Notes

Comparison of Octadecyl-bonded Alumina and Silica for Reversed-phase Liquid Chromatography Based on the Linear Solvation Energy Relationships

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Recently, Wiserman *et al.* introduced an "octadecylalumina" (ODA) material for reversed-phase liquid chromatography in which monomeric octadecyl functionalities are covalently bonded to the surface of a porous, microspherical alumina, which has been known to have a better pH stability (pH 2-14) and contain less chromatographically active sites than silica counterpart (ODS)[1]. The higher stability of the ODA to alkaline eluents and the absence of acidic silanol sites on its surface are very useful properties for a more efficient separation of organic bases than is generally possible with ODS. Haky *et al.*[2] compared chromatographic properties of the ODA and ODS for reversed phase liquid chromatography and found that although retention property of ODA is similar to standard ODS stationary phases, there are differences in solute-stationary phase interactions, especially in hydrogen bonding interactions on the two phases. These differences were ascribed to the differences in the chemical properties of silica and alumina base material[2].

In this paper, we reexamined the chromatographic properties of these two stationary phases based on the linear solvation energy relationsips (LSERs)[3,4] and Kalmet-Taft solvatochromic parameters, π^*, α, and β[5] to gain a better understanding of the differences in solute-stationary phase interactions on the two phases. Kamlet, Taft and their coworkers have applied the LSER approach to some 600 processes[4] including a large number of systems of immediate relevance to chromatography, such as Rohrschneider's gas-liquid partition coefficients[6], retention of McReynold's solutes on polymeric silicone oil gas chromatographic phases[7], and retention in normal[8] and reversed phase liquid chromatography[9-12]. According to the LSER formalism, when applied to phase-transfer processes, a general solute or solvent property (SP) can be correlated via the use of three types of terms as folllows[3,4]:

$$SP = SP_o + \text{cavity term} + \text{dipolar term} + \text{hydrogen bonding term(s)} \quad (1)$$

SP_o denotes the value of SP when all the three terms in the equation are zero. The cavity term is usually taken as the product of the solute van der Waals molar volume (V_i) and the square of the Hildebrand solubility parameter (δ_H) of the solvent. The dipolar term is the product of the solute π^* and the solvent π^*. The π^* parameter measures a combination of dipolarity/polarizability of a compound. The hydrogen bonding (HB) terms are written as a cross product of the solute α and the solvent β (type B HB) and the product of the solute β and the solvent α (type A HB). The parameters α and β measure HB donor acidity and HB acceptor basicity of the compound, respectively. In the case of the chromatographic retention, SP in the equation below denotes a logarithmic capacity factor and the subscript 2 designates a solute property. The subscripts s and m denote the stationary and mobile phases, respectively.

$$\log k' = \log k'_o + M(\delta_s^2 - \delta_m^2) V_{I,2}/100 + S(\pi_s^* - \pi_m^*)\pi_2^* + B(\alpha_s - \alpha_m)\beta_2 + A(\beta_s - \beta_m)\alpha_2 \quad (2)$$

The coefficients M, S, A, and B are the fitting parameters.

When a system with a fixed pair of mobile and stationary phases is considered, eq. 2 is reduced to

$$\log k' = \log k'_o + mV_{I,2}/100 + s\pi_2^* + b\beta_2 + a\alpha_2 \quad (3)$$

The coefficients m, s, a, and b 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 (or mobile) phase internations affecting retention for a given pair of mobile-stationary phase condition. Thus, when these coefficients are different for capacity factors for a given solute set measured on the ODA and ODS with the same mobile phase, the differences indicate different contributions from various solute-stationary phase interactions to retention on the two phases. As shown below simple regression analyses based on the LSER can readily reveal the differences in the chromatographic properties of bonded stationary phases derived from different base material.

Results and Discussion

Haky *et al.* reported capacity factors for 31 organic compounds on both the ODA and ODS stationary phases using methanol-aqueous buffer (pH 7.4) as the mobile phase[2]. Capacity factors for 22 solutes whose solvatochromic parameters are available are listed in Table 1. Retention parameters on the ODA stationary phase are larger than those on the ODS phase since the solutes were eluted using the mobile phase containing a smaller amount of the stronger solvent methanol (50% on the ODA *vs.* 70% on the ODS).

The LSER equations obtained for the ODS and ODA stationary phases are:

$$\log k'\ (ODS) = -0.31(\pm 0.11) + 2.64(\pm 0.15) V_{I,2}/100 - 2.19(\pm 0.14)\beta_2 - 0.33(\pm 0.08)\alpha_2 \quad (4)$$

$$n = 22,\ r = 0.991,\ s.d. = 0.089$$

$$\log k'\ (ODA) = -0.58(\pm 0.16) + 3.57(\pm 0.23) V_{I,2}/100$$

Table 1. The solute properties

Solute	$V_I/100$	π^*	β	α	logk' ODS	logk' ODA
benzamide	0.676	0.94	0.75	0.49	-0.274	0.044
aniline	0.562	0.73	0.50	0.16	-0.058	0.079
benzyl alcohol	0.634	0.99	0.52	0.35	0.088	0.230
phenol	0.536	0.72	0.33	0.61	-0.022	0.373
benzonitrile	0.590	0.90	0.37	0.00	0.185	0.376
acetophenone	0.690	0.90	0.49	0.00	0.285	0.447
p-cresol	0.634	0.68	0.34	0.58	0.363	0.729
benzene	0.491	0.59	0.10	0.00	0.731	0.772
m-cresol	0.634	0.68	0.34	0.58	0.351	0.692
quinoline	0.734	0.92	0.44	0.00	0.433	0.655
methyl benzoate	0.736	0.76	0.39	0.00	0.609	0.861
trichloroethylene	0.492	0.53	0.05	0.00	0.855	1.045
chlorobenzene	0.581	0.71	0.07	0.00	1.071	1.249
ethyl benzoate	0.834	0.74	0.41	0.00	1.007	1.200
1-naphthol	0.798	0.82	0.33	0.61	0.769	1.461
toluene	0.592	0.55	0.11	0.00	0.946	1.183
2-naphthol	0.798	0.92	0.33	0.61	0.705	1.366
bromobenzene	0.624	0.79	0.06	0.00	1.142	1.386
naphthalene	0.753	0.70	0.15	0.00	1.358	1.641
biphenyl	0.920	1.18	0.20	0.00	1.625	n.a.*
phenanthrene	1.015	0.80	0.20	0.00	1.807	n.a.
anthracene	1.015	0.80	0.20	0.00	1.807	n.a.

*Not available.

$$-2.52(\pm 0.16)\beta_2+0.16(\pm 0.08)\alpha_2 \qquad (5)$$

$$n=19,\quad r=0.988,\quad s.d.=0.087$$

The coefficients for π^* turned out to be not significant (statistically zero) and thus do not appear in the equations.

It is seen in eq. 4 and 5, as might be expected from a priori considerations, that increasing solute size (V_{I2}) causes an increase in retnetion (k'), i.e., free energy concepts favor solute transfer from the more cohesive mobile phase to the less cohesive stationary phase. The size of the coefficient m on the ODA in eq. 5 is significantly greater than that in eq. 4 because the mobile phase used on the ODA cntained a greater amount of more cohesive water than the one used on the ODS. Opposing this effect, increases in solute hydrogen bond donor basicity (β_2) lead to lower k' values because the solutes have increased affinities for the more hydrogen bond donating aqueous mobile phase. The sizes of the coefficient b in the two equations are similar. Type A HB interactions occur mainly between the HB basic functionality of the solute and water, which is a stronger HB donor acid than any other components in both chromatographic phases such as methanol, bonded octadecyl and unreacted surface silanol group of silica. Thus, as long as the mobile phase contains water the relative amount of water is not important in hydrogen bond formation because the solute concentration is always smaller than that for water in the mobile phase.

The magnitude of the coefficient a for α_2 term in both equations (eqs. 4 and 5) is small compared to the coefficients m and b, indicating that type B HB interactions are less important in determining retention compared to cavity formation and type A HB interactions. However, the effect of type B HB on retention is quite different on the two stationary phases. The sign of the coefficient a is negative on the ODS but positive on the ODA. Increasing solute HB donor acidity leads to lower retention on the ODS while leads to increase retention on the ODA. If HB interactions only between the solute and the mobile phase are affecting the solute retention the coefficient a must have the same sign (negative) on both stationary phases since both mobile phase used on the two stationary phases contain water and type B HB interactions should lead to lower k'. The positive sign of the coefficient a on the ODA is a clear indication of contribution of strong HB interactions between the solute and the unreacted basic sites of the alumina surface. This also indicates type B HB interactions between the solute and alumina surface are stronger than those between the solute and water in the mobile phase. This is in agreement with an inherent basicity of unbonded alumina[8,13,14]. The unreacted surface silanol groups of silica also interact through type A HB with solutes' HB acceptor functionalities, but with their smaller HB donor acidity than water, type A HB interactions with surface silanol groups on the ODS are likely to be less important than type B HB interactions on the ODA.

The above LSER equations have clearly shown that the active sites of the ODA stationary phase participate in the determination of retention although alumina does not possess strong hydrogen-bond active sites like residual silanol groups on the ODS. Understanding the effect of different chemical properties of base material for stationary phases on retention, shown here with the ODS and ODA, is

useful for studying retention processes in RPLC and can be utilized for obtaining optimum separations for a given sample with these stationary phases.

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Chemical Shifts in Carbon-13 Nuclear Magnetic Resonance Spectra of Aminopolycarboxylate Anions

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Prediction of chemical shifts based on emperical additive substituent parameters has been proved to be quite successful in ^{13}C-NMR. It was demonstrated in the pioneering work of Grant and Paul[1] that the chemical shift of a paraffinic carbon in a linear or branched hydrocarbon can be estimated by the emperical substituent rule. Lindeman and Adams[2] extended the work of Grant and Paul to estimate the chemical shifts of substituted alkanes by calculating the shift of the parent alkane and by adding the appropriate substituent parameters. Extensive studies for estimation of chemical shift have been made for compounds containing several functional groups such as alcohols,[3] amines,[4] carboxylates,[5] pyridines,[6] etc. But in our best knowledge the estimation of chemical shifts for more complicated compounds such as aminopolycarboxylic acids has not been reported.

In this paper we predict ^{13}C chemical shifts of 11 aminopolycarboxylate anions in aqueous solution which contain several functional groups (N, O, COO^-) using the emperical substituent parameters.

Table 1. Names and Abbreviations(in parantheses) of Aminopolycarboxylic Acids

Methyliminodiacetic acid(MIDA)
Ethyliminodiacetic acid(EtIDA)
Nitrilotriacetic acid(NTA)
Ethylenediaminetetraacetic acid(EDTA)
1,2-Propylenediaminetetraacetic acid(PDTA)
Diethylenetriaminepentaacetic acid(DTPA)
2-Hydroxyethylethylenediamintriacetic acid(HEDTA)
2-Hydroxyethyliminodiacetic acid(HEIDA)
Ethyletherdiaminetetraacetic acid(EEDTA)
Ethylenebis(oxyethylenenitrilo) tetraacetic acid(EGTA)
2-Hydroxy-1,3-propanediaminetetraacetic acid(HPDTA)

Experimental

The names and abbreviations of aminopolycarboxylic acids studied are listed in Table 1.

Sample solutions for NMR spectra were prepared by dissolving the weighed amounts of aminopolycarboxylic acid in 20% D_2O/80% H_2O to provide 0.5 M solution. The pH of the solution was adjusted with 50% NaOH or concentrated H_2SO_4 solution. Fully deprotonated forms were obtained by raising the pH value to two units above the highest *pKa* value.[7]

^{13}C NMR spectra were obtained at 25.2 MHz on a Varian XL-100 FT spectrometer at 40 ± 2 °C probe temperature. The experimental details for obtaining spectra are same as those given elsewhere.[8] For individual solutions spectral reproducibility was better than ±0.1 ppm.

Results and Discussion

The ^{13}C NMR spectra of 11 fully deprotonated aminopolycarboxylate anions were measured and ^{13}C chemical shifts of these compounds are summarized in Table 2.

Chemical shifts of carboxylate carbons can be predicted by Rabenstein equation (1)[5(b)]

$$\delta_{coo} = 182.09 + \Sigma n_i d_i \quad (1)$$

where d are additive parameters for given functional groups at specific numbers of bonds B from COO moiety and n_i is the number of functional groups. The d parameters are given in Table 3.

Chemical shifts of non-carboxylate carbons in aminopolycarboxylate can be predicted by two methods. The chemical