatic hydrocarbons as ΔR_M vs. ΔR_M correlations. They performed linear regressions for all monofunctional analytes on polar bonded columns, separately, for electronodonor and dipolar compounds. They concluded increased retention of electrondonor, as well as, protondonor compounds on the amino column in comparison to the cyano column, and increased retention of dipolar compounds on the cyano column in comparison to diol. On the basis of the experiments, it appears that basic and acidic solutes are preferentially retained by the amino phase and dipolar solutes are preferentially retained by the cyano phase, whereas the diol phase exhibits intermediate properties.

In our previous paper[8] silica, alumina, and magnesium silicate (Florisil) stationary phases were compared by ΔR_M vs. ΔR_M correlations obtained for aniline, phenol, and quinoline substituted with various functional groups in isoeluotropic eluents. It was concluded that adsorption energy depends not only on the character of a functional group but also on the chemical character of the substituted molecule. Linear relationships of ΔR_M vs. ΔR_M correlations for substituted anilines and heterocyclic bases prove there is similarity of acidic surface active centres on alumina and silica, and for substituted anilines, phenols, and heterocyclic bases prove the similarity of surface active centres on silica and Florisil surfaces. Similar comparison of ΔR_M vs. ΔR_M nonlinear correlations for phenols on alumina and Florisil prove that O^{2-} ions, which determine retention of proton-donor substances on alumina surface, are absent from Florisil surfaces. However, similarity in adsorption of heterocyclic bases and anilines with predominantly electrondonor properties, reveals similarities between acidic centres on alumina (Al^{3+} ions and OH groups) and Florisil (Mg^{2+} ions and OH groups).

The aim of this work was the comparison of ΔR_M values of bifunctional solutes: *para*-substituted anilines, phenols, and quinolines in isoeluotropic

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binary eluents. Binary mixtures of *n*-heptane and solvents from different selectivity classes, such as 2-propanol, dioxane, tetrahydrofuran, ethyl acetate, ethylmethyl ketone, acetone, diisopropyl ether, and dichloromethane, were used as mobile phases to obtain equal retention of phenol, aniline, and quinoline to choose the effect of modifier. ΔR_M vs. ΔR_M correlation enables comparison of surface active sites on polar bonded stationary phases' surfaces.

EXPERIMENTAL

Thin layer chromatography was performed on 10 × 10 cm glass diol F_{254}, CN F_{254}, and NH_2 F_{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 solutions of the solutes in methanol were spotted to the adsorbent layer. Plates were conditioned for 15 min in eluent vapours to eliminate the demixing effect, and developed face-down to a distance of 8 cm from the origin at 20°C ± 1°C. Binary mixtures of polar modifiers: 2-propanol (*i*PrOH), ethyl acetate (AcOEt), ethyl methyl ketone (MEK), dioxane (DX), tetrahydrofuran (THF), acetone (Me_2CO), diisopropyl ether (*i*Pr_2O), or dichloromethane (DCM) with *n*-heptane (H) as diluents were used as mobile phases. Solvents were analytical grade from Polish Reagents (POCh, Gliwice, Poland). Table 1 lists some properties of the solvents investigated.

The *para* derivatives of the phenols, aromatic amines, and heterocyclic bases listed in Table 2, were chromatographed as model solutes. The location of the spots was determined under UV light ($\lambda = 254$ nm). In all cases, the spots were symmetric and did not exhibit tailing. R_F coefficients (average from three measurements) were predicted with standard error $\sigma \leq 4 \times 10^{-4}$).

RESULTS AND DISCUSSION

The measurements were carried out on thin layers of cyanopropyl, diol, and aminopropyl-silica. The eluent strength of binary mixture, polar modifier–*n*-heptane, was selected to obtain the value of capacity factor *k* about 1 for phenol, quinolone, and aniline analogously, as was proposed by Saunders.[9] The isoeluotropic series for phenol, for aniline, and for quinolone, obtained for various adsorbents and solvents from different groups of selectivity, are presented in Tables 3–5. The differences in eluotropic series for phenol, aniline, and quinoline are noticeable, which indicate various eluent strengths on investigated adsorbents. The solvation effects are the result of competing interactions: modifier–solute–surface active sites. It is often

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Table 1. Some properties of the solvents investigated.

No.	Name	Abbreviation	μ^a (D)	η^b (cP)	ρ^c (g cm^{-3})	Solubility parameters[d] δ	δ_d	δ_0	δ_a	δ_h	Boiling point (°C)[e]
1	2-Propanol	*i*PrOH	1.66	2.40	0.785	10.2[f]	7.2[f]	2.5[f]	4[f]	4[f]	82.3
2	Dioxane	DX	0.45	1.37	1.034	9.8	7.8	4	3	0	101.3
3	Tetrahydrofuran	THF	1.75	0.55	0.889	9.1	7.6	4	3	0	66.0
4	Ethyl acetate	AcOEt	1.82	0.45	0.902	8.6	7.0	3	2	0	77.1
5	Ethyl methyl ketone	MEK	2.86	0.43	0.718	—	—	—	—	—	79.6
6	Acetone	Me_2CO	2.69	0.36	0.791	9.4	6.8	5	2.5	0	56.3
7	Diisopropyl ether	iPr_2O	1.22	0.37	0.725	7.0	6.9	0.5	0.5	0	68.3
8	Dichloromethane	DCM	1.14	0.44	1.325	9.6	6.4	5.5	0.5	0	39.7
9	*n*-Heptane	H	0.00	0.40	0.684	7.4	7.4	0	0	0	98.0

[a] Dipole moment: internet.

[b] Viscosity.

[c] Density: Aldrich Catalogue 1996/97.

[d] δ, solubility parameter; δ_d, dispersion solubility parameter; δ_a, proton-acceptor solubility parameter; δ_h, proton-donor solubility parameter.

[e] Aldrich Catalogue 1996/97.

[f] Data for 1-propanol.

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Table 2. The compounds investigated.

No.	Name	Symbol	Type of polar group
Phenols			
1	Phenol	Ph	AB
2	4-Bromophenol	4BrPh	AB
3	4-Iodophenol	4IPh	AB
4	4-Chlorophenol	4ClPh	AB
5	4-Nitrophenol	$4NO_2Ph$	AB, AB
6	4-Aminophenol	$4NH_2Ph$	AB, AB
7	4-Ethylphenol	4EtPh	AB
8	4-Methylphenol	4MePh	AB
Anilines			
1	Aniline	An	AB
2	4-Iodoaniline	4IAn	AB
3	4-Bromoaniline	4BrAn	AB
4	4-Nitroaniline	4NtAn	B, AB
5	4-Aminoaniline	$4NH_2An$	AB, AB
6	4-Ethylaniline	4EtAn	AB
7	4-Methylaniline	4MeAn	AB
8	4-Methoxyaniline	4MeOAn	AB, B
Quinolines			
1	Quinoline	Q	B
2	5-Aminoquinoline	$5NH_2Q$	B, AB
3	4-Hydroxyquinoline	4OHQ	B, AB
4	6-Nitroquinoline	$6NO_2Q$	B, B
5	5-Hydroxyquinoline	5OHQ	B, AB

accompanied by displacement of modifier molecules from the monolayer adsorbed on the surface's active centres, or with co-adsorption of solute molecules on the film of polar modifier.[10–12] Also, the proton donor–acceptor properties and polarity of the solvent determine the differences in eluent strengths of polar solvents. It should be mentioned that in relation to aniline, solvents from B group[13] such as tetrahydrofuran, ethyl acetate, ethylmethyl ketone, and diisopropyl ether have equal eluent strength. Isopropanol, from group AB with predomination of acidic properties, has equal eluent strength on all polar bonded phases examined in the case of quinoline. In the case of phenol dichloromethane, solvent from group A, has the same eluent strength on all polar bonded phases. However, the same eluent strength was still obtained for tetrahydrofuran, ethyl acetate, and acetone on CN- and diol-phases. It is noticeable, that in most cases, phenol and its derivatives are

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Table 3. ΔR_M ($R_{M(PhX)}$-$R_{M(Ph)}$) values for *p*-substituted phenols in isoeluotropic mobile phases.

CN functional group	25% *i*PrOH	30% Dx	25% THF	30% AcOEt	30% MEK	40% Me_2CO	60% *i*Pr_2O	80% DCM
Br	−0.04	0.00	0.00	0.00	0.00	−0.04	0.035	0.19
I	0.07	0.18	−0.14	−0.02	−0.02	−0.07	−0.16	0.017
Cl	0.07	0.14	−0.11	−0.05	−0.05	−0.07	−0.16	0.02
NH_2	1.06	1.02	1.02	1.12	0.57	0.82	0.59	1.06
NO_2	0.30	0.59	0.18	0.21	0.14	0.05	0.03	0.21
CH_3	0.04	0.07	−0.11	−0.05	−0.02	−0.07	−0.16	0.02
C_2H_5	0.00	0.02	−0.25	−0.05	−0.05	−0.07	−0.16	0.02
Diol functional group	20% *i*PrOH	25% Dx	25% THF	30% AcOEt	25% MEK	40% Me_2CO	55% *i*Pr_2O	80% DCM
Br	0.00	0.09	0.12	0.00	−0.03	0.00	0.00	0.33
I	0.07	0.35	0.46	0.10	0.16	0.00	0.29	0.35
Cl	0.07	0.27	0.29	0.10	0.02	0.00	0.12	0.16
NH_2	1.09	1.18	1.36	0.88	0.91	1.02	1.40	0.94
NO_2	0.19	0.70	0.64	0.36	0.23	0.00	0.41	0.51
CH_3	0.04	0.23	0.37	0.10	0.05	0.00	0.16	0.27
C_2H_5	0.04	0.20	0.25	0.07	0.09	0.00	0.12	−0.02
NH_2 functional group	30% *i*PrOH	25% Dx	40% THF	50% AcOEt	50% MEK	50% Me_2CO	100% *i*Pr_2O	80% DCM
Br	0.19	0.36	0.34	0.63	0.34	0.09	0.64	0.35
I	0.38	1.11	0.67	0.23	0.44	0.20	0.81	0.46
Cl	0.19	0.65	0.46	0.16	0.23	0.00	0.33	0.06
NH_2	0.88	1.25	1.04	0.96	0.63	0.26	0.99	0.46
NO_2	0.95	1.43	1.04	0.60	0.92	0.70	0.99	0.72
CH_3	0.12	0.71	0.46	0.00	0.17	0.00	0.41	0.17
C_2H_5	0.12	0.51	0.41	−0.04	0.07	−0.23	0.25	−0.11

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Table 4. ΔR_M ($R_{M(AnX)}$-$R_{M(An)}$) values for *p*-substituted amines in isoeluotropic mobile phases.

CN functional group	25% *i*PrOH	30% Dx	25% THF	30% AcOEt	30% MEK	40% Me_2CO	60% *i*Pr_2O	80% DCM
Br	−0.04	0.00	0.00	0.00	0.00	−0.04	0.035	0.19
I	0.07	0.18	−0.14	−0.02	−0.02	−0.07	−0.16	0.017
Cl	0.07	0.14	−0.11	−0.05	−0.05	−0.07	−0.16	0.02
NH_2	1.06	1.02	1.02	1.12	0.57	0.82	0.59	1.06
NO_2	0.30	0.59	0.18	0.21	0.14	0.05	0.03	0.21
CH_3	0.04	0.07	−0.11	−0.05	−0.02	−0.07	−0.16	0.02
C_2H_5	0.00	0.02	−0.25	−0.05	−0.05	−0.07	−0.16	0.02
Diol functional group	**20% *i*PrOH**	**25% Dx**	**25% THF**	**30% AcOEt**	**25% MEK**	**40% Me_2CO**	**55% *i*Pr_2O**	**80% DCM**
Br	0.00	0.09	0.12	0.00	−0.03	0.00	0.00	0.33
I	0.07	0.35	0.46	0.10	0.16	0.00	0.29	0.35
Cl	0.07	0.27	0.29	0.10	0.02	0.00	0.12	0.16
NH_2	1.09	1.18	1.36	0.88	0.91	1.02	1.40	0.94
NO_2	0.19	0.70	0.64	0.36	0.23	0.00	0.41	0.51
CH_3	0.04	0.23	0.37	0.10	0.05	0.00	0.16	0.27
C_2H_5	0.04	0.20	0.25	0.07	0.09	0.00	0.12	−0.02
NH_2 functional group	**30% *i*PrOH**	**25% Dx**	**40% THF**	**50% AcOEt**	**50% MEK**	**50% Me_2CO**	**100% *i*Pr_2O**	**80% DCM**
Br	0.19	0.36	0.34	0.63	0.34	0.09	0.64	0.35
I	0.38	1.11	0.67	0.23	0.44	0.20	0.81	0.46
Cl	0.19	0.65	0.46	0.16	0.23	0.00	0.33	0.06
NH_2	0.88	1.25	1.04	0.96	0.63	0.26	0.99	0.46
NO_2	0.95	1.43	1.04	0.60	0.92	0.70	0.99	0.72
CH_3	0.12	0.71	0.46	0.00	0.17	0.00	0.41	0.17
C_2H_5	0.12	0.51	0.41	−0.04	0.07	−0.23	0.25	−0.11

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Table 5. ΔR_M ($R_{M(QX)}$-$R_{M(Q)}$) values for *p*-substituted quinolines in isoeluotropic mobile phases.

CN functional group	20% *i*PrOH	25% Dx	25% THF	20% AcOEt	25% MEK	40% Me_2CO	80% *i*Pr_2O	60% DCM
$5NH_2$	0.09	1.23	1.23	1.67	0.83	0.79	1.60	1.21
4OH	1.09	0.55	0.55	0.12	−0.14	0.58	—	1.78
$6NO_2$	0.39	0.09	0.09	0.37	0.07	0.42	0.37	1.57
5OH	0.30	0.67	0.67	1.36	0.57	0.94	1.42	0.91
Diol functional group	20% *i*PrOH	30% Dx	40% THF	30% AcOEt	35% MEK	50% Me_2CO	100% *i*Pr_2O	70% DCM
$5NH_2$	1.62	—	1.02	1.02	—	1.02	—	1.67
4OH	0.99	1.71	1.40	1.40	1.36	1.14	—	—
$6NO_2$	0.36	−0.03	−0.03	−0.03	−0.03	−0.07	1.57	0.70
5OH	0.32	0.68	0.68	0.68	0.53	−0.03	0.23	—
NH_2 functional group	20% *i*PrOH	15% Dx	35% THF	30% AcOEt	30% MEK	40% Me_2CO	70% *i*Pr_2O	60% DCM
$5NH_2$	0.42	1.60	0.45	0.10	0.82	0.45	—	0.44
4OH	1.41	—	—	0.27	—	—	0.14	1.23
$6NO_2$	0.07	−0.17	0.33	0.27	0.07	0.00	0.16	0.10
5OH	0.28	0.46	0.95	1.04	1.04	0.60	0.35	1.23

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more strongly adsorbed on the aminopropyl layer and need higher concentration of modifiers (in seven for eight cases) to obtain the same eluent strength in relation to phenol, in comparison to CN- and diol-silica.

However, the mixtures of comparable eluent strength have different selectivity of separation, which the Snyder's Eq. (2) indicates[5,6] (where S and A are parameters depending on chromatographed solutes). The selectivity of separation in isoeluotropic eluents was also compared for phenols, for anilines, and for heterocyclic bases as ΔR_M values. It can be noticed, that for phenols the highest ΔR_M values are obtained on the aminopropyl layer, especially when dioxane as an eluent modifier was used (see Tables 3–5). Similarly, for aromatic amines, the highest ΔR_M values are obtained on the aminopropyl layer, in the case when acetone or diisopropyl ether as eluent modifiers were used. For quinoline bases, the most selective system is CN-silica/dichloromethane. Selectivity of separation can be read over the R_M spectra presenting separation selectivity in isoeluotropic systems examined for phenols, anilines, and quinoline bases. From the diagrams, the systems with the highest selectivity of separation of particular groups of substances can be found (see Figs. 1–3). For example, aromatic amines are most selectively separated on aminopropyl-silica layers, especially with diisopropyl ether and 2-propanol as eluent modifiers (see Fig. 1C). From the spectra presented for amines on CN-silica, eluent systems with dioxane, and diol eluent systems with 2-propanol and ethyl acetate as the most selective are perceptible (Fig. 1A and B). From the next diagram for phenols, it is clearly seen that all nonpolar phenols are practically eluted together on the cyanopropyl layer (see Fig. 2A). The most selective are diol layers with the eluents containing tetrahydrofuran or dioxane, as well as aminopropyl layers with the eluents containing ethylmethyl ketone or dioxan as eluent modifiers. The separation selectivity for quinolines are presented in Fig. 3. It is seen from the spectra, that the most selective for the separation of quinoline bases are cyanopropyl layers, especially with 2-propanol, ethyl acetate, diisopropyl ether, or dichloromethane as eluent modifiers.

Retention mechanisms in different chromatographic systems can be compared by $\Delta R_{M\,I}$ vs. $\Delta R_{M\,II}$ correlation diagrams. Table 6 presents parameters of correlation lines $\Delta R_{M\,I}$ vs. $\Delta R_{M\,II}$ for investigated groups of compounds in the chromatographic systems examined.

When CN- and diol-silica are compared, it is seen that the linear equation $\Delta R_{M\,CN} = a\Delta R_{M\,Diol} + b$ has quite different parameters for particular groups of substances. There are only few cases when regression coefficient R is higher than 0.9. However, for amines, F-statistic values in most cases are higher than F critical, which prove a good correlation and similarity of retention mechanisms of aromatic amines on cyanopropyl and diol phases. It means, that the adsorption energies on CN- and diol-silica for particular functional groups

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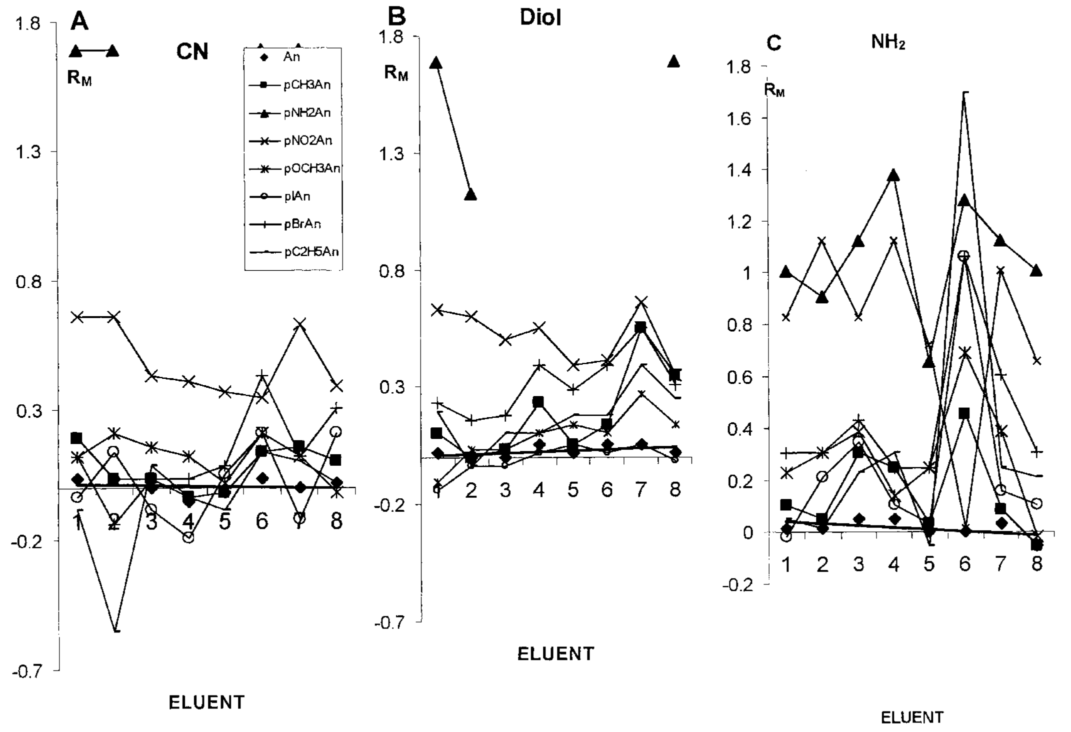

Figure 1. Graphical comparison of R_M values obtained for anilines (see Table 2) in following chromatographic systems: A, CN-silica; B, diol-silica; C, NH_2-silica; isoeluotropic eluents with modifiers: 1, IPrOH; 2, DX; 3, THF; 4, AcOEt; 5, MEK; 6, Me_2CO; 7, iPr_2O; 8, DCM in *n*-heptane, concentrations as in Table 3.

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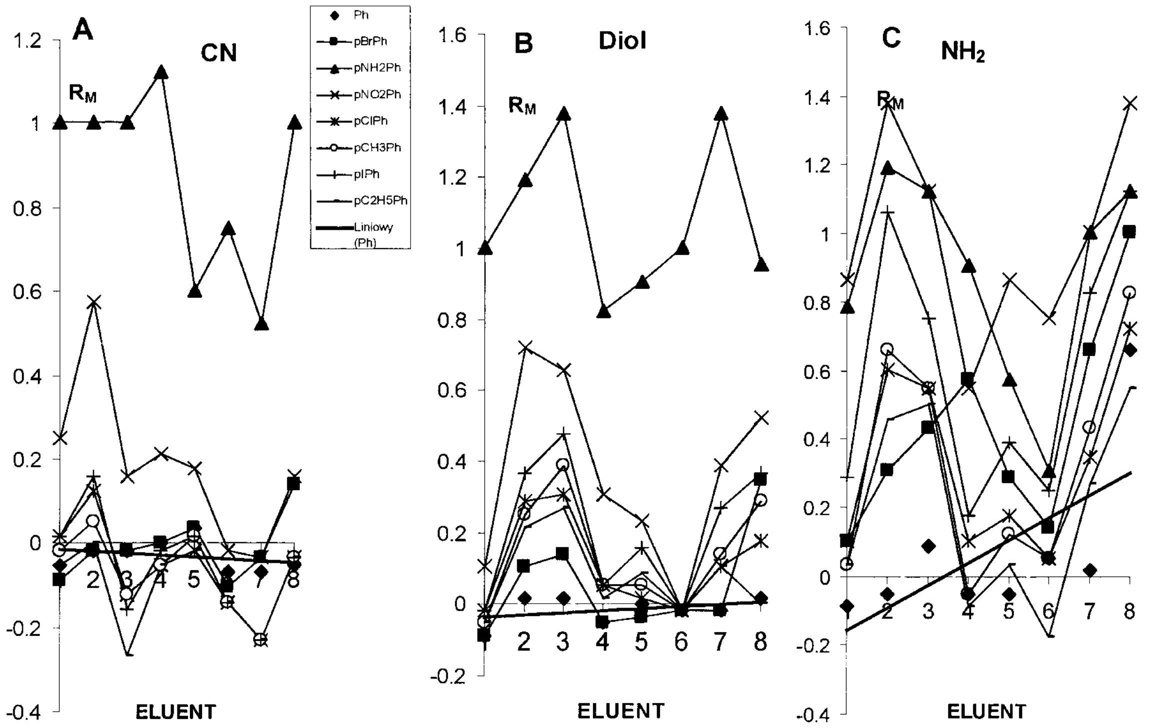

Figure 2. Graphical comparison of R_M values obtained for phenols (see Table 2) in following chromatographic systems: A, CN-silica; B, diol-silica; C, NH_2-silica; isoeluotropic eluents with modifiers: 1, IPrOH; 2, DX; 3, THF; 4, AcOEt; 5, MEK; 6, Me_2CO; 7, *i*Pr_2O; 8, DCM in *n*-heptane, concentrations as in Table 3.

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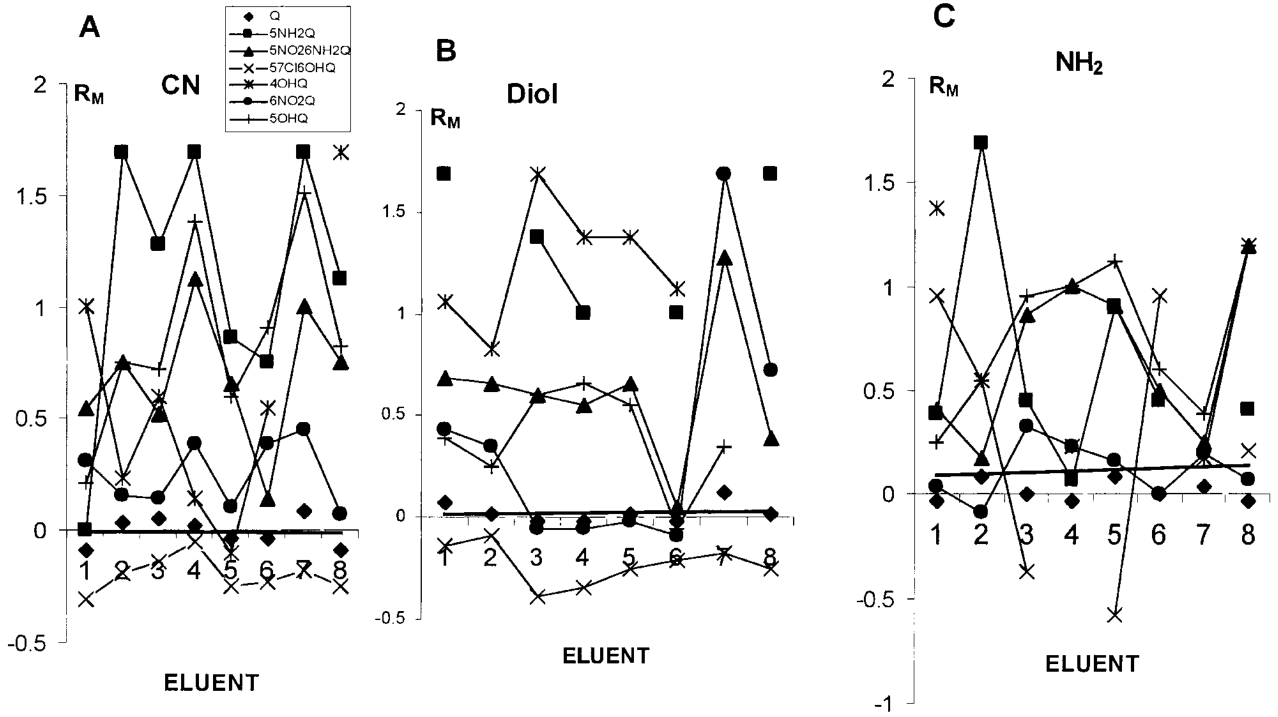

Figure 3. Graphical comparison of R_M values obtained for quinolines (see Table 2) in following chromatographic systems: A, CN-silica; B, diol-silica; C, NH_2-silica; isoeluotropic eluents with modifiers: 1, IPrOH; 2, DX; 3, THF; 4, AcOEt; 5, MEK; 6, Me_2CO; 7, *i*Pr_2O; 8, DCM in *n*-heptane, concentrations as in Table 3.

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substituted to aniline molecule are similar. This is due to similar surface active centres of these adsorbents, cyano groups on the CN-silica surface and diol ligands on diol-silica, in both cases electron-donor sites[14] strongly interacting with amine NH_2 groups (class AB with predominating basic properties). However, the situation is quite different when the functional groups are substitued to heterocyclic bases. The correlation points are strongly dispersed and regression coefficients in all cases are low ($R < 0.66$). It indicates various adsorption mechanisms of compounds of class B (heterocyclic bases), which are adsorbed on CN- and diol-silica acidic centres. Dissimilarity is also confirmed by low F-statistic values and high values of standard error. For phenols, substances of class AB with predomination of acidic properties, regression coefficients for $\Delta R_{\mathrm{M\,Diol}}$ vs. $\Delta R_{\mathrm{M\,CN}}$ correlations are, in most cases, relatively low. However, F-statistic values in three cases are above F-critical. Thus, it can be concluded there are certain similarities of retention mechanism of phenols on both investigated phases.

The lines of $\Delta R_{\mathrm{M\,NH2}}$ vs. $\Delta R_{\mathrm{M\,CN}}$ correlations have, in most cases, low regression coefficients (there are two out of 23 cases when $r > 0.9$) for all investigated groups of substances. However, in some cases, F-statistic values prove the linearity of $\Delta R_{\mathrm{M\,NH2}}$ vs. $\Delta R_{\mathrm{M\,CN}}$ correlations in four cases for phenols, in four cases for amines, and in two cases for quinolines. This indicates similar energies of adsorption of functional groups on active sites of CN-silica and NH_2-silica.

The comparison of energies of adsorption on surface active centres of NH_2- and diol also gives interesting observations. The data show that the correlation points $\Delta R_{\mathrm{M\,NH2}}$ vs. $\Delta R_{\mathrm{M\,Diol}}$ for quinolines and amines do not form linear relationships, and regression coefficients are relatively low because of dissimilar mechanisms of adsorption of quinoline bases and aromatic amines, with predomination of electrondonor properties on active sites of aminopropyl and diol phases. F-statistic values prove these conclusions, because only three out of eight cases for amines and in all cases for quinolines are below F-critical values. The adsorption of phenols on both layers is, however, similar, which is indicated by F-statistic values (in five out of eight cases higher than F-critical). It proves the similarity of basic centres of both phases.

The $\Delta R_{\mathrm{M\,I}}$ vs. $\Delta R_{\mathrm{M\,II}}$ relationships permit estimation of the influence of polar solvents on energy of adsorption of functional groups on individual adsorbents. When correlations are linear with relatively high regression coefficients and F-statistic values $>$ F-critical, conclusions about the influence of modifiers on the energy of adsorption of investigated derivatives can be formulated. Such a condition for $\Delta R_{\mathrm{M\,Diol}}$ vs. $\Delta R_{\mathrm{M\,CN}}$ relationships is fulfilled for amines and, in some cases, for phenols. Low values of slopes of correlation lines indicate high adsorption energies on CN layers for investigated compounds and, on the contrary, mean a strong solvation effect of solute by

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modifier and its strong elution from diol-silica in a given eluent system. For phenols, the strong solvation effect and elution from diol-silica is shown for MEK and dioxane. 2-propanol, tetrahydrofuran, and ethyl acetate have similar elution properties for both adsorbents. For phenols, the strong solvation effect and elution from diol-silica is shown for 2-propanol, dioxane, and acetone.

For correlations of $\Delta R_{\mathrm{M\,NH2}}$ vs. $\Delta R_{\mathrm{M\,CN}}$, high F-values were obtained for phenols, and anilines in some cases. Therefore, solvation and adsorption effects for these substances in some eluent systems can be discussed. For these correlations, low slope values of lines prove high adsorption energies of individual functional groups on CN-silica, but stronger elution from the aminopropyl surface. Low slope values for ΔR_{M} correlation lines for phenols were obtained for ethyl acetate, 2-propanol, tetrahydrofuran, and dioxane as modifiers. This confirms strong elution with these solvents in systems with NH_2-silica. Low slope values for amines are obtained for 2-propanol, dioxane, diisopropyl ether, indicating high solvation of these solvents from aminopropyl phases.

When adsorption energies of substituents on NH_2-silica and diol phases were compared, poor correlations of $\Delta R_{\mathrm{M\,NH2}}$ vs. $\Delta R_{\mathrm{M\,Diol}}$ relationships for amines but good ones for phenols with relatively high F-statistic values, were obtained. Adsorption energies of phenols are, in most cases, higher on diol phases, slope values are low ($a < 1$).

Taking into account $\Delta R_{\mathrm{M\,I}}$ vs. $\Delta R_{\mathrm{M\,II}}$ linear relationships, stronger adsorption of functional groups of phenols on CN in comparison to diol and NH_2-silica, and of substituents of amines on CN-silica in comparison to diol phases in most investigated isoeluotropic eluent systems, can generally be confirmed.

CONCLUSIONS

Differences in eluent strengths of polar modifiers (2-propanol, ethyl acetate, dioxane, tetrahydrofuran, acetone, methyl ethyl ketone, dichloromethane, and diisopropyl ether) depends on the electron-donor character of solutes and types of stationary phases.

Selectivity of separation can be analysed by ΔR_{M} values and by R_{M} spectra. For the separation of phenols and aromatic amines, the most selective were aminopropyl phases, for quinolines, cyanopropyl phases are used.

Chromatographic properties of polar bonded stationary phases were analysed by means of $\Delta R_{\mathrm{M\,I}}$ vs. $\Delta R_{\mathrm{M\,II}}$ correlations. High F-statistic values for $\Delta R_{\mathrm{M\,Diol}}$ vs. $\Delta R_{\mathrm{M\,CN}}$, $\Delta R_{\mathrm{M\,NH2}}$ vs. $\Delta R_{\mathrm{M\,Diol}}$, and $\Delta R_{\mathrm{M\,NH2}}$ vs. $\Delta R_{\mathrm{M\,CN}}$ correlations for substances from the AB group (aromatic amines and phenols) in most cases confirm similarity of surface electrondonor centres on surfaces of polar bonded stationary phases.

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