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Characterization of some normal-phase liquid chromatographic stationary phases based on linear solvation energy relationships

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Abstract

Characterization of a number of normal-phase liquid chromatography (NP-LC) stationary phases was attempted by estimating characteristic interaction constants for the stationary phases based on linear solvation energy relationships. Five characteristic interaction constants of the stationary phases, the lipophilicity (*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 capacity factors (k') for a set of test solutes measured on them in the mobile phase of a given composition 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 vary with the type of the stationary phases. The effect of polar modifier in the mobile phases on the interaction properties of the sorbents was also investigated. © 1998 Elsevier Science B.V.

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1. Introduction

While the importance of the stationary phase in reversed-phase liquid chromatography (RP-LC) is just now being recognized, it plays a primary role in normal-phase liquid chromatography (NP-LC). Solid adsorbents such as silica and alumina have thus been studied extensively as the stationary phase in liquid–solid chromatography and a number of theories have been developed for prediction of retention of various solutes [1]. Recently, polar bonded phases have been increasingly used as stationary phases in NP-LC [2]. Three polar bonded types, diol (dihydroxypropyl propyl ether), aminopropyl and cyanopropyl, have found wide applications. These bonded phases exhibit properties similar to solid adsorbents, but they possess some important advantages over solid adsorbents, which include (a) much less irreversible adsorption of very polar solutes, (b) faster column equilibration, and (c) enhanced chromatographic selectivity obtained by adjusting both mobile and stationary phases [3].

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Retention in adsorption chromatography is best described by the models by Snyder and co-workers [1,4–6]. It was originally designed for solid sorbents such as silica and alumina. The model starts from the assumption that retention of a solute is governed by competitive adsorption on the active sites on the sorbent. It has been shown that this general assumption also works on polar bonded silica phases [5,7–11].

A number of studies have been devoted to characterize the retention properties of sorbents for NP-LC. Since direct measurement of interaction properties of bulk bonded material is often difficult and often less sensitive than chromatographic measurements, characterization of stationary phases has most often been attempted by measuring their retentivity and selectivity for a particular class of compounds. Cooper and Smith [7,8] used nitrobenzenes to investigate selectivity characteristics of diol, amino and cyano bonded sorbents as a function of the more polar mobile phase modifier. These authors also determined extended solubility parameters for the same sorbents [9]. Salotto et al. [10] used group retention values to characterize selectivity differences. Lubke et al. [3] studied selectivity and mobile phase effects for diol, amino and cyano bonded sorbents using pentane–diethyl ether eluents. Carlsson and Oestman [12] studied two aminoalkyl bonded phases (aminopropyl and dimethylaminopropyl silica). Grimvall and Oestman [13] studied retention behavior of halogenated environmental pollutants on seven different solid and bonded phases. Hamoir and Massart [14] used retention of β-adrenergic drugs to study the properties of a cyano bonded phase.

In the present work we use a linear solvation energy relationship (LSER) model [15,16] to characterize chromatographic properties of the NP-LC stationary phases in terms of the type and relative strength of the stationary phase interactions with solutes. This model has been used to describe a large number of systems of immediate relevance to chromatography, such as Rohrschneider's gas–liquid partition coefficients [17], retention of McReynolds solutes on polymeric silicone oil gas chromatographic phases [18], retention in reversed-phase (RP) LC [19–22] and supercritical fluid chromatography (SFC) [23]. The LSER model has also been successfully used to characterize the chromatographic properties of stationary phases used in RP-LC [24], surface polarity of carbon fibers for use in gas–solid chromatography [25] and sorption properties of sorbents for solid-phase extraction [26]. We compared the interaction properties of silica and alumina by correlating Snyder's ε^0 [4] values for solvents on these solid phases [27].

According to the LSER formalism [15,16], when applied to the chromatographic retention, logarithmic capacity factors of solutes are described by the following equation:

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

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 [28,29], δ, Hildebrand solubility parameter, R, an excess molar refraction, π^*, the solute dipolarity/polarizability, $\Sigma\alpha_2^h$, the effective hydrogen bond (HB) donor acidity, and $\Sigma\beta_2^h$, the effective HB acceptor basicity [15]. 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

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

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 conditions. 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. 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 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, represent 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 [30]. The *r* coefficient refers to the ability of the phase to interact with the solute π- and n-electron pairs and provides an indication of polarizability. These interaction constants can be useful in understanding the selectivity of the sorbents used in NP-LC.

2. Experimental

Retention measurements were obtained with a Hewlett-Packard Series 1090 HPLC system composed of an injector equipped with a 10-μl sample loop and a UV–Vis detector set to a wavelength of 254 nm. A Waters R401 differential refractometer was connected to the UV–Vis detector in series and a Hewlett-Packard 3396 Series II integrator was used to record chromatograms. Columns investigated are a Hypersil silica (200 mm×4.6 mm I.D., 5 μm, Hewlett-Packard, Palo Alto, CA, USA), a Hypersil APS(NH_2) (100 mm×2.1 mm I.D., 5 μm, Hewlett-Packard), a Lichrospher 100 Diol (150 mm×4.6 mm I.D., 5 μm, Alltech Associates, Deerfield, IL, USA), a Lichrospher CN (125 mm×4 mm I.D., 5 μm, Hewlett-Packard), a Ultrasphere CN (150 mm×4.6 mm I.D., 5 μm, Beckman, Fullerton, CA, USA), a Hypersil CN (150 mm×4.6 mm I.D., 5 μm, Alltech Associates) and a Spherisorb CN (150 mm×4.6 mm I.D., 5 μm, Alltech Associates). Some of the properties of these columns are listed in Table 1, as supplied by the manufacturers.

The column was placed in a waterjacket, and the temperature was controlled at 30±0.1°C. The eluents used were 1% (v/v) methanol–hexane or 10–40% (v/v) chloroform–hexane. The eluent flow-rate was 1–2 ml/min. An aliquot of pentane was injected to determine the column void volume. The capacity factors were calculated from the mean retention times of triplicate injections. Relative standard deviation (R.S.D.) 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 each day and we observed that retention times of toluene agreed within 2% before and after the whole series of experiments. All the solutes were reagent grade from Aldrich (Milwaukee, WI, USA) and used without further purification. Hexane and chloroform were HPLC grade and from J.T. Baker (Phillipsburg, NJ, USA).

We have been careful to choose compounds of widely varying physicochemical properties. Values of the solute parameters [30] are given in Table 2.

3. Results and discussion

3.1. Chromatographic properties of the NP-LC sorbents in 1% (v/v) methanol–hexane

Results of regressions of log k' on the seven sorbent columns in 1% (v/v) methanol–hexane vs. the solute properties are listed Table 3, where the coefficients in Eq. (2) are given together with *n* the number of solutes used, ρ the correlation coefficient, S.D. the overall standard deviation, *F* the Fisher *F*-statistic and the range of k' values used. The data for pyridine, benzylamine and butyl ether on silica, benzaldehyde on amino column, and pyridine and benzylamine on the remaining columns are obvious outliers, based on Student's *t*-test and Cook's distance [31], and thus were not used in the regressions. Retention times of nonpolar solutes (e.g., alkylben-

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

No.	Stationary phase	Particle size (μm)	Ligand	Surface area (m^2 g^{-1})	Carbon loading (%)
I	Hypersil Silica	5	Bare silica	170	0
II	Hypersil APS NH_2	5	Aminopropyl	170	1.6–1.9
III	Lichrospher Diol	5	Dihydroxypropyl propyl ether	250	INA[a]
IV	Lichrospher CN	5	Cyanopropyl	350	INA
V	Ultrasphere CN	5	Cyanopropyl	200	4.4
VI	Hypersil CN	5	Cyanopropyl	170	3.5
VII	Spheisorb CN	5	Cyanopropyl	220	INA

[a] Information not available.

zenes) are very short and close to that of dead time marker and the capacity 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 NP-LC columns is well represented by the LSER model.

In order to gain understanding of factors rendering the differences in retention properties of various NP-LC stationary phases let us examine the signs and magnitudes of the coefficients listed in Table 3. A bar graph for these coefficients is shown in Fig. 1. The magnitudes of the coefficients *s*, *b* and *a* are greater than that for *v*. The *r* coefficients for all the sorbents are statistically nil or very small compared to the remaining coefficients, indicating that interactions of the sorbents with the solute π- and n-electron pairs play an insignificant role in determining retention and selectivity and in turn the polarizability is not a significant factor in characterizing the stationary phase. The Ehrenson test [32] also indicated that the R_2 parameter is not significant at the 99% confidence level. Thus in further regressions we excluded the R_2 parameter and used the remaining four solute parameters. 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 negative signs of the *v* coefficients indicate that increasing solute size (V_x) causes a decrease in retention. This can be explained in the perspective of displacement model [33]. An increase in solute size requires more solvent molecules to be displaced, and hence the energy for endoergic displacement of solvent molecules is greater than exoergic interactions by solutes with active sites on the sorbent surface. This will result in reduced retention with increasing the solute size, leading to a decrease in the *v* coefficient. Note that the magnitude of the *v* coefficients is generally smaller than that for the *s*, *b* and *a* coefficients and does not vary much with the type of the sorbents.

The signs of the *s*, *b* and *a* coefficients are all positive, indicating that an increase in the solute dipolarity (π^*), HB donor acidity (α) and HB acceptor basicity (β) leads to increased retention

Table 2
The solute parameters

Solute	R_2	π_2^*	$\Sigma\alpha_2^h$	$\Sigma\beta_2^h$	V_{x2}
Diethyl ether	0.041	0.25	0.00	0.45	0.731
Dibutyl ether	0.000	0.25	0.00	0.45	1.294
Nitromethane	0.313	0.95	0.06	0.31	0.424
Acetone	0.179	0.70	0.04	0.49	0.547
2-Butanone	0.166	0.70	0.00	0.51	0.688
Methyl acetate	0.142	0.64	0.00	0.45	0.606
Ethyl acetate	0.106	0.62	0.00	0.45	0.747
Acetophenone	0.818	1.01	0.00	0.48	1.014
Propiophenone	0.804	0.95	0.00	0.51	1.155
Butyrophenone	0.792	0.95	0.00	0.51	1.296
2-Phenyl ethanol	0.811	0.91	0.30	0.64	1.057
Benzyl alcohol	0.803	0.87	0.33	0.56	0.916
Phenol	0.805	0.89	0.60	0.30	0.775
p-Cresol	0.820	0.87	0.57	0.31	0.916
Chlorobenzene	0.718	0.65	0.00	0.07	0.839
Bromobenzene	0.882	0.73	0.00	0.09	0.891
Nitrobenzene	0.871	1.11	0.00	0.28	0.891
Benzene	0.610	0.52	0.00	0.14	0.716
Toluene	0.601	0.52	0.00	0.14	0.857
Ethyl benzene	0.613	0.51	0.00	0.15	0.998
Ethyl benzoate	0.689	0.85	0.00	0.46	1.219
Pyridine	0.631	0.84	0.00	0.52	0.675
Aniline	0.955	0.96	0.26	0.41	0.816
Benzylamine	0.829	0.88	0.10	0.72	0.957
4-Bromoaniline	1.190	1.19	0.31	0.35	0.991
1-Naphthol	1.520	1.05	0.61	0.37	1.144
p-Chlorophenol	0.915	1.08	0.67	0.20	0.898
p-Toluidine	0.923	0.95	0.23	0.45	0.957
Phenetole	0.681	0.70	0.00	0.32	1.057
Benzaldehyde	0.820	1.00	0.00	0.39	0.873
Propylbenzene	0.599	0.50	0.00	0.15	1.139
n-Butylbenzene	0.595	0.51	0.00	0.15	1.280
Mesitylene	0.649	0.52	0.00	0.20	1.139
Benzonitrile	0.742	1.11	0.00	0.33	0.871
Anisole	0.708	0.75	0.00	0.29	0.916
p-Xylene	0.613	0.52	0.00	0.17	0.998
Anthracene	2.290	1.34	0.00	0.26	1.454

because the solutes have greater affinities for the more polar and hydrogen bonding sorbent surfaces. The positive signs of these three coefficients also indicate that the magnitude of net attractive polar interactions between the solute and the stationary phase is greater than that between the solute and the mobile phase. The magnitudes of the *a* coefficients are greater than those of the *b* coefficients. This indicates that the net HB interactions between the solute as HB donor and the stationary phase as HB acceptor (type A HB) predominate over HB interactions between the solute as HB acceptor and the stationary phase as HB donor interactions (type B HB) for all seven sorbents studied. Comparison of the magnitudes of the three coefficients indicates that the most important factor influencing NP-LC retention for the solutes studied is the type A HB interactions, followed by the type B HB interactions, and the dipolar interactions are somewhat less important than the two types of HB interactions.

The magnitudes of the *s*, *b* and *a* coefficients vary substantially with the type of the active moiety of the sorbents and with the brand for the stationary phases of the same ligand (four cyano-bonded phases). For sorbents with polar bonded ligands, it is well known that endcapping can not block the surface silanol groups completely and that there is substantial variability in the concentration of surface silanol groups on the initial silica. This will certainly affect the polarity (π_s^*) and HB properties of the stationary phase (α_s and β_s), rendering these ostensibly equivalent cyano phases to exhibit different interaction strengths toward the solute and hence yielding different values of these coefficients for different brands. Comparison of the magnitude of the *a* coefficients indicates that the amino phase is the most basic, followed by diol and silica. The HB basicity of the cyano phases is slightly smaller than the other phases and vary somewhat with the brand. Magnitude of the *b* coefficients (the sorbent HB acidity) for bare silica and the diol phase is similar each other and greater than that for the amino phase and all the cyano phases except a particular cyano phase, Spherisorb CN, the *b* coefficient of which is even greater than bare silica. This is unusual in that a part of active sites such as silanol groups on the bonded phases is deactivated by the bonded moiety, which would lead to decreased HB acidity, compared to the bare silica phase. Unusually high HB acidity of this cyano phase is likely to be due to higher amount of HB acidic impurities (trace metals) present in the silica support of this phase than in the bare silica phase [34]. The *s* coefficients (the sorbent dipolarity) are in general somewhat greater for the cyano phases than for amino and diol phases and similar in magnitude to bare silica.

These results are in general agreement with those observed in previous studies on diol, cyano, amino and bare silica phases. Salotto et al. [10] found that with methylene chloride as polar modifier the amino

Table 3
LSER coefficients for various sorbents in hexane[a]

Stationary phase[b]	*c*	*s*	*a*	*b*	*v*	*ρ*	S.D.	*n*	*F*	*k′* range
I	−1.21 (0.10)[c]	1.06 (0.10)	2.23 (0.10)	1.56 (0.13)	−0.83 (0.09)	0.990	0.11	34	356	0.04–7.0
II	−1.14 (0.09)	0.94 (0.08)	2.94 (0.09)	1.20 (0.11)	−0.72 (0.08)	0.993	0.10	36	217	0.04–26.7
III	−0.94 (0.09)	1.07 (0.07)	2.37 (0.09)	1.47 (0.11)	−0.85 (0.07)	0.993	0.09	35	535	0.07–16.3
IV	−0.89 (0.10)	0.99 (0.12)	1.94 (0.08)	1.04 (0.13)	−0.64 (0.10)	0.991	0.09	35	418	0.10–10.1
V	−1.10 (0.09)	1.03 (0.11)	1.97 (0.08)	1.08 (0.12)	−0.60 (0.09)	0.992	0.09	35	446	0.08–8.3
VI	−1.16 (0.08)	0.95 (0.10)	1.86 (0.07)	1.15 (0.11)	−0.61 (0.08)	0.993	0.08	35	503	0.07–5.4
VII	−0.99 (0.10)	1.00 (0.08)	2.13 (0.09)	1.69 (0.12)	−0.84 (0.08)	0.991	0.10	35	396	0.07–9.7

[a] Hexane containing 1% (v/v) methanol.
[b] Column designations are as in Table 1.
[c] Numbers in parentheses are standard deviations associated with the coefficient estimates.

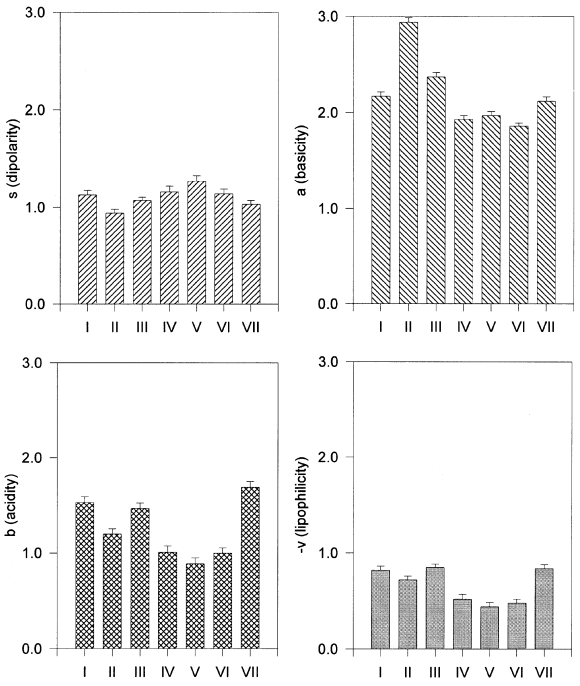

Fig. 1. LSER coefficients for various sorbents.

and diol phases each preferentially retain basic solutes while the cyano column retains preferentially dipolar solutes. The amino phase was found to strongly retain acidic solutes. Smith and Cooper [9] determined extended solubility parameters for diol, amino and cyano phases and placed the phases in a selectivity triangle. Cyano bonded silica phase was found to be essentially dipolar while amino and diol silica phases were essentially equally basic and dipolar. However, it must be pointed out that a meaningful comparison can only be made for specific sorbent–mobile phase combinations, not for sorbents as a whole since the same stationary phase can exhibit very different chromatographic properties with different mobile phases.

3.2. Effect of polar modifier in mobile phases on the chromatographic properties of the sorbents

Fig. 2 shows plots of log k' for two typical solutes, 2-phenylethanol and nitromethane vs. logarithmic mole fraction (ϕ) of chloroform in hexane

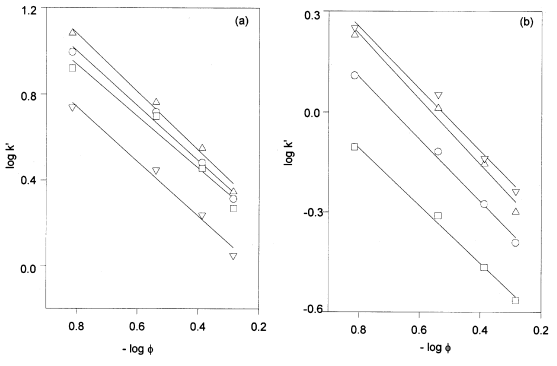

Fig. 2. Plots of log k' of (a) 2-phenylethanol and (b) nitromethane vs. log ϕ (mole fraction) of chloroform in hexane for silica (I) (○), amino (II) (▽), diol (III) (□) and cyano (IV) (△) sorbents.

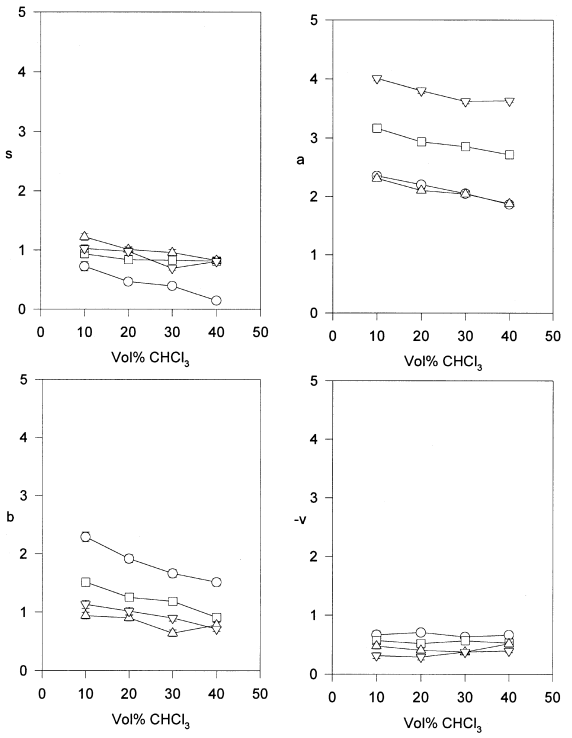

Fig. 3. Effect of polar modifier on the LSER coefficients for silica (I) (○), amino (II) (▽), diol (III) (□) and cyano (IV) (△) sorbents.

for Hypersil silica (I), Hypersil APS amino (II), Lichrospher diol (III) and Lichrospher CN (IV) sorbents. Snyder's displacement model [4] predicts that when the polarity (ε^0) of the polar modifier is much greater than that for a nonpolar solvent in the mixture and mole fraction of the polar modifier is quite high, a plot of log k' vs. logarithmic mole fraction of the polar modifier should yield a straight line. Quite good linear relationships are seen in plots of log k' vs. log ϕ, indicating that the Snyder's model is quite satisfactory for both solid adsorbents and polar bonded phases in hexane–chloroform eluents.

Correlation coefficients for regressions of log k' on the bare silica, amino, diol and cyano columns vs. the solute properties in 10–40% (v/v) chloroform–hexane are close to unity ($\rho = 0.986$–0.995), indicating that retention of the solutes on these columns in these eluents is also well represented by the LSER. Pyridine and benzylamine on the all columns were found to be outliers based on Student's t-test and Cook's distance and were excluded in the regressions. Fig. 3 shows variation of four LSER coefficients with volume fraction of chloroform in hexane for Hypersil silica, Hypersil APS amino, Lichrospher diol and Lichrospher CN sorbents.

While the magnitudes of the s coefficients (the sorbent dipolarity/polarizability) in chloroform–hexane are not appreciably different from those in 1% (v/v) methanol–hexane for amino, diol and cyano sorbents, the magnitude of the s coefficient for bare silica is somewhat lower in chloroform–modified hexane than in 1% methanol–hexane. The magnitude of the s coefficient becomes smaller with increasing amount of chloroform. Chloroform is a relatively dipolar solvent ($\pi^* = 0.58$) [35]. In view of dipolarity of chloroform, it can be speculated that the magnitude of the s coefficients for the sorbents would increase due to the increased amount of adsorbed chloroform with increasing chloroform content. However, it is possible that association of chloroform onto the sorbents may act to reduce the dipolarity of the formed sorbents with adsorbed chloroform. Decreasing s coefficients seems to indicate that the latter is the case for the sorbents studied. Decreasing polarity of the sorbents with increasing polar modifier content may also be related to the heterogeneity of the silica surface. For polar bonded silica phases surface silanol groups are not completely covered and residual silanols are always

present for even endcapped phases. Even on bare silica activity of silanol groups on the surface are not homogeneous. Polar chloroform molecules occupy preferentially the most active sites on the surface, i.e., the most active silanol groups on the bare silica and residual silanol groups on the polar bonded silica phases. This will act to reduce the polarity of the sorbent surfaces.

The magnitudes of the *a* coefficients (the sorbent HB basicity) are much greater for all four sorbents in chloroform–hexane than in 1% (v/v) methanol–hexane and decreases with increasing chloroform content. Chloroform is a relatively weak HB acid ($\alpha = 0.20$) but a very weak HB base ($\beta = 0.10$) [35]. Decreasing *a* coefficients with increasing chloroform content can also be attributed to decreased amount of silanol groups by adsorbed chloroform, as discussed in the case of the *s* coefficients. It is also likely that a formed sorbent by adsorbing chloroform becomes an even stronger HB base than the sorbent itself upon initial addition of chloroform in hexane. Diol, amino and cyano groups are in general stronger HB base than chloroform. The β values for free-form analogues for these groups, ethanediol, propylamine and butanitrile, are 0.52, 0.72 and 0.40, respectively. A further increase in chloroform in hexane results in increased coverage of HB base sites on the sorbent, exhibiting a decrease in the sorbent HB basicity.

A different explanation for the decrease in the magnitudes of the *s* and *a* coefficients can be presented based on restricted-access delocalization effect of the polar modifier [5]. Restricted-access delocalization occurs on both a solid adsorbent such as silica and polar bonded phases [3]. With increasing coverage of the adsorbent surface, adsorbed polar modifier molecules interfere with further localization of modifier molecules, and further adsorption occurs without localization. Then the effective solvent strength of the modifier decreases with increasing surface coverage. This will lead to reduced retention of a solute, which will, in turn, yield apparently decreased magnitude of the coefficients related to polar interaction strengths.

The magnitudes of the *b* coefficients for the four sorbents in chloroform–hexane are not very different from those in 1% methanol–hexane and again generally decreases with increasing chloroform content. The magnitudes of the *v* coefficients do not vary appreciably upon addition of chloroform in hexane.

3.3. Comparison of the coefficients in NP-LC and RP-LC

It may be interesting to compare the four coefficients obtained in NP-LC with the corresponding coefficients obtained in RP-LC. In RP-LC [19–21], the *v* coefficient is always positive in sign and very large, indicating that as the solute size increases retention increases while it is negative in sign and quite small in NP-LC. This is related to 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 RP-LC and mobile phase in NP-LC. In RP-LC, retention is mainly driven by nonpolar dispersive interactions of the solute with the nonpolar alkyl bonded phase [36–38] while in NP-LC 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 that the magnitudes of the *v* coefficients are greater in RP-LC than in NP-LC.

The sign of the coefficients relevant to polar interaction strengths (*s*, *b* and *a*) are all positive in NP-LC but all negative in RP-LC. This is again 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 RP-LC while it will be more strongly adsorbed onto the sorbent due to its increased interactions with the more polar and strong hydrogen bonding sites on the surface in NP-LC. The magnitudes of the *s* coefficients in RP-LC are thus, in general, much smaller than that in NP-LC. As shown in Eq. (1), the *s* coefficient is related to the difference in dipolarity between the stationary and mobile phase, $(\pi_s^* - \pi_m^*)$. In RP-LC, this difference is usually small. Dipolarities of aqueous organic phases over the composition range are only slightly greater

in magnitude than those for alkyl-bonded stationary phases, which possess absorbed water and organic solvent molecules and residual surface silanol groups [39–41]. 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 NP-LC, dipolarity of a sorbent is usually much greater, no matter which is a solid adsorbent or polar bonded phase, than the organic mobile phase modified with another polar organic solvent. The HB donor acidity and acceptor basicity of aqueous organic mobile phases used in RP-LC are much greater than those of the solvated alkyl-bonded phases while the stationary phases used in NP-LC are much stronger HB bases and acids than the organic mobile phases in NP-LC.

4. Conclusions

A number of NP-LC stationary phases were characterized by estimating characteristic interaction constants for the stationary phases based on linear solvation energy relationships. Comparison of the interaction constants for the sorbents showed that the sorbent HB acidities for bare silica and the diol phase are similar each other and greater than those for the amino and cyano phases. For the sorbent HB basicity, the amino phase is the most basic, followed by diol and silica. The sorbent dipolarity is in general somewhat greater for the cyano phases than for amino and diol phases and similar to bare silica. While the dipolarity of the sorbents does not vary appreciably, the HB basicity and acidity of the sorbents significantly increase upon addition of polar modifier (chloroform) in hexane and gradually decrease with further addition of the polar modifier. These phase interaction constants provide an overview of the selectivity for the commonly used NP-LC sorbents and may provide some information on choosing a selective sorbent for a given sample type.

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References

[1] L.R. Snyder, in Cs. Horváth (Ed.), High-Performance Liquid Chromatography, Vol. III, Academic Press, New York, 1983, pp. 157–223 and references therein.
[2] J.G. Dorsey, W.T. Cooper, Anal. Chem. 66 (1994) 857A.
[3] M. Lubke, J.-L. le Quere, D. Barron, J. Chromatogr. A 690 (1995) 41.
[4] L.R. Snyder, Principles of Adsorption Chromatography, Marcel Dekker, New York, 1968.
[5] L.R. Snyder, T. Schunk, Anal. Chem. 54 (1982) 1764.
[6] L.R. Snyder, J.L. Glajch, J.J. Kirkland, J. Chromatogr. 218 (1981) 299.
[7] P.L. Smith, W.T. Cooper, J. Chromatogr. 410 (1987) 249.
[8] W.T. Cooper, P.L. Smith, J. Chromatogr. 355 (1986) 57.
[9] P.L. Smith, W.T. Cooper, Chromatographia 25 (1988) 55.
[10] A.W. Salotto, E.L. Weiser, K.P. Caffey, R.L. Carty, S.C. Racine, L.R. Snyder, J. Chromatogr. 498 (1990) 55.
[11] L.D. Olsen, R.J. Hurtubise, J. Chromatogr. 479 (1989) 5.
[12] H. Carlssonand, C. Oestman, J. Chromatogr. A 715 (1995) 31.
[13] E. Grimvall, C. Oestman, J. Chromutogr. A 675 (1994) 55.
[14] T. Hamoir, D.L. Massart, J. Chromatogr. A 673 (1994) 1.
[15] M.J. Kamlet, J.L.M. Abboud, R.W. Taft, Prog. Phys. Org. Chem. 13 (1981) 591.
[16] M.J. Kamlet, R.W. Taft, Acta Chem. Scand. B39 (1985) 611.
[17] M.J. Kamlet, R.W. Taft, P.W. Carr, M.H. Abraham, J. Chem. Soc. Faraday Trans. I 78 (1982) 1689.
[18] J.E. Brady, D. Bjorkman, C.D. Herter, P.W. Carr, Anal. Chem. 56 (1984) 278.
[19] P.C. Sadek, P.W. Carr, R.M. Doherty, M.J. Kamlet, R.W. Taft, M.H. Abraham, Anal. Chem. 57 (1985) 2971.
[20] P.W. Carr, R.M. Doherty, M.J. Kamlet, R.W. Taft, W. Melander, Cs. Horváth, Anal. Chem. 58 (1986) 2674.
[21] J.H. Park, P.W. Carr, M.H. Abraham, R.W. Taft, R.M. Doherty, M.J. Kamlet, Chromatographia 25 (1988) 373.
[22] J.H. Park, M.D. Jang, S.T. Kim, Bull. Korean Chem. Soc. 11 (1990) 297.
[23] D. Pyo, W. Li, M.L. Lee, J.D. Weckwerth, P.W. Carr, J. Chromatogr. A 753 (1996) 291.
[24] J.H. Park, J.J. Chae, T.H. Nah, M.D. Jang, J. Chromatogr. A 664 (1994) 149.
[25] J.H. Park, Y.K. Lee, J.B. Donnet, Chromatographia 33 (1992) 154.
[26] J.H. Park, Y.C. Weon, Anal. Sci. 12 (1996) 733.
[27] J.H. Park, P.W. Carr, J. Chromatogr. 465 (1989) 123.
[28] J.C. McGowan, J. Chem. Technol. Biotechnol. 34A (1984) 38.
[29] M.H. Abraham, J.C. McGowan, Chromatographia 23 (1987) 243.
[30] M.H. Abraham, Chem. Soc. Rev. 22 (1993) 73.

[31] S. Weisberg, Applied Linear Regression, Wiley, New York, 1980.
[32] S. Ehrenson, J. Org. Chem. 44 (1979) 1793.
[33] L.R. Snyder, H.D. Warren, J. Chromatogr. 15 (1964) 344.
[34] H. Engelhardt, H. Low, W. Gotzinger, J. Chromatogr. 544 (1991) 371.
[35] Y. Marcus, Chem. Soc. Rev. 93 (1993) 409.
[36] P.W. Carr, J. Li, A.J. Dallas, D.I. Eiknes, L.C. Tan, J. Chromatogr. A 656 (1993) 113.
[37] P.W. Carr, L.C. Tan, J.H. Park, J. Chromatogr. A 724 (1996) 1.
[38] 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.
[39] R.S. Helburn, S.C. Rutan, J. Pompano, D. Mitchem, W.T. Patterson, Anal. Chem. 66 (1994) 610.
[40] H. Lu, S.C. Rutan, Anal. Chem. 68 (1996) 1387.
[41] J.H. Park, A.J. Dallas, P. Chau, P.W. Carr, J. Phys. Org. Chem. 7 (1994) 757.