



ELSEVIER

Journal of Chromatography A, 915 (2001) 35–42

JOURNAL OF
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Selectivity of amino-, cyano- and diol-bonded silica in reversed-phase liquid chromatography

In Whan Kim^a, Hyun Sook Lee^b, Young Kyu Lee^b, Myung Duk Jang^c, Jung Hag Park^{b,*}

^aDepartment of Chemistry Education, Taegu University, Kyongsan 712-714, South Korea

^bDepartment of Chemistry and Institute of Basic Science, Yeungnam University, 214-1 Daedong, Kyongsan 712-749, South Korea

^cDepartment of Environmental Engineering, Andong Info Tech, Andong 762-830, South Korea

Received 13 November 2000; received in revised form 11 January 2001; accepted 29 January 2001

Abstract

Amino-, cyano- and diol-bonded silica stationary phases were characterized by estimating their characteristic interaction constants in reversed-phase liquid chromatography (RPLC) based on linear solvation energy relationships. Five characteristic interaction constants of the stationary phases, the hydrophobicity (v), polarizability (r), dipolarity (s), hydrogen bond (HB) acceptor basicity (a) and HB donor acidity strength (b) were determined by multiple regression analyses of logarithmic retention factors (k) for a set of test solutes measured on them in 10% (v/v) methanol–water vs. the solute properties represented by characteristic molecular volume (V_x), excess polarization (R_2), dipolarity/polarizability (π^*), HB donor acidity (α) and HB acceptor basicity (β). Magnitudes of the five constants for the phases in RPLC were compared with those in normal-phase LC to see the differences in chromatographic selectivity in the two LC modes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Stationary phases, LC; Linear solvation energy relationships; Hydrophobicity; Polarizability; Dipolarity; Hydrogen bond acceptor basicity; Hydrogen bond donor acidity

1. Introduction

Practicing chromatographers have noted the significant differences in retention characteristics among stationary phases having the same bonded functionalities [1,2]. This variability comes naturally since the retention in RPLC is determined by both non-specific and specific, chemical interactions undergoing between the solute molecule and the interactive sites of the stationary phase. These involve not only

nonspecific interactions between solute molecules and the organic bonded phase but also hydrogen bonding interactions with unreacted silanol groups and complexation with trace metals on the silica surfaces [3,4]. Relative contribution of these two types of interactions depends on the characteristics of the stationary phase, which include the nature of base silica particle such as the specific surface area and pore size and volume, the nature of bonded organic ligand, and the bonding process.

The heterogeneous nature of the bonded stationary phases makes them difficult to study. In addition, different mobile phases will solvate the stationary phase to different extents [5–8]. Therefore, the

*Corresponding author. Tel.: +82-53-810-2360; fax: +82-53-811-3141.

E-mail address: jhpark@yu.ac.kr (J.H. Park).

characteristics of those solvated surface phases need to be considered in order to obtain a more complete understanding of bonded-phase chromatography. Characterization of solvated stationary phases can be performed by either chromatographic or by spectroscopic measurements. A good summary of chromatographic methods can be found in a recent book by Unger [9]. Recently, the linear solvation energy relationship (LSER) [10,11] and Kamlet–Taft solvatochromic parameters have been used to characterize the stationary phases used in normal and reversed-phase LC. Park and co-workers [12–14] correlated retention factors of a set of test compounds on a number of stationary phases having variegated types of bonded moieties vs. solutes' parameters based on LSER. From the coefficients obtained from multiple linear regression analyses, they determined the so-called “characteristic interaction constants” for the stationary phases, which measure the phases' lipophilicity, dipolarity/polarizability, hydrogen bond (HB) accepting basicity and HB donating acidity. Other recent studies on LC stationary phases' interaction properties using LSER approach include works by Abraham and co-workers [15,16], Oumada et al. [17], Cheong and Choi [18], Valko et al. [19], Sandi and Szepeszy [20,21], Spange and co-workers [22–24], Reta et al. [25], and Al-Haj et al. [26].

Polar bonded phases such as cyano (cyanopropyl), diol (dihydroxypropyl propyl ether) and amino (aminopropyl)-bonded silica have been increasingly used in both NPLC and RPLC [27,28]. The cyano- and amino-bonded phases are used in both normal and reversed-phase LC. The diol-bonded phase is usually used in normal-phase mode but it can be also used in reversed-phase mode for separation of polar and ionizable solutes using water-rich organic or pure water mobile phases. Recently, there has been a growing interest in using water-rich mobile phases by using alkyl-bonded packings having very low phase ratio, by using elevated temperature, or by adding surfactants [28–31].

We thought that it would be useful to compare interaction properties of these polar bonded stationary phases in NP and RPLC modes in understanding differences in their chromatographic selectivity in the two LC modes in both qualitative and quantitative perspectives, even though in a relative sense. In the

present work we used LSER to characterize characteristic interactions constants in RPLC of the three polar bonded silica stationary phases in a highly aqueous mobile phase and compared them with those obtained in NPLC [32].

According to the LSER formalism [10,11], when applied to the chromatographic retention, logarithmic capacity factors of solutes are described by the following equation:

$$\begin{aligned} \log k = & c + V(\delta_s^2 - \delta_m^2) V_{x2} + L(R_s - R_m)R_2 \\ & + S(\pi_s^* - \pi_m^*) \pi_2^* + B(\alpha_s - \alpha_m) \sum \beta_2^h \\ & + A(\beta_s - \beta_m) \sum \alpha_2^h \end{aligned} \quad (1)$$

The subscripts *s*, *m* and 2 designate the stationary phase, mobile phase and the solute, respectively. The descriptors included are V_x , the characteristic molecular volume [33,34], δ , Hildebrand solubility parameter, R , an excess molar refraction, π^* , the solute dipolarity/polarizability, $\sum \alpha_2^h$, the effective hydrogen bond donor acidity, and $\sum \beta_2^h$, the effective HB acceptor basicity [35]. The coefficients V , L , S , B , and A are the fitting parameters. The c term includes the volume phase ratio and dipolar interactions between the solute and the chromatographic phases when π^* is zero. When a system with a fixed pair of mobile and stationary phases is considered, Eq. (1) is reduced to:

$$\log k = c + vV_{x2} + rR_2 + s\pi_2^* + b \sum \beta_2^h + a \sum \alpha_2^h \quad (2)$$

The coefficients v , r , s , b , and a are obtained by multiple linear regression of $\log k$ vs. the solute parameters. The sign and magnitude of the coefficients measure the direction and relative strength of different types of solute–stationary (and mobile) phase interactions affecting retention for a given pair of mobile–stationary phase condition. When capacity factors for a set of solutes measured on a number of different stationary phase columns using the mobile phase of the same composition are examined, the mobile phase parameters in Eq. (2) (δ_m^2 , R_m , π_m^* , α_m , and β_m) are fixed. Then any variations in the coefficients v , r , s , b , and a with different columns are due only to variations in the properties (δ_s^2 , R_s , π_s^* , α_s , and β_s) of the stationary phases. Modification of the stationary phase by the mobile phase

components varies with the type of bonded functional group on the sorbents in a given mobile phase. However, when the mobile phase is constant for all the columns studied what we measure is the actual bonded phase environment (the bonded phase and sorbed mobile phase components), which really controls retention. Different magnitudes of these coefficients for different columns are indicative of the differences in the extent of contributions to retention from various types of interactions of the stationary phase with the solute. The values of the coefficients v , r , s , b , and a thus, can be regarded as measures of relative strength of corresponding interaction properties of the column. The a and b coefficients, being complementary to the solute hydrogen bond acidity and basicity, represents the stationary phase hydrogen bond basicity and acidity, respectively. The s coefficient is related to the stationary phase dipolarity/polarizability. The v coefficient is related to a combination of dispersive interactions and the cavity effect and essentially measures the phase lipophilicity [35]. The r coefficient refers to the ability of the phase to interact with the solute π - and n -electrons.

2. Experimental

Retention measurements were obtained with a Tosoh HPLC system composed of a CCPD dual pump, CO 8010 column oven, a Rheodyne injector equipped with a 10- μ l sample loop, SD 8013 degasser, and a UV 8010 detector set to a wavelength of 254 nm and a RI 8010 detector connected in series. A Hewlett-Packard 3396 Series II integrator was used to record chromatograms. Columns investigated are a Lichrospher 100 Diol (150 \times 4.6 mm I.D., 5 μ m, Alltech Associates, Inc., Deerfield, IL, USA), a Hypersil CN (150 \times 4.6 mm I.D., 5 μ m, Alltech Associates, Inc., Deerfield, IL, USA) and a Supelcosil LC-NH₂ (250 \times 4.6 mm I.D., 5 μ m, Supelco, Inc., Bellefonte, PA, USA). These are the same columns as used in our previous study in NPLC [32].

The column was maintained at 30 \pm 0.1 $^{\circ}$ C. The eluent used was 10% v/v methanol–water at flow-rate of 1–2 ml min⁻¹. An aliquot of deuterium oxide was injected to determine the column void volume by noting the baseline disturbance due to the refrac-

tive index difference. The retention factors were calculated from the mean retention times of triplicate injections. Relative standard deviation in three replicate retention time measurements was usually about better than 1.5% for all solutes. In order to check the stability of the column we injected toluene before and after the day's measurement and found the retention times of toluene were reproducible within 1% for a day. This check was done everyday and we observed that retention times of toluene agreed within 2% before and after the whole series of experiment. All the solutes were reagent grade from Aldrich (Milwaukee, WI, USA) and used without further purification. Methanol was HPLC grade and from J.T. Baker (Phillipsburg, NJ, USA). HPLC grade water was obtained using an Elgastat UHQ II water purification system (Bucks, UK).

We have been careful to choose compounds of widely varying physicochemical properties. Values of the solute parameters [35] are given in Table 1.

3. Results and discussion

3.1. The RPLC LSER coefficients in 10% v/v methanol–water

Results of regressions of log k on the three sorbent columns in 10% v/v methanol–water vs. the solute properties are listed Table 2, where the coefficients in Eq. (2) are given together with n the number of solutes used, ρ the correlation coefficient, SD the overall standard deviation, F the Fisher F -statistic and the range of k values used. The data for aniline, 1-naphthol, pyridine and p -toluidine on diol column, benzene, benzylamine, 4-bromoaniline, p -toluidine, benzaldehyde, pyridine and n -butylbenzene on amino column, and aniline, 1-naphthol, pyridine and anthracene on cyano column are obvious outliers, based on Student's t -test and Cook's distance [36], and thus were not used in the regressions. Retention times of most of aliphatic solutes are very short and close to that of dead time maker and the retention factors for these solutes may be subject to some uncertainty. Nevertheless, correlation coefficients are mostly close to unity, indicating that retention behavior of the solutes on the columns is well represented by the LSER model.

Table 1
The solute parameters

No.	Solute	R_2	π_2^*	$\Sigma \alpha_2^h$	$\Sigma \beta_2^h$	V_{x2}
1	Diethyl ether	0.041	0.25	0.00	0.45	0.731
2	Dibutyl ether	0.000	0.25	0.00	0.45	1.294
3	Nitromethane	0.313	0.95	0.06	0.31	0.424
4	Acetone	0.179	0.70	0.04	0.49	0.547
5	2-Bethnone	0.166	0.70	0.00	0.51	0.688
6	Methyl acetate	0.142	0.64	0.00	0.45	0.606
7	Ethyl acetate	0.106	0.62	0.00	0.45	0.747
8	Acetophenone	0.818	1.01	0.00	0.48	1.014
9	Propiophenone	0.804	0.95	0.00	0.51	1.155
10	Butyrophenone	0.792	0.95	0.00	0.51	1.296
11	2-Phenyl ethanol	0.811	0.91	0.30	0.64	1.057
12	Benzyl alcohol	0.803	0.87	0.33	0.56	0.916
13	Phenol	0.805	0.89	0.60	0.30	0.775
14	<i>p</i> -Cresol	0.820	0.87	0.57	0.31	0.916
15	Chlorobenzene	0.718	0.65	0.00	0.07	0.839
16	Bromobenzene	0.882	0.73	0.00	0.09	0.891
17	Nitrobenzene	0.871	1.11	0.00	0.28	0.891
18	Benzene	0.610	0.52	0.00	0.14	0.716
19	Toluene	0.601	0.52	0.00	0.14	0.857
20	Ethyl benzene	0.613	0.51	0.00	0.15	0.998
21	Ethyl benzoate	0.689	0.85	0.00	0.46	1.219
22	Pyridine	0.631	0.84	0.00	0.52	0.675
23	Aniline	0.955	0.96	0.26	0.41	0.816
24	Benzylamine	0.829	0.88	0.10	0.72	0.957
25	4-Bromoaniline	1.190	1.19	0.31	0.35	0.991
26	1-Naphthol	1.520	1.05	0.61	0.37	1.144
27	<i>p</i> -Chlorophenol	0.915	1.08	0.67	0.20	0.898
28	<i>p</i> -Toluidine	0.923	0.95	0.23	0.45	0.957
29	Phenetole	0.681	0.70	0.00	0.32	1.057
30	Benzaldehyde	0.820	1.00	0.00	0.39	0.873
31	Propylbenzene	0.599	0.50	0.00	0.15	1.139
32	<i>n</i> -Butylbenzene	0.595	0.51	0.00	0.15	1.280
33	Mesitylene	0.649	0.52	0.00	0.20	1.139
34	Bezonitrile	0.742	1.11	0.00	0.33	0.871
35	Anisole	0.708	0.75	0.00	0.29	0.916
36	<i>p</i> -Xylene	0.613	0.52	0.00	0.17	0.998
37	Anthracene	2.290	1.34	0.00	0.26	1.454

In order to gain understanding of factors rendering the differences in retention properties of the three stationary phases let us examine the signs and magnitudes of the coefficients listed in Table 2. A bar graph for these coefficients is shown in Fig. 1. The magnitudes of the coefficients v and r are in general greater than those for s , a and b for all phases. In all the regressions we checked for possible interrelations between the descriptors by computing the cross-correlation coefficients. The highest correlation coefficient is that between π_2^* and $\Sigma \alpha_2^h$ (0.393) with $\rho^2=0.154$. This indicates that the solute set chosen for this work does not involve strong cross correlations of descriptors.

The positive signs of the v and r coefficients indicate that increasing solute size (V_x) and polarizability (R) cause an increase in retention. Even though the functional groups of the ligates are polar nonpolar dispersive and polarizing interactions between the solute and stationary phase are predominant over polar interactions between them. The magnitude of the v coefficients is the greatest for cyano column followed by diol and amino column indicating that the cyano phase is the least polar among the three and the best in discriminating solute size when all other solute properties are to be the same. The v coefficients for nonpolar ODS phases are very large. This similarity in the v coefficient between cyano and nonpolar ODS phase explains why the cyano phase can be used routinely in both the NPLC and RPLC mode with eluents of higher organic compositions than that used in this study. The r coefficient is much greater for the diol phase than those for the cyano and amino phase. This is expected since the diol phase possesses two pairs of

Table 2
LSER coefficients for the stationary phases in 10% v/v methanol–water

Stationary phase	c	r	s	a	b	v	ρ	SD	n	F	k range
Amino	-1.93 (0.11)	0.67 (0.06)	NS	-0.56 (0.15)	NS	0.46 (0.12)	0.96	0.12	30	99.20	0.02–1.90
Diol	-1.18 (0.18)	2.12 (0.19)	-1.17 (0.21)	-0.60 (0.20)	-0.23 (0.15)	1.34 (0.17)	0.96	0.14	33	124.06	0.03–7.95
Cyano	-1.21 (0.10)	1.06 (0.11)	-0.33 (0.12)	-0.82 (0.12)	-0.14 (0.09)	1.59 (0.10)	0.99	0.09	33	242.32	0.13–19.51

NS, not significant. Numbers in parentheses are standard deviations associated with the coefficient estimates.

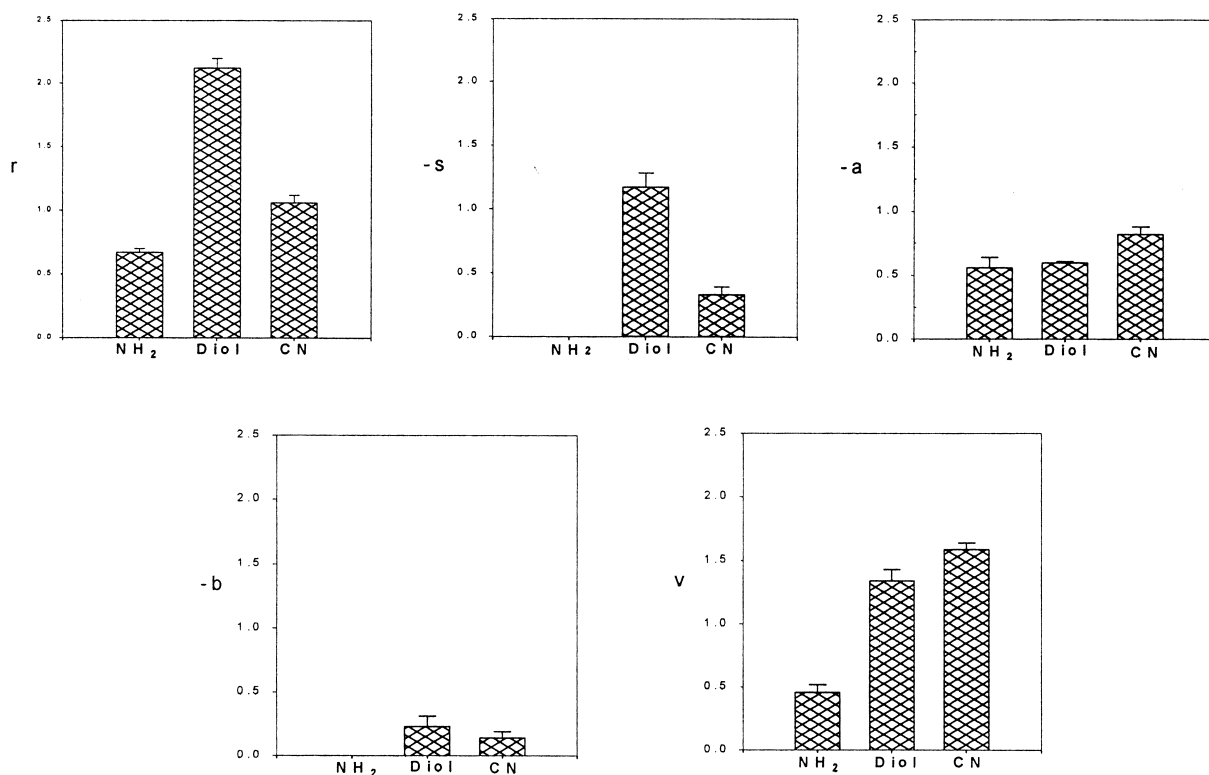


Fig. 1. LSER coefficients for amino-, cyano- and diol-bonded phase.

n -electrons while the other two phases have one pair, thus the former undergoes greater interactions with the solute n - or π -electron pairs. This indicates that the diol phase is best in differentiating the solutes that have different polarizabilities and/or different numbers of n -electron pairs if all the other properties are similar.

The magnitude of the a coefficients for the three phases are quite similar, with that for the cyano phase being somewhat greater than those for the other two phases. The a coefficient is determined by the difference in the HB basicity between the stationary and mobile phase, ($\beta_s - \beta_m$). The β values for propylamine (0.72) and ethylene glycol (0.52), the free-form analogues for the amino and diol phases, are greater than that for butyronitrile (0.40), the free-form analog of the cyano group [37]. A greater β_s value will yield a smaller absolute value for the coefficient a . This suggests that cyano phase will be the better discriminator against the solutes'

HB donor acidity with all the other solute properties being similar.

The magnitude of the s coefficient is the biggest for the diol phase, followed by the cyano phase. The amino phase shows a statistically insignificant s value. The s values for the phases decrease in the same order as the π^* values for the free-form analogs for diol, cyano and amino phases, which are 0.92, 0.71 and 0.31, respectively [37]. This infers that the diol phase will be the better discriminator against the solutes' polarity with all the other properties being similar. The b coefficients for all three phases are very small or negligible, indicating that the solutes' HB basicities are not well differentiated on these columns.

3.2. Comparison of the LSER coefficients in RP and NPLC

It may be interesting to compare the five co-

Table 3
Comparison of the LSER coefficients in NPLC and RPLC

Stationary phase	r_N	r_R	s_N	s_R	a_N	a_R	b_N	b_R	v_N	v_R
Amino	NS	0.67 (0.06)	0.94 (0.08)	NS	2.94 (0.09)	-0.56 (0.15)	1.20 (0.11)	NS	-0.72 (0.08)	0.46 (0.12)
Diol	NS	2.12 (0.19)	1.07 (0.07)	-1.17 (0.21)	2.37 (0.09)	-0.60 (0.20)	1.47 (0.11)	-0.23 (0.15)	-0.85 (0.07)	1.34 (0.17)
Cyano	-0.17 (0.07)	1.06 (0.11)	1.14 (0.10)	-0.33 (0.12)	1.86 (0.07)	-0.82 (0.12)	1.00 (0.11)	-0.14 (0.09)	-0.48 (0.08)	1.59 (0.10)

Subscript N, NPLC; data from Ref. [32]. Subscript R, RPLC. NS, not significant. Numbers in parentheses are standard deviations associated with the coefficient estimates.

efficients for the three columns obtained in NPLC with those obtained in RPLC (Table 3). The same columns were investigated in both RPLC and NPLC study. Bar graphs for comparison of these coefficients in the two modes of LC are shown in Fig. 2. In RPLC [15,16,38–41], the v and r coefficients are always positive in sign and large, indicating that as the solute size increases retention increases while in NPLC the v coefficients are negative in sign and comparable in size to those in RPLC, and the r coefficients are very small or negligible. This is related to the relative polarities of the mobile and

stationary phases used in the two modes of LC. The larger the solute is, the greater is its lipophilicity. This should favor partition of solute into the less polar phase, that is, the stationary phase in RPLC and mobile phase in NPLC. In RPLC, retention is mainly driven by nonpolar dispersive interactions of the solute with the nonpolar alkyl bonded phase [42–44] while in NPLC retention is mainly driven by competitive, polar and hydrogen bonding interactions between the solute and mobile phase molecules towards polar adsorption sites and nonpolar dispersive interactions are much less important. It follows

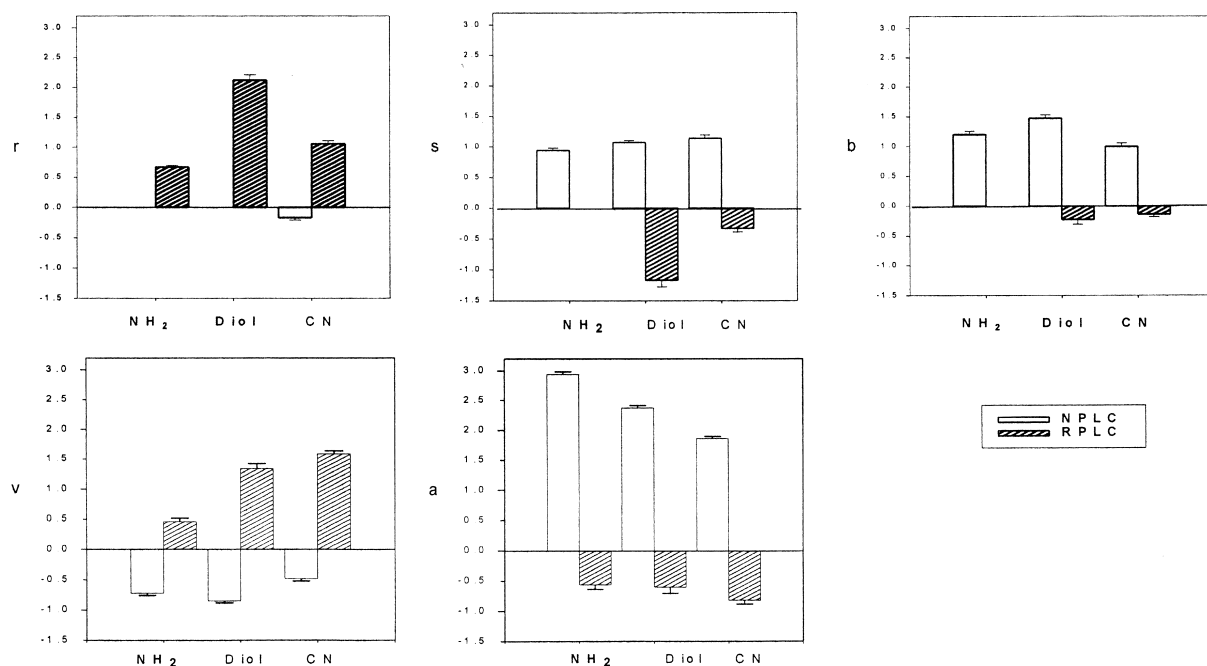


Fig. 2. Comparison of the LSER coefficients in NPLC and RPLC.

that the magnitudes of the v coefficients are greater in RPLC than in NPLC.

The sign of the coefficients relevant to polar interaction strengths (s , b and a) are all positive in NPLC but all negative in RPLC. This is also related to the relative polarities of the mobile phase and stationary phases in the two LC modes. As the dipolarity, HB acidity and HB basicity of the solute increase the solute favors partition into the more polar and hydrogen bonding aqueous–organic mobile phase in RPLC while it will be more strongly attracted onto the stationary phase due to its increased interactions with the more polar and hydrogen-bonding functional groups on the surface in NPLC. The magnitude of the s coefficients in RPLC is thus, in general, smaller than that in NPLC. As shown in Eq. (1), the s coefficient is related to the difference in the dipolarity between the stationary and mobile phase, $(\pi_s^* - \pi_m^*)$. In RPLC, this difference is usually small. Dipolarities of aqueous organic phases over the composition range are only slightly greater in magnitude than those for stationary phases, which possess polar functional groups, absorbed water and organic solvent molecules and residual surface silanol groups [45–47]. The relative magnitudes of the a and b coefficients in the two LC modes can be rationalized in a similar manner to the case of the s coefficient. In NPLC, dipolarity of the stationary phase is usually much greater, no matter which is a solid adsorbent or polar bonded phase, than the mobile phase of a nonpolar organic solvent modified with another polar organic solvent. The HB acidity and basicity of aqueous organic mobile phases used in RPLC are much greater than those of the solvated alkyl-bonded phases while the stationary phases used in NPLC are much stronger HB bases and acids than the organic mobile phases in NPLC.

Comparison of relative sizes of the LSER coefficients in two modes of LC provides information for differences in chromatographic selectivity. The magnitudes of the a coefficients in NPLC are much greater than those in RPLC, indicating that these polar bonded phases better differentiate solutes having different HB acidities in NPLC than in RPLC. The b coefficients are also greater in NPLC than in RPLC, suggesting that solutes having different HB basicities are better resolved when these polar bonded phases are employed in NPLC than in RPLC.

The magnitudes of the s coefficients in NPLC are also, in general, greater than those in RPLC, indicating that these polar bonded phases better differentiate solutes having different dipolarities in NPLC than in RPLC. The magnitudes of the v and r coefficients are in general greater in RPLC than in NPLC, indicating that solutes having different sizes and polarizabilities are better separated in RPLC than in NPLC.

Recently Oumada et al. [17] compared interaction properties of a number of polar bonded phases in NPLC including amino, cyano and diol phases using their own and literature k data based on the LSER methodology. The k values used were measured in mobile phases of different composition than those used in our work [32]. Although the values of the coefficients obtained in their work are somewhat different from those obtained in our work the trend in variation of the coefficients with bonded functionalities are similar. It must be, however, pointed out that a meaningful comparison can only be made for specific stationary–mobile phase combinations. Even stationary phases possessing the same bonded ligands show widely different retention properties due to variations in the nature of the base silica particles and the bonding process [1,2]. The extents of solvation by the mobile phase components of the stationary phase, which affect the properties of the stationary phase, also vary widely with the composition of the mobile phase [5–8].

4. Conclusions

Reversed-phase liquid chromatographic selectivities for amino-, cyano- and diol-bonded silica stationary phases in a highly aqueous eluent were characterized by estimating five characteristic interaction constants based on linear solvation energy relationships. Magnitudes of the constants for the phases in RPLC were compared with those in NPLC to see the differences in chromatographic selectivity in the two LC modes. The comparison indicated the following differences in chromatographic selectivities: For solutes having different HB acidities with the other interaction properties being similar separation on these polar phases in NPLC may provide better resolution than in RPLC. Solutes

having different HB basicities are also better resolved in NPLC than in RPLC. These polar bonded phases better differentiate solutes having different dipolarities in NPLC than in RPLC. Solute's size and polarizability are however better discriminated in RPLC than in NPLC. It is hoped that these phase interaction constants provide an understanding of differences in the selectivity for the three stationary phases and may provide some useful information for choosing a selective phase and mode of LC for a given sample type.

Acknowledgements

This work was supported by the Korea Research Foundation grant (KRF-99-005-D-000-55) and the Taegu University research grant, 2000.

References

- [1] M.F. Delaney, A.N. Papas, M.J. Walters, *J. Chromatogr.* 31 (1987) 410.
- [2] R.M. Smith, S.L. Miller, *J. Chromatogr.* 464 (1989) 297.
- [3] P.E. Antle, A.P. Goldberg, L.R. Snyder, *J. Chromatogr.* 321 (1985) 1.
- [4] H. Engelhardt, H. Low, W. Gotzinger, *J. Chromatogr.* 544 (1991) 371.
- [5] R.M. McCormick, B.L. Karger, *Anal. Chem.* 52 (1980) 2249.
- [6] R.M. McCormick, B.L. Karger, *J. Chromatogr.* 199 (1980) 259.
- [7] C.R. Yonker, T.A. Zwier, M.F. Burke, *J. Chromatogr.* 241 (1982) 257.
- [8] C.R. Yonker, T.A. Zwier, M.F. Burke, *J. Chromatogr.* 241 (1982) 269.
- [9] K. Unger (Ed.), *Packings and Stationary Phases in Chromatographic Techniques*, Marcel Dekker, New York, 1990.
- [10] M.J. Kamlet, J.L.M. Abboud, R.W. Taft, *Prog. Phys. Org. Chem.* 13 (1981) 591.
- [11] M.J. Kamlet, R.W. Taft, P.W. Carr, M.H. Abraham, *J. Chem. Soc., Faraday Trans. I* 78 (1982) 1689.
- [12] J.H. Park, J.J. Chae, T.H. Nah, M.D. Jang, *J. Chromatogr. A* 664 (1994) 149.
- [13] J.H. Park, P.W. Carr, *J. Chromatogr.* 465 (1989) 123.
- [14] J.H. Park, M.H. Yoon, Y.K. Ryu, B.E. Kim, J.W. Ryu, M.D. Jang, *J. Chromatogr. A* 796 (1998) 249.
- [15] M.H. Abraham, M. Roses, *J. Phys. Org. Chem.* 7 (1994) 672.
- [16] M.H. Abraham, M. Roses, C.F. Poole, S. K Poole, *J. Phys. Org. Chem.* 10 (1997) 358.
- [17] F.Z. Oumada, M. Roses, E. Bosch, M.H. Abraham, *Anal. Chim. Acta* 382 (1999) 301.
- [18] W.J. Cheong, J.D. Choi, *Anal. Chim. Acta* 342 (1997) 51.
- [19] K. Valko, M. Plass, C. Bevan, D. Reynolds, M.H. Abraham, *J. Chromatogr. A* 797 (1998) 41.
- [20] A. Sandi, L. Szepesy, *J. Chromatogr. A* 818 (1998) 1.
- [21] A. Sandi, L. Szepesy, *J. Chromatogr. A* 818 (1998) 19.
- [22] S. Spange, A. Reuter, E. Vilsmeier, *Colloid Polym. Sci.* 274 (1996) 59.
- [23] S. Spange, A. Reuter, *Langmuir* 15 (1999) 141.
- [24] S. Spange, A. Reuter, D. Lubda, *Langmuir* 15 (1999) 2103.
- [25] M. Reta, P.W. Carr, P.C. Sadek, S.C. Rutan, *Anal. Chem.* 71 (1999) 3484.
- [26] M.A. Al-Haj, R. Kalisz, A. Nasal, *Anal. Chem.* 71 (1999) 2976.
- [27] J.G. Dorsey, W.T. Cooper, *Anal. Chem.* 66 (1994) 857A.
- [28] M.D. Foster, R.E. Synovec, *Anal. Chem.* 68 (1996) 2838.
- [29] R.M. Smith, R.J. Burgess, *J. Chromatogr. A* 785 (1997) 49.
- [30] D.J. Miller, S.B. Hawthorne, *Anal. Chem.* 69 (1997) 623.
- [31] W. Hu, K. Hasebe, D.M. Reynolds, H. Haraguchi, *Anal. Chim. Acta* 353 (1997) 143.
- [32] J.H. Park, M.H. Yoon, Y.K. Ryu, B.E. Kim, J.W. Ryu, M.D. Jang, *J. Chromatogr. A* 796 (1998) 249.
- [33] J.C. McGowan, *J. Chem. Technol. Biotechnol.* 34A (1984) 38.
- [34] M.H. Abraham, J.C. McGowan, *Chromatographia* 23 (1987) 243.
- [35] M.H. Abraham, *Chem. Soc. Rev.* 22 (1993) 73.
- [36] S. Weisberg, *Applied Linear Regression*, Wiley, New York, 1980.
- [37] Y. Marcus, *Chem. Soc. Rev.* 22 (1993) 409.
- [38] P.C. Sadek, P.W. Carr, R.M. Doherty, M.J. Kamlet, R.W. Taft, M.H. Abraham, *Anal. Chem.* 57 (1985) 2971.
- [39] P.W. Carr, R.M. Doherty, M.J. Kamlet, R.W. Taft, W. Melander, C. Horvath, *Anal. Chem.* 58 (1986) 2674.
- [40] J.H. Park, P.W. Carr, M.H. Abraham, R.W. Taft, R.M. Doherty, M.J. Kamlet, *Chromatographia* 25 (1988) 373.
- [41] J.H. Park, M.D. Jang, S.T. Kim, *Bull. Korean Chem. Soc.* 11 (1990) 297.
- [42] P.W. Carr, J. Li, A.J. Dallas, D.I. Eikens, L.C. Tan, *J. Chromatogr. A* 656 (1993) 113.
- [43] P.W. Carr, L.C. Tan, J.H. Park, *J. Chromatogr. A* 724 (1996) 1.
- [44] J.H. Park, Y.C. Weon, Y.K. Lee, L.C. Tan, L. Li, J. Li, P.W. Carr, J.F. Evans, *J. Chromatogr. A* 767 (1997) 1.
- [45] R.S. Helburn, S.C. Rutan, J. Pompano, D. Mitchem, W.T. Patterson, *Anal. Chem.* 66 (1994) 610.
- [46] H. Lu, S.C. Rutan, *Anal. Chem.* 68 (1996) 1387.
- [47] J.H. Park, A.J. Dallas, P. Chau, P.W. Carr, *J. Phys. Org. Chem.* 7 (1994) 757.