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Short communication

Insights into the retention mechanism of neutral organic compounds on polar chemically bonded stationary phases in reversed-phase liquid chromatography

Zahid Ali, C.F. Poole*

Department of Chemistry, Room 183, Wayne State University, Detroit, MI 48202, USA

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Abstract

The solvation parameter model is used to characterize the retention properties of a 3-aminopropylsiloxane-bonded (Alltima amino), three 3-cyanopropylsiloxane-bonded (Ultrasphere CN, Ultremex-CN and Zorbax SB-CN), a spacer bonded propanediol (LiChrospher DIOL) and a multifunctional macrocyclic glycopeptide (Chirobiotic T) silica-based stationary phases with mobile phases containing 10 and 20% (v/v) methanol–water. The low retention on the polar chemically bonded stationary phases compared with alkylsiloxane-bonded silica stationary phases arises from the higher cohesion of the polar chemically bonded phases and an unfavorable phase ratio. The solvated polar chemically bonded stationary phases are considerably more hydrogen-bond acidic and dipolar/polarizable than solvated alkylsiloxane-bonded silica stationary phases. Selectivity differences are not as great among the polar chemically bonded stationary phases as they are between the polar chemically bonded phases and alkylsiloxane-bonded silica stationary phases.

Keywords: Solvation parameter model; Reversed-phase liquid chromatography; Retention mechanism; Polar chemically bonded stationary phases

1. Introduction

Retention in reversed-phase liquid chromatography is usually optimized by varying the composition of the mobile phase (solvent type, solvent strength, and additives), and to a lesser extent temperature, for a given stationary phase [1,2]. For small, nonionic molecules the selected stationary phase is almost always a alkylsiloxane-bonded silica stationary phase, but when optimization fails using the above approach, alternative stationary phases are then explored. These might include other alkylsiloxane-bonded silica stationary phases with alkyl groups of the same or different chain lengths, but often to achieve a significant change in band spacing, chemically bonded phases containing different polar functional groups, porous polymers, or porous graphitic carbon are utilized. There is, however, only a limited understanding of the retention mechanism on polar chemically bonded stationary phases to offer an alternative to trial-and-error procedures for stationary phase selection.

The solvation parameter model provides a general approach for characterizing the retention properties of stationary phases in reversed-phase liquid chromatography [1,3,4]. The model is essential a partition model, but makes no assumption about the distribution process, and is set out below in a form suitable for describing the retention of neutral solutes in reversed-phase liquid chromatography:

$$\log k = c + eE + sS + aA + bB + vV \quad (1)$$

The model equation is made up of product terms representing solute properties (descriptors), indicated by capital letters, and the complementary properties characteristic of the separation system, indicated by the lower case letters in italics. Each product term defines the relative contribution of

* Corresponding author. Tel.: +1 313 577 2881; fax: +1 313 577 1377.
E-mail address: cfp@chem.wayne.edu (C.F. Poole).

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a specified intermolecular interaction to the correlated property, in this case the retention factor, log *k*. The contribution from electron lone pair interactions is defined by *eE*, interactions of a dipole-type by *sS*, hydrogen-bond interactions by *aA* and *bB*, and differences in cavity formation and dispersion interactions in the mobile and stationary phases by *vV*. The solute descriptors are formally defined as the excess molar refraction, *E*, dipolarity/polarizability, *S*, effective hydrogen-bond acidity, *A*, effective hydrogen-bond basicity, *B*, and McGowan's characteristic volume, *V*. Descriptors are available for over 4000 compounds with others accessible through calculation and estimation methods [3,5,6].

The system constants characterize the retention properties of the separation system. These are defined as the difference in contributions from electron lone pair interactions, *e*, dipole-type interactions, *s*, hydrogen-bond basicity, *a*, hydrogen-bond acidity, *b*, and cohesion and dispersion interactions, *v*, for the mobile and solvated stationary phases. The system constants are obtained by multiple linear regression analysis for a varied group of solutes selected to satisfy the statistical and chemical requirements of the model [1,3,5–7]. System constants for a wide range of mobile phase compositions are available for alkylsiloxane-bonded silica [1–3], the porous polymer PLRPS [8,9] and porous graphic carbon [10] stationary phases but are relatively sparse for chemically bonded phases. Kim et al. [11] determined system constants for silica-based 3-aminopropylsiloxane-bonded, 3-cyanopropylsiloxane-bonded and spacer bonded propanediol stationary phases with a mobile phase containing 10% (v/v) methanol–water. Sandi and Szepesy [12] determined system constants for a 3-cyanopropylsiloxane-bonded silica column (Zorbax SB 300 CN) with a mobile phase containing 30% (v/v) acetonitrile–water. Al-Haj et al. [13] used a modified form of Eq. (1) that lacked terms for dipole-type and electron loan pair interactions to compare the retention properties of a 3-cyanopropylsiloxane-bonded silica stationary phase (Discovery cyano) to several alkylsiloxane-bonded silica stationary phases. Valko et al. [14,15] used gradient elution conditions to characterize the retention properties of a variety of polar chemically bonded stationary phases to identify suitable columns for estimating solute descriptors. While the system constants of Eq. (1) are fully-defined for isocratic conditions, it remains unclear if they have physical significance when gradient elution is used [16]. System constants for a large number of mobile phase compositions were described for 3-cyanopropylsiloxane-bonded silica thin-layer chromatography plates and used in simulations for computer-aided method development [17,18]. System constants for 3-cyanopropylsiloxane-bonded [19,20] and spacer bonded propanediol [21] silica-based sorbents are available for a wide range of mobile phase compositions. These constants were used for computer-aided method development in solid-phase extraction [22]. Although some similarity in retention properties for chemically bonded sorbents developed for thin-layer chromatography and solid-phase extraction is expected, the physical and chemical properties of these products are optimized for a different set of requirements to column liquid chromatography, and they likely provide only a rough guide to the retention properties of column packings for liquid chromatography.

The above studies will be discussed in more detail in the body of the article were comparisons seem reasonable. The solvation parameter model has also been used to characterize polar chemically bonded phases using non-aqueous solvents for normal-phase chromatography [23–26]. The characteristics of the retention mechanism for normal and reversed-phase conditions are quite different because of the dominant role played by water in reversed-phase separations. Thus, these studies provide little insight into the retention mechanism for reversed-phase liquid chromatography [1,3]. They are identified here for completeness only.

2. Experimental

Common chemicals were reagent grade and obtained from several sources. Water was prepared using a Milli-Q system (Millipore, Bedford, MA, USA). The water had a pH of 5.3–5.4 and a resistance of 18.2 mΩ/cm. Methanol was OmniSolv grade and obtained from EMD Chemicals (Gibbstown, NJ, USA). The 250 mm × 4.6 mm i.d. Zorbax SB-CN, Ultrasphere CN and Alltima Amino columns, 5 μm particles, were obtained from Alltech Associates (Deerfield, IL, USA). The 250 mm × 4.6 mm i.d. Ultremex-CN column, 5 μm particles, was obtained from Phenomenex (Torrance, CA, USA). The 250 mm × 4.6 mm i.d. LiChrospher DIOL column, 5 μm particles, was obtained from EMD Chemicals (Gibbstown, NJ, USA). The 250 mm × 4.6 mm i.d. Chirobiotic T column, 5 μm particles, was obtained from Advanced Separations Technologies (Whippany, NJ, USA).

For liquid chromatography, a Hitachi D-7000 liquid chromatograph (Hitachi Instruments, San Jose, CA, USA) consisting of a L-7100 dual-head reciprocating piston pump, L-7455 diode array detector and L-7300 column was used. A Dell OptiPlex pentium II computer (Round Rock, TX, USA) running Hitachi System Manager software v. 4.1 was used for instrument control and data acquisition. All separations were performed at a flow rate of 1.0 ml/min and temperature of 25 °C. The column hold-up time was determined by injection of an aqueous solution of sodium nitrate (26 mg/ml).

Multiple linear regression analysis and statistical calculations were performed on a Gateway E-4200 computer (North Sioux City, SD, USA) using the program SPSS v11 (SPSS, Chicago, IL, USA). The solute descriptors were taken from an in-house data base and are summarized in Table 1.

3. Results and discussion

Examples of the three common types of polar chemically bonded stationary phases (3-aminopropylsiloxane-bonded, 3-cyanopropylsiloxane-bonded and spacer bonded propane-

Table 1
Solutes for column characterization and their descriptors values

Solute	Descriptors				
	V	*E*	*S*	*A*	*B*
Acetanilide	1.113	0.870	1.40	0.50	0.67
Acetophenone	1.014	0.820	1.01	0	0.48
Anisole	0.916	0.710	0.75	0	0.29
Benzamide	0.973	0.990	1.50	0.49	0.67
Benzene	0.716	0.610	0.52	0	0.14
Benzonitrile	0.871	0.740	1.11	0	0.33
Benzophenone	1.481	1.447	1.50	0	0.50
Benzyl benzoate	1.680	1.264	1.42	0	0.51
Benzyl chloride	0.980	0.821	0.82	0	0.33
Biphenyl	1.324	1.360	0.99	0	0.26
1-Bromonaphthalene	1.260	1.598	1.13	0	0.13
3-Bromophenol	0.950	1.060	1.15	0.70	0.16
Butyrophenone	1.300	0.800	0.95	0	0.51
1-Chloronaphthalene	1.208	1.417	1.06	0	0.13
2-Chlorophenol	0.898	0.853	0.88	0.32	0.31
4-Chlorophenol	0.898	0.920	1.08	0.67	0.20
Dibutyl phthalate	2.270	0.700	1.40	0	0.86
3,4-Dichloroaniline	1.061	1.158	1.24	0.35	0.25
Diethyl phthalate	1.711	0.729	1.40	0	0.88
2,6-Dimethylphenol	1.057	0.860	0.79	0.39	0.39
Ethylbenzene	0.998	0.613	0.51	0	0.15
Hexanophenone	1.580	0.720	0.95	0	0.50
2-Methoxynaphthalene	1.285	1.390	1.13	0	0.35
3-Methylphenol	0.916	0.822	0.88	0.57	0.34
4-Methylphenol	0.916	0.820	0.87	0.57	0.31
Naphthalene	1.085	1.340	0.92	0	0.20
1-Naphthol	1.144	1.520	1.05	0.61	0.37
2-Naphthol	1.144	1.520	1.08	0.61	0.40
2-Nitroaniline	0.990	1.180	1.37	0.30	0.36
4-Nitroaniline	0.990	1.220	1.91	0.42	0.38
Nitrobenzene	0.891	0.871	1.11	0	0.28
4-Nitrobenzyl alcohol	1.090	1.064	1.39	0.44	0.62
2-Nitrophenol	0.949	1.015	1.05	0.05	0.37
4-Nitrophenol	0.949	1.070	1.72	0.82	0.26
4-Nitrotoluene	1.032	0.870	1.11	0	0.28
Octanophenone	1.859	0.720	0.95	0	0.50
Phenol	0.775	0.810	0.89	0.60	0.30
2-Phenylethanol	1.057	0.811	0.91	0.30	0.65
4-Phenylphenol	1.383	1.560	1.41	0.59	0.45
Propriophenone	1.160	0.800	0.95	0	0.51
Valerophenone	1.440	0.800	0.95	0	0.50

diol silica column packings) and a silica-based multifunctional stationary phase (Chirobiotic T) are included in this study. The main difficulty in determining system constants for these column types was the weak retention of many solutes commonly used for column characterization in reversed-phase liquid chromatography. The solutes finally selected for this purpose, Table 1, are a subset of the solutes used by us to characterize the retention properties of alkylsiloxane-bonded silica stationary phases [16,27] augmented by a few additional solutes to provide adequate cover of the descriptor and retention space. Even so, it proved impractical to perform measurements at volume fractions of methanol higher than 20% (v/v) [10% (v/v) in the case of the 3-aminopropylsiloxane-bonded silica stationary phase]. This resulted in retention factor values in the range $-0.75 < \log k < 1.00$. For alkylsiloxane-bonded silica stationary phase values of $-0.75 < \log k < 2.75$ for the same solutes are more typical. Peak shapes were acceptable for all solutes except bases, which exhibited tailing, most likely due to electrostatic interactions with charged groups (e.g. silanols) of the stationary phase. Since electrostatic interactions are not represented in the solvation parameter model, compounds of this type were excluded from the data analysis.

The system constants for the polar chemically bonded stationary phases with mobile phases containing 10% (v/v) and 20% (v/v) methanol–water are summarized in Table 2. The models make chemical sense and are statistically sound. System constants for a representative alkylsiloxane-bonded silica stationary phase (Synergi Hydro-RP) are included in Table 2 for comparison purposes [27]. As a generic group the properties of alkylsiloxane-bonded silica stationary phases cannot be represented by a single column [3,4,27], but large differences in the system constants between the polar chemically bonded stationary phases and the Synergi Hydro-RP stationary phase can safely be interpreted as general differences between the different solvated stationary phase chemistries.

To aid the interpretation of the system constants in Table 2 some key features of the separation system should be noted. The stationary phase in reversed-phase liquid chromatography is solvated by the mobile phase, and although the chemistry of the bonded groups may play a key role in this process as well as in pore wetting, it is important not to become too fixated on the identity of the chemically bonded group as its role in direct solute interactions may be subservient to its general role in establishing an organized solvated interphase region for solute transfer from the mobile phase. In addition, water is both the most cohesive and hydrogen-bond acidic of the common solvents used in reversed-phase liquid chromatography. Although water is expected to be present in the interphase region, it is generally believed that solvation of the stationary phase occurs by differential absorption of mobile phase components such that at equilibrium the mobile phase possesses a higher water content than the interphase region. The strong intermolecular interactions between water molecules tend to promote self-association over interactions with dissimilar solvent or solute molecules. The preference for water to reform water–water interactions assists in the transfer of solutes to the stationary phase and is the main driving force for retention in reversed-phase liquid chromatography. This is opposed by the selective distribution of hydrogen-bond basic solutes to the water rich mobile phase, which is the main interaction that opposes transfer to the solvated stationary phase and reduces retention.

The effect of the cohesive properties of water is reflected in the v system constant determined by the difference in cavity formation and dispersion interactions in the mobile and solvated stationary phases. The v system constant is positive for all polar chemically bonded phases, Table 2, but is about five-fold smaller than for the alkylsiloxane-bonded silica stationary phase. Since it is generally assumed that dispersion interactions are roughly self-canceling for transfer between

Table 2
System constants for the polar chemically bonded stationary phases with methanol–water mobile phases

Stationary phase	System constants						Statistics[a]			
	v	*e*	*s*	*a*	*b*	*c*	*ρ*	S.E.	*F*	*n*
10% (v/v) methanol–water										
Alltima amino	0.38 (0.02)	0.37 (0.02)	0	0	−0.52 (0.04)	−0.89 (0.03)	0.982	0.035	299	39
Ultrasphere CN	0.85 (0.07)	0.58 (0.06)	−0.09 (0.06)	−0.18 (0.06)	−0.78 (0.11)	−0.73 (0.07)	0.972	0.080	121	41
Ultremex-CN	0.50 (0.03)	0.26 (0.03)	0	−0.17 (0.03)	−0.51 (0.06)	−0.52 (0.04)	0.978	0.042	179	39
Zorbax SB-CN	0.62 (0.03)	0.21 (0.02)	0	−0.17 (0.03)	−0.60 (0.05)	−0.59 (0.03)	0.985	0.038	273	39
LiChrospher DIOL	0.49 (0.06)	0.89 (0.05)	−0.37 (0.05)	−0.26 (0.05)	−0.50 (0.10)	−0.59 (0.06)	0.978	0.072	152	41
Chirobiotic T	0.69 (0.05)	0.26 (0.05)	0.26 (0.05)	−0.40 (0.05)	−0.60 (0.09)	−0.83 (0.06)	0.976	0.065	147	41
Synergi Hydro-RP[b]	3.64 (0.20)	0.29 (0.10)	−0.58 (0.06)	−0.59 (0.07)	−1.99 (0.09)	−0.46 (0.14)				
20% (v/v) methanol–water										
Ultrasphere CN	0.95 (0.07)	0.49 (0.06)	−0.15 (0.06)	−0.10 (0.05)	−0.75 (0.11)	−0.93 (0.07)	0.973	0.076	123	40
Ultremex-CN	0.56 (0.04)	0.33 (0.04)	0.06 (0.05)	−0.17 (0.04)	−0.65 (0.09)	−0.99 (0.05)	0.975	0.053	126	38
Zorbax SB-CN	0.56 (0.04)	0.22 (0.04)	−0.08 (0.04)	−0.16 (0.04)	−0.53 (0.08)	−0.78 (0.04)	0.973	0.046	107	38
LiChrospher DIOL	0.56 (0.03)	0.41 (0.03)	−0.17 (0.04)	0	−0.73 (0.06)	−0.58 (0.04)	0.986	0.043	285	38
Chirobiotic T	0.49 (0.03)	0.16 (0.03)	0.24 (0.03)	−0.33 (0.03)	−0.48 (0.06)	−0.86 (0.04)	0.979	0.045	164	41
Synergi Hydro-RP[b]	3.18 (0.20)	0.34 (0.10)	−0.67 (0.06)	−0.58 (0.06)	−2.13 (0.08)	−0.29 (0.13)				

[a] ρ is the multiple correlation coefficient; S.E. the standard error in the estimate; F the Fischer statistic and n the number of solutes. The numbers in parenthesis are the standard deviations for the system constants.
[b] Data from ref. [27].

condensed phases, the solvated polar chemically bonded stationary phases must be significantly more cohesive than the alkylsiloxane-bonded silica stationary phase. This is a major reason for the lower retention observed for polar chemically bonded stationary phases.

The effect of the hydrogen-bond acidity of water is reflected in the *b* system constant, which is negative for all the polar chemically bonded stationary phases in Table 2. The *b* system constant is about four-fold smaller (less negative) than for the alkylsiloxane-bonded silica stationary phase. The solvated polar chemically bonded stationary phases are, therefore, significantly more hydrogen-bond acidic than the alkysiloxane-bonded silica stationary phase. Although there are differences in the *b* system constant for the different types of chemically bonded phases, the range of values is narrow compared to the difference between the polar chemically bonded stationary phases and the alkylsiloxane-bonded stationary phase. This suggests that the hydrogen-bond acidity of the solvated stationary phase is not a strong function of the identity of the polar bonded group. More likely, both the difference in the *v* and *b* system constants is a product of the attraction of a larger volume fraction of water into the interphase region for the polar chemically bonded stationary phases compared with alkylsiloxane-bonded silica stationary phases.

The *e* system constant is positive for all the stationary phases in Table 2 and contributes favorably to retention. It seems to be more important for the 10% (v/v) methanol–water mobile phase composition and for the spacer bonded propanediol stationary phase. In general, the contribution of electron loan pair interactions to retention in reversed-phase liquid chromatography is small, but useful selectivity differences exist for the different types of polar chemically bonded stationary phases. In terms of its ability to affect band spacing on different column types, only small changes due to this parameter can be expected.

The *s* system constant varies significantly among the polar chemically bonded stationary phases and between these phases and the alkylsiloxane-bonded silica stationary phase. The *s* system constant is determined by the difference in capacity of the mobile and solvated stationary phases for dipole-type interactions. All the solvated polar chemically bonded stationary phases are more dipolar/polarizable than typical solvated alkylsiloxane-bonded silica stationary phases. The solvated Chirobiotic T stationary phase is the most competitive and has a positive *s* value significantly larger than any of the other polar chemically bonded stationary phases. The Chirobiotic T stationary phase has a complex structure (macrocyclic glycopeptide) and so the reason for its selectivity for dipole-type interactions is not easy to pinpoint except to note that it has a large number of possible polar functional groups for dipole-type interactions. The 3-cyanopropylsiloxane-bonded silica stationary phases have either zero *s* values or small negative values. Since alkylsiloxane-bonded silica stationary phases have significant negative *s* values, this is an indication that dipole-type interactions are more important for the 3-cyanopropylsiloxane-bonded silica stationary phases, which in general, are about as dipolar/polarizable as the mobile phase. Dipole-type interactions, therefore, do not play a large part in the retention mechanism on the solvated 3-cyanopropylsiloxane-bonded stationary phases but will play a significant role in method development when transferring a method from a alkylsiloxane-bonded silica stationary phase (weak interaction) to a 3-cyanopropylsiloxane-bonded silica stationary phase (stronger interaction). Dipole-type interactions for the solvated 3-aminopropylsiloxane-bonded silica stationary phase are about the same as those for the solvated 3-cyanopropylsiloxane-bonded silica station-

ary phases. Dipole-type interactions for the solvated spacer bonded propanediol stationary phase are weaker than for the solvated 3-cyanopropylsiloxane-bonded silica stationary phases while stronger than typical solvated alkylsiloxane-bonded silica stationary phases.

The hydrogen-bond basicity of the solvated polar chemically bonded stationary phases is generally significantly greater than for typical solvated alkylsiloxane-bonded silica stationary phases, but the polar chemically bonded stationary phases are not competitive with the mobile phase (*a* system constant is usually negative). The exceptions are the 3-aminopropylsiloxane-bonded silica stationary phase and 10% (v/v) methanol–water mobile phase and the solvated spacer bonded propanediol stationary phase and 20% (v/v) methanol–water mobile phase, which are about as hydrogen-bond basic as the mobile phase. Otherwise the range of *a* system constant values is small with the solvated Chirobiotic T stationary phase, being the least competitive with the mobile phase, and the status of the solvated spacer bonded propanediol stationary phase showing a significant change at the two mobile phase compositions. The 3-cyanopropylsiloxane-bonded silica stationary phases are more hydrogen-bond basic than the solvated Chirobiotic T stationary phase and are virtually unaffected by the change in mobile phase composition.

The *c* term (model constant) is unrelated to the intermolecular interactions responsible for the solute equilibrium distribution between the two phases. When the dependent variable is the retention factor, the *c* term is dominated by the phase ratio for the chromatographic system, but also contains contributions from all sources of lack-of-fit of the model equation to the experimental data. Assuming that the value of the *c* term is controlled predominantly by the phase ratio, then the phase ratio for the solvated polar chemically bonded phases is less favorable for retention compared with the solvated alkylsiloxane-bonded silica stationary phase. This provides a further reason for the lower retention, in general, on the polar chemically bonded stationary phases compared with alkylsiloxane-bonded silica stationary phases.

Selectivity differences between separation systems are preferably correlated through the differences in their system constant ratios (*e*/*v*, *s*/*v*, *a*/*v* and *b*/*v*) [3,4,28]. Effective changes in band spacing on any compared separation systems requires a significant difference in at least two system constant ratios [29]. The system constant ratios for the stationary phases studied here, with further values taken from the literature, are summarized in Table 3. Selectivity differences are noted among the polar chemically bonded stationary phases as well as between these phases and the alkylsiloxane-bonded silica stationary phase. The range of selectivity differences for the 3-cyanopropyslsiloxane-bonded silica stationary phases is not large and is similar to differences observed among a larger number of alkylsiloxane-bonded silica stationary phases [3,4]. These selectivity differences can, and do, arise from differences in the physical properties of the silica substrate (pore structure, surface area, silanol concentration) and differences in the chemistry used to prepare the bonded phases and their bonding density. There is a signif-

Table 3
System constant ratios for the stationary phases studied in this report and literature values

Stationary phase	System constant ratios					Reference
	v	*e*/*v*	*s*/*v*	*a*/*v*	*b*/*v*	
10% (v/v) methanol–water						
Alltima amino	0.38	0.97	0	0	−1.37	
Supelcosil LC-NH_2	0.46	1.46	0	−1.22	0	[11]
Ultrasphere CN	0.85	0.68	−0.11	−0.21	−0.92	
Ultremex-CN	0.50	0.52	0	−0.34	−1.02	
Zobax SB-CN	0.62	0.34	0	−0.27	−0.97	
Hypersil CN	1.59	0.67	−0.21	−0.52	−0.09	[11]
J.T. Baker CN (SPE sorbent)	1.78	0.23	0	−0.16	−0.90	[20]
E. Merck CN HPTLC plates	2.39	0	0	0	−0.69	[17]
LiChrospher DIOL	0.49	1.82	−0.76	−0.53	−1.02	
LiChrospher 100 DIOL	1.34	1.58	−0.87	−0.48	−0.17	[11]
J.T. Baker DIOL (SPE sorbent)	1.53	0.31	0	−0.19	−0.77	[21]
Chirobiotic T	0.69	0.38	0.38	−0.58	−0.87	
Synergi Hydro-RP	3.64	0.08	−0.16	−0.16	−0.55	[27]
20% (v/v) methanol–water						
Ultrasphere CN	0.95	0.52	−0.16	−0.11	−0.79	
Ultremex-CN	0.56	0.59	0.11	−0.30	−1.16	
Zobax SB-CN	0.56	0.39	−0.14	−0.29	−0.95	
J.T. Baker CN (SPE sorbent)	1.65	0.21	0	−0.15	−0.93	[20]
E. Merck CN HPTLC plates	1.99	0.15	0	0	−0.82	[17]
LiChrospher DIOL	0.56	0.73	−0.30	0	−1.30	
J.T. Baker DIOL (SPE sorbent)	1.54	0.24	0	−0.13	−0.81	[21]
Chirobiotic T	0.49	0.33	0.49	−0.67	−0.98	
Synergi Hydro-RP	3.18	0.11	−0.21	−0.18	−0.67	[27]

icant difference in the system constant ratios for the chemically bonded phases studied in ref. [11] and those calculated here. These differences are probably larger than can be explained by differences in column properties. Reviewing the data in ref. [11] there is a significant difference in the choice of descriptor values for a number of solutes (there is a systematic problem in the *B* values for weak bases in ref. [11]; the quoted values are not appropriate for water containing phases). In addition, weak bases are susceptible to contributions to retention from electrostatic interactions not taken into account by the solvation parameter model. Lastly, the range of retention factor values is small (e.g. 0.02–1.90 on the Supelcosil LC-NH_2 column) with many solutes too weakly retained for accurate measurements. These factors may have resulted in poor modeling conditions. There is little agreement between the system constant ratios for thin-layer chromatography and solid-phase extraction sorbents and the column sorbents. This is not unexpected, since the products are manufactured to different specifications. The materials for thin-layer chromatography are prepared using bifunctional silanizing reagents, and with a low degree of silanization, to promote adequate migration of the mobile phase by capillary forces [1]. Materials for solid-phase extraction are optimized for retention and have a polymeric surface coating based on a high surface area type A silica substrate [22]. These differences in chemistries mean that the results from thin-layer chromatography or solid-phase extraction offer a poor system for predicting separations on high-performance liquid chromatography columns and vice versa.

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