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Study of retention in micellar liquid chromatography on a C_8 column by the use of linear solvation energy relationships ☆

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Abstract

Linear solvation energy relationships (LSERs) are used to investigate the fundamental chemical interactions governing the micellar liquid chromatographic retention of 22 aromatic compounds (11 benzene derivatives and 11 aromatic polycyclic hydrocarbons) in 80 mobile phases on a C_8 column. The systems studied involve combinations of 0.050 to 0.140 *M* sodium dodecyl sulfate or cetyltrimethylammonium bromide, with 0 to 10% methanol, *n*-propanol, and *n*-butanol as mobile phase modifiers. The ability of the LSERs to account for the chemical interactions underlying solute retention is shown. A comparison of predicted and experimental retention factors suggests that LSER formalism is able to reproduce adequately the experimental retention factors of the solutes studied in the different experimental conditions investigated.

Keywords: Micellar liquid chromatography; Linear solvation energy relationships; Mobile phase composition

1. Introduction

Micellar liquid chromatography (MLC) is an alternative technique to conventional reversed-phase liquid chromatography (RPLC) in which the mobile phase is an aqueous solution of a surfactant at a concentration above its critical micellar concentration, that is, in a medium where micelles exist [1,2].

MLC techniques present some advantages over RPLC techniques such as: (a) it is possible to separate cationic, anionic, and neutral species simultaneously [3,4]; (b) rapid elution gradients can be achieved because the concentration of free surfactant monomers in the mobile phase remains essentially constant in the post-critical concentrations region [5] and thus, the amount of sorbed surfactant in the stationary phase remains constant, and little column re-equilibration time is required before a new separation is started [5–7]; (c) luminescence detection can be improved for some solutes [8] when they are incorporated into the micelles, and more typically because of the complex phase-transfer phenomenon occurring within the column; and (d) biological fluids can be directly injected into the chromatographic system because of the solubilization of proteins by surfactants [9,10].

An important drawback of MLC, however, is the

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decrease in chromatographic efficiency observed as compared to that obtained in RPLC [5,11], especially with mobile phases formed only of water and the surfactant. This limitation can be avoided by the addition of small amounts of organic modifiers to the mobile phase [4,5], which, in addition to improving the efficiency of MLC separations, can also increase chromatographic selectivity and reduce analysis time.

The aim of this work is to investigate the fundamental chemical interactions responsible for retention in micellar systems modified by alcohols. The variations of these interactions are studied as a function of the nature and concentration of the surfactant [sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB)] and organic modifier (methanol, *n*-propanol and *n*-butanol). For this study, we have used linear solvation energy relationships (LSERs) [12–15] to explain retention in MLC systems using aqueous mobile phases containing SDS or CTAB in the absence and in the presence of 3, 5 and 10% (v/v) methanol, *n*-propanol, or *n*-butanol. The data in this study cover 80 different micellar mobile phases using 22 aromatic compounds (11 benzene derivatives and 11 polycyclic aromatic hydrocarbons).

LSER methodology has been extensively applied in conventional RPLC [12,16–21], gas chromatography (GC) [22,23], and more recently to supercritical fluid chromatography [24–27]. LSER studies regarding the transfer of solutes from water to micellar systems have also been published. In these studies, different chromatographic techniques have been used: MLC [15,28,29], micellar electrokinetic chromatography (MEKC) [15,30–33] and headspace gas chromatography (HS-GC) [34].

With respect to MLC LSER studies, in a previous paper [28], we studied the fundamental chemical interactions governing the retention of 15 aromatic compounds in 40 micellar RPLC chromatographic systems using SDS, CTAB, methanol, *n*-propanol and *n*-butanol as mobile phase modifiers with a C_{18} stationary phase. We found that solute size and basicity are the two most important solute parameters determining the retention in the MLC systems studied. These results were similar to those obtained by other authors [29] with the zwitterionic surfactant *n*-dodecyl-*N*,*N*-dimethylamino-3-propane-1-sulfonate (C-12 DAPS).

The general LSER equation used in this work is [35]:

$$\log k = \log k_0 + m(V_X/100) + s\pi_2^H + a\sum\alpha_2^H + b\sum\beta_2^H + rR_2$$

where k is the experimental retention factor. The V_X, π_2^H, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$ and R_2 terms are the solute descriptors, where V_X represents the solute's size/polarizability, π_2^H is the dipolarity/polarizability, $\Sigma\alpha_2^H$ is the hydrogen bond (HB) donating ability, $\Sigma\beta_2^H$ is the HB accepting ability, and R_2 is the excess molar refraction. The subscript ''2'' simply signifies that these parameters are solute descriptors.

The coefficients of these descriptors *m*, *s*, *a*, *b*, and *r* reflect differences in the two bulk phases between which the solute is transferring [30] and are obtained through a multiparameter linear regression. The log k_0 term is simply the intercept of the regression and is comprised of constant contributions from the solutes and the chromatographic system.

We note that since the parameters V_X and π_2^H are blends of two different interactions, the coefficients of these parameters are also blends of the corresponding properties. Specifically, *m* is the difference in the cohesivity/dispersive ability of the two bulk phases, and *s* is the difference in the ability of the two phases to interact through dipole–dipole and dipole–induced dipole interactions. Many reviews and examples of LSERs and their interpretations are available [16–20].

The interpretation of MLC LSERs is complicated by the fact that the system is commonly described using a three-phase model (mobile, stationary, and micellar phases) with three accompanying partition coefficients (mobile to stationary phase, mobile to micelle phase, and stationary to micelle phase transfers) [28]. Regarding the interpretations of the role of the stationary phase in determining changes in the LSER coefficients as a function of surfactant concentration, we assumed, in the same mode that other authors [36–38] that the stationary phase environment in MLC is independent of micelle concentration in the mobile phase and, thus, the stationary phase does not change with the surfactant concen-

tration and the amount of surfactant adsorbed by the stationary phase remains constant above the critical micelle concentration (CMC). Finally, different modifiers and different modifier concentrations with the same surfactant system can cause changes in the total amount of sorbed surfactant, but we make the simplifying assumption that this amount does not vary substantially as a function of the surfactant concentration [28,39].

2. Experimental

Benzene derivatives and polycyclic aromatic hydrocarbons were: (1) benzene, (2) benzyl alcohol, (3) benzamide, (4) toluene, (5) benzonitrile, (6) nitrobenzene, (7) phenol, (8) 2-phenylethanol, (9) chlorobenzene, (10) phenylacetonitrile, (11) 3,5-dimethylphenol, (12) naphthalene, (13) 1-naphthol, (14) 2-naphthol, (15) 1-naphthylamine, (16) pyrene, (17) phenanthrene, (18) 2,3-benzofluorene, (19) fluorene, (20) fluoranthene, (21) acenaphthene, (22) antracene. SDS, CTAB, *n*-propanol, and *n*-butanol were from Merck and methanol was from Scharlau. All were of the highest purity available and used as received.

Experimental MLC data used in this work were previously determined in Ref. [40] in the case of 15 benzene and naphthalene derivatives and in Ref. [41] in the case of polycyclic aromatic hydrocarbons. Tables 1 and 2 group the experimental conditions (80 mobile phases) in which the retention factors for the 22 compounds studied were determined.

The chromatographic system consisted of a Model 1050 pump, a Model 1050 automatic injector, a Model 1050 spectrophotometric detector of variable wavelength and a HP 3394 integrator (all from Hewlett-Packard). Retention data employed were averages of at least three determinations and were obtained with two columns (one for each surfactant) 15 cm×4.0 mm I.D. Spherisorb C_8 ($d_p = 5$ μm) (Teknokroma). Column void volumes of 1.09 ml determined for the SDS column and 0.97 ml for the CTAB column were used for all retention factor calculations. The columns and mobile phases were water-jacketed and maintained at 25°C with a circulating water bath.

LSERs were determined using the regression algorithm in Excel and solute parameters from Abraham et al. [35].

3. Results and discussion

The coefficients for the LSER equations obtained for each of the 80 mobile phases used in this work are grouped in Tables 1 and 2. In most cases, these parameters were obtained by using the 22 aromatic solutes studied in this work, but for some mobile phases the retention factor could not be determined for all compounds. In these cases, the parameters for the LSER equations were obtained using a minor number of solutes, which is indicated in the tables.

Table 1 shows the results obtained for CTAB mobile phases, for which correlation coefficients ranged from 0.908 to 0.952 with standard errors ranging from 0.045 to 0.097. Table 2 shows that correlation coefficients for SDS mobile phases ranged from 0.881 to 0.976 with standard errors ranging from 0.047 to 0.181.

In all the systems investigated the coefficients of π_2^H and $\Sigma\beta_2^H$ were negative, that is, an increase in the solute dipolarity/polarizability and HB basicity decreases the overall retention of the molecule. Furthermore, the coefficients of V_X and R_2 were positive in all the systems studied, indicating that increases in the solute volume and excess molar refractivity lead to increases in retention. However, the coefficient of $\Sigma\alpha_2^H$ is negative in SDS systems while in the CTAB systems it is statistically equal to zero or very slightly negative. In terms of the magnitude of the coefficients, solute volume and HB basicity generally play the largest role in determining the retention of solutes in all the systems studied. Solute dipolarity/polarizability is also an important factor in the CTAB systems with coefficients comparable in magnitude to those of solute volume.

These trends parallel observations in RPLC LSER studies in which solute volume and HB basicity typically have the largest coefficients. The trends also parallel our previous MLC LSER studies involving a C_{18} stationary phase [36]. Finally, the results also match chemical intuition in that they reflect the hydrophobic effect, which increases retention of

Table 1
LSER equations for 35 different CTAB mobile phases and a C_8 stationary phase[a]

	Log k_0	m	s	a	b	r	R	SD
[CTAB] no modifier								
0.050[1]*	0.69 (0.18)	1.01 (0.27)	−0.18 (0.12)	0.14 (0.09)	−1.06 (0.18)	0.09 (0.11)	0.929	0.070
0.067[1]*	0.66 (0.16)	0.89 (0.24)	−0.16 (0.10)	0.14 (0.08)	−0.96 (0.16)	0.08 (0.10)	0.930	0.063
0.080[1]*	0.63 (0.15)	0.82 (0.22)	−0.15 (0.09)	0.14 (0.07)	−0.90 (0.14)	0.07 (0.08)	0.934	0.056
0.100[1]*	0.61 (0.13)	0.73 (0.19)	−0.14 (0.08)	0.12 (0.06)	−0.81 (0.13)	0.06 (0.08)	0.935	0.050
0.120[1]*	0.58 (0.12)	0.66 (0.17)	−0.12 (0.07)	0.10 (0.06)	−0.74 (0.12)	0.05 (0.07)	0.936	0.045
[CTAB] 3% *n*-propanol								
0.050	1.12 (0.16)	0.48 (0.24)	−0.38 (0.14)	0.16 (0.11)	−0.83 (0.20)	0.19 (0.12)	0.908	0.092
0.067	1.03 (0.14)	0.42 (0.21)	−0.34 (0.12)	0.12 (0.09)	−0.74 (0.17)	0.16 (0.10)	0.914	0.079
0.080	0.98 (0.13)	0.39 (0.19)	−0.31 (0.11)	0.11 (0.08)	−0.71 (0.16)	0.15 (0.09)	0.918	0.072
0.100[1]*	0.55 (0.13)	0.76 (0.20)	−0.17 (0.08)	0.04 (0.06)	−0.88 (0.13)	0.08 (0.08)	0.945	0.051
0.120	0.83 (0.10)	0.33 (0.15)	−0.25 (0.08)	0.06 (0.06)	−0.60 (0.12)	0.12 (0.07)	0.931	0.055
[CTAB] 5% *n*-propanol								
0.050	1.11 (0.17)	0.50 (0.26)	−0.43 (0.14)	0.10 (0.11)	−0.88 (0.21)	0.19 (0.12)	0.913	0.096
0.067	1.04 (0.14)	0.43 (0.22)	−0.37 (0.12)	0.08 (0.09)	−0.80 (0.10)	0.17 (0.11)	0.918	0.083
0.080	0.96 (0.13)	0.42 (0.20)	−0.34 (0.11)	0.07 (0.09)	−0.75 (0.16)	0.16 (0.09)	0.925	0.074
0.100	0.90 (0.12)	0.37 (0.18)	−0.30 (0.10)	0.06 (0.08)	−0.71 (0.15)	0.13 (0.09)	0.921	0.068
0.120	0.83 (0.10)	0.35 (0.16)	−0.28 (0.09)	0.04 (0.07)	−0.66 (0.13)	0.12 (0.08)	0.932	0.060
[CTAB] 10% *n*-propanol								
0.050	1.04 (0.17)	0.52 (0.26)	−0.46 (0.15)	−0.02 (0.11)	−0.93 (0.21)	0.20 (0.12)	0.925	0.097
0.067	0.97 (0.15)	0.44 (0.23)	−0.42 (0.13)	−0.00 (0.10)	−0.85 (0.19)	0.19 (0.11)	0.924	0.088
0.080	0.90 (0.13)	0.42 (0.20)	−0.37 (0.11)	−0.05 (0.09)	−0.79 (0.16)	0.16 (0.10)	0.933	0.076
0.100[2]*	0.89 (0.13)	0.25 (0.20)	−0.35 (0.10)	−0.12 (0.09)	−0.68 (0.15)	0.20 (0.09)	0.945	0.065
0.120	0.77 (0.11)	0.36 (0.16)	−0.32 (0.09)	−0.07 (0.07)	−0.69 (0.13)	0.13 (0.08)	0.942	0.061
[CTAB] 3% *n*-butanol								
0.050	1.01 (0.15)	0.40 (0.23)	−0.39 (0.13)	0.08 (0.10)	−0.76 (0.18)	0.20 (0.11)	0.915	0.085
0.067	0.93 (0.13)	0.35 (0.20)	−0.35 (0.11)	0.08 (0.09)	−0.71 (0.16)	0.18 (0.09)	0.921	0.074
0.080	0.89 (0.12)	0.32 (0.18)	−0.33 (0.10)	0.07 (0.08)	−0.67 (0.14)	0.18 (0.09)	0.928	0.066
0.100[3]*	0.79 (0.13)	0.32 (0.19)	−0.31 (0.11)	0.06 (0.08)	−0.59 (0.17)	0.16 (0.09)	0.923	0.067
0.120	0.74 (0.09)	0.27 (0.14)	−0.27 (0.08)	0.06 (0.06)	−0.58 (0.12)	0.15 (0.07)	0.934	0.054
[CTAB] 5% *n*-butanol								
0.050	0.97 (0.16)	0.41 (0.23)	−0.44 (0.13)	−0.01 (0.10)	−0.81 (0.19)	0.22 (0.11)	0.924	0.089
0.067	0.91 (0.13)	0.35 (0.20)	−0.38 (0.12)	0.01 (0.09)	−0.75 (0.17)	0.20 (0.10)	0.928	0.077
0.080	0.86 (0.12)	0.32 (0.19)	−0.35 (0.11)	0.00 (0.08)	−0.71 (0.15)	0.19 (0.09)	0.929	0.071
0.100	0.82 (0.11)	0.29 (0.16)	−0.33 (0.09)	−0.01 (0.07)	−0.62 (0.13)	0.16 (0.08)	0.932	0.061
0.120	0.72 (0.12)	0.33 (0.17)	−0.29 (0.10)	0.02 (0.08)	−0.67 (0.14)	0.12 (0.08)	0.917	0.066
[CTAB] 10% *n*-butanol								
0.050	0.82 (0.14)	0.35 (0.22)	−0.41 (0.12)	−0.08 (0.09)	−0.81 (0.18)	0.23 (0.10)	0.934	0.082
0.067	0.73 (0.13)	0.35 (0.19)	−0.36 (0.11)	−0.12 (0.08)	−0.72 (0.15)	0.18 (0.09)	0.940	0.071
0.080[4]*	0.95 (0.14)	−0.09 (0.24)	−0.30 (0.12)	−0.04 (0.09)	−0.83 (0.17)	0.32 (0.11)	0.941	0.066
0.100	0.66 (0.10)	0.26 (0.16)	−0.30 (0.09)	−0.14 (0.07)	−0.62 (0.13)	0.16 (0.07)	0.945	0.058
0.120[2]*	0.60 (0.09)	0.24 (0.14)	−0.27 (0.08)	−0.17 (0.06)	−0.57 (0.11)	0.13 (0.07)	0.952	0.052

[1]*15 solutes, [2]*21 solutes, [3]*19 solutes, [4]*18 solutes.
[a] Standard deviations for each coefficient are shown in parentheses.

Table 2
LSER equations for 45 different SDS mobile phases and a C_8 stationary phase[a]

	Log k_0	m	s	a	b	r	R	SD
[SDS] no modifier								
0.050[1]*	0.24 (0.16)	1.72 (0.24)	−0.30 (0.10)	−0.34 (0.08)	−1.32 (0.16)	0.18 (0.10)	0.975	0.063
0.067[1]*	0.33 (0.16)	1.45 (0.23)	−0.29 (0.10)	−0.33 (0.08)	−1.18 (0.16)	0.20 (0.10)	0.972	0.061
0.080[1]*	0.32 (0.15)	1.38 (0.21)	−0.28 (0.09)	−0.34 (0.07)	−1.11 (0.14)	0.16 (0.09)	0.973	0.056
0.100[1]*	0.30 (0.14)	1.28 (0.21)	−0.26 (0.09)	−0.34 (0.07)	−1.03 (0.14)	0.15 (0.09)	0.972	0.055
0.120[1]*	0.34 (0.12)	1.13 (0.18)	−0.25 (0.08)	−0.29 (0.06)	−0.98 (0.12)	0.16 (0.07)	0.976	0.047
[SDS] 10% methanol								
0.050	0.98 (0.32)	0.51 (0.48)	−0.72 (0.27)	−0.77 (0.21)	−0.31 (0.39)	0.52 (0.23)	0.881	0.181
0.067	0.94 (0.29)	0.45 (0.42)	−0.66 (0.24)	−0.45 (0.18)	−0.32 (0.34)	0.47 (0.20)	0.891	0.158
0.080	0.90 (0.25)	0.43 (0.38)	−0.63 (0.21)	−0.44 (0.16)	−0.35 (0.30)	0.44 (0.18)	0.903	0.141
0.100	0.84 (0.23)	0.39 (0.35)	−0.57 (0.20)	−0.42 (0.15)	−0.38 (0.27)	0.41 (0.17)	0.909	0.130
0.120[2]*	0.78 (0.22)	0.33 (0.33)	−0.52 (0.19)	−0.40 (0.14)	−0.37 (0.27)	0.40 (0.16)	0.914	0.124
[SDS] 3% *n*-propanol								
0.050	0.82 (0.19)	0.90 (0.29)	−0.52 (0.17)	−0.30 (0.13)	−0.86 (0.24)	0.25 (0.14)	0.952	0.109
0.067	0.78 (0.17)	0.80 (0.26)	−0.47 (0.15)	−0.29 (0.11)	−0.80 (0.21)	0.22 (0.12)	0.955	0.097
0.080	0.75 (0.16)	0.75 (0.24)	−0.43 (0.13)	−0.30 (0.10)	−0.76 (0.19)	0.21 (0.11)	0.958	0.088
0.100	0.70 (0.14)	0.69 (0.20)	−0.38 (0.12)	−0.30 (0.09)	−0.73 (0.16)	0.19 (0.10)	0.962	0.079
0.120	0.61 (0.13)	0.73 (0.19)	−0.38 (0.11)	−0.29 (0.08)	−0.70 (0.16)	0.15 (0.09)	0.964	0.073
0.140[3]*	0.63 (0.15)	0.64 (0.21)	−0.38 (0.12)	−0.29 (0.09)	−0.67 (0.16)	0.17 (0.10)	0.964	0.074
[SDS] 5% *n*-propanol								
0.050	0.91 (0.20)	0.86 (0.31)	−0.61 (0.17)	−0.30 (0.13)	−1.00 (0.25)	0.30 (0.15)	0.953	0.115
0.067	0.87 (0.17)	0.77 (0.27)	−0.54 (0.15)	−0.32 (0.12)	−0.98 (0.21)	0.28 (0.13)	0.959	0.101
0.080	0.84 (0.17)	0.72 (0.26)	−0.54 (0.15)	−0.34 (0.11)	−0.89 (0.20)	0.26 (0.12)	0.958	0.096
0.100[3]*	0.80 (0.15)	0.63 (0.23)	−0.47 (0.13)	−0.32 (0.10)	−0.86 (0.19)	0.26 (0.11)	0.961	0.087
0.120	0.75 (0.14)	0.60 (0.21)	−0.43 (0.12)	−0.32 (0.09)	−0.80 (0.17)	0.23 (0.10)	0.965	0.078
0.140	0.69 (0.12)	0.59 (0.18)	−0.40 (0.10)	−0.30 (0.08)	−0.78 (0.14)	0.21 (0.08)	0.972	0.066
[SDS] 10% *n*-propanol								
0.050	0.72 (0.18)	0.92 (0.27)	−0.61 (0.15)	−0.34 (0.12)	−1.07 (0.22)	0.29 (0.13)	0.966	0.103
0.067[2]*	0.68 (0.16)	0.84 (0.25)	−0.54 (0.14)	−0.34 (0.11)	−0.99 (0.20)	0.25 (0.12)	0.966	0.093
0.080	0.66 (0.15)	0.77 (0.23)	−0.51 (0.13)	−0.33 (0.10)	−0.96 (0.19)	0.24 (0.11)	0.967	0.087
0.100	0.63 (0.14)	0.70 (0.21)	−0.47 (0.12)	−0.33 (0.09)	−0.90 (0.17)	0.22 (0.10)	0.968	0.080
0.120[3]*	0.58 (0.15)	0.62 (0.21)	−0.42 (0.12)	−0.32 (0.09)	−0.82 (0.17)	0.22 (0.10)	0.969	0.078
[SDS] 3% *n*-butanol								
0.050	0.82 (0.19)	0.79 (0.30)	−0.57 (0.17)	−0.30 (0.13)	−0.93 (0.24)	0.27 (0.14)	0.948	0.112
0.067	0.77 (0.18)	0.72 (0.27)	−0.52 (0.15)	−0.30 (0.12)	−0.86 (0.22)	0.25 (0.13)	0.951	0.100
0.080	0.75 (0.16)	0.68 (0.25)	−0.49 (0.14)	−0.30 (0.11)	−0.84 (0.20)	0.23 (0.12)	0.953	0.094
0.100	0.69 (0.14)	0.60 (0.22)	−0.43 (0.12)	−0.29 (0.09)	−0.77 (0.18)	0.22 (0.10)	0.958	0.082
0.120	0.64 (0.13)	0.58 (0.20)	−0.40 (0.12)	−0.29 (0.09)	−0.74 (0.16)	0.20 (0.10)	0.959	0.077
0.140	0.60 (0.13)	0.54 (0.19)	−0.38 (0.11)	−0.28 (0.08)	−0.72 (0.15)	0.19 (0.09)	0.961	0.072
[SDS] 5% *n*-butanol								
0.050	0.84 (0.19)	0.79 (0.30)	−0.59 (0.17)	−0.27 (0.13)	−1.021 (0.24)	0.26 (0.14)	0.947	0.113
0.067	0.83 (0.18)	0.63 (0.28)	−0.51 (0.16)	−0.27 (0.12)	−0.97 (0.23)	0.26 (0.13)	0.946	0.105
0.080	0.80 (0.16)	0.62 (0.25)	−0.50 (0.14)	−0.29 (0.10)	−0.92 (0.20)	0.25 (0.12)	0.955	0.093
0.100	0.78 (0.16)	0.54 (0.24)	−0.46 (0.13)	−0.27 (0.10)	−0.90 (0.19)	0.24 (0.11)	0.954	0.089
0.120	0.67 (0.15)	0.58 (0.23)	−0.39 (0.13)	−0.26 (0.10)	−0.88 (0.19)	0.19 (0.11)	0.951	0.087
0.140	0.67 (0.14)	0.53 (0.21)	−0.40 (0.12)	−0.28 (0.09)	−0.81 (0.17)	0.19 (0.10)	0.955	0.080

Table 2. Continued

	Log k_0	m	s	a	b	r	R	SD
[SDS] 10% *n*-butanol								
0.050	0.77 (0.18)	0.56 (0.28)	−0.52 (0.16)	−0.21 (0.12)	−1.00 (0.22)	0.26 (0.13)	0.941	0.104
0.067	0.70 (0.16)	0.48 (0.25)	−0.47 (0.14)	−0.23 (0.11)	−0.91 (0.20)	0.24 (0.12)	0.943	0.093
0.080	0.64 (0.16)	0.45 (0.24)	−0.41 (0.14)	−0.22 (0.10)	−0.88 (0.19)	0.20 (0.11)	0.938	0.090
0.100	0.62 (0.15)	0.41 (0.22)	−0.42 (0.12)	−0.24 (0.09)	−0.83 (0.18)	0.21 (0.11)	0.945	0.083
0.120	0.57 (0.14)	0.39 (0.21)	−0.39 (0.12)	−0.25 (0.09)	−0.80 (0.17)	0.20 (0.10)	0.945	0.080
0.140	0.58 (0.15)	0.29 (0.23)	−0.41 (0.13)	−0.27 (0.10)	−0.68 (0.19)	0.24 (0.11)	0.929	0.088

[1]*15 solutes, [2]*21 solutes, [3]*20 solutes.

[a] Standard deviations for each coefficient are shown in parentheses.

larger organic molecules, and they also reflect the HB donating ability of water, which decreases the retention of HB accepting solutes.

3.1. Variation of the coefficients of LSER equations as a function of the surfactant concentration in SDS and CTAB systems

In all systems studied, the absolute value of all the coefficients decreases as the surfactant concentration increases, except for the coefficients of $\Sigma\alpha_2^H$ which remain practically unchanged and very nearly equal to zero in CTAB systems. As an example, Fig. 1 shows the variation of the LSER coefficients as a function of the SDS concentration in media modified by a 10% methanol, *n*-propanol and *n*-butanol. Fig. 2 shows the same variation but for CTAB systems in media modified by a 5% propanol and butanol. Chromatographically, the decrease in coefficients indicates that the interactions between the solute and the mobile phase become more similar to the solute–stationary phase interactions as the surfactant concentration increases. This result matches chemical intuition given the structural similarities of surfactant micelles and the stationary phase. It also parallels results obtained in a similar study using the same surfactants and a C_{18} stationary phase [28] as opposed to the C_8 phase used here.

As shown in Tables 1 and 2, the largest changes in the coefficients as a function of surfactant concentration are observed for *m*, *b* and *s*, while the smaller changes are obtained for *r* and *a*. Chemically, the *m* coefficient decreases because increasing the surfactant concentrations increases the concentration of micelles. This allows more solutes to partition into the less cohesive/more dispersive micellar microenvironment in the mobile phase, resulting in an overall decrease in the effective mobile phase cohesivity and an increase in the mobile phase dispersive ability relative to the cohesivity/dispersion of the stationary phase. This also explains the behavior of *s* and *b* since, as more solutes partition out of the aqueous environment of the mobile phase into the micellar microenvironments, the average solute environment appears to be less polar and have less HB donating ability. The constant *a* coefficient implies that the overall effective basicity of the mobile phase environment experienced by the solutes does not change as a function of the surfactant concentration. The *r* coefficient shows that the stationary phase is slightly better able to interact with polarizable molecules than is the mobile phase and that this behavior remains relatively constant as a function of surfactant concentration.

3.2. Effect of the addition of alcohols on the values of the LSER coefficients in SDS and CTAB systems

Regarding the effect of the alcohol modifiers, the LSERs reveal very little difference among the three modifiers in terms of their effect on the LSER coefficients. Thus, in the case of CTAB for which *n*-propanol and *n*-butanol were used as modifiers, no significant differences were found between the values of the coefficients when these were compared in presence of the two alcohols (see as an example, Fig. 2). However, in general, these coefficients presented differences as compared to those corresponding to mobile phases not modified by alcohols. In fact, the

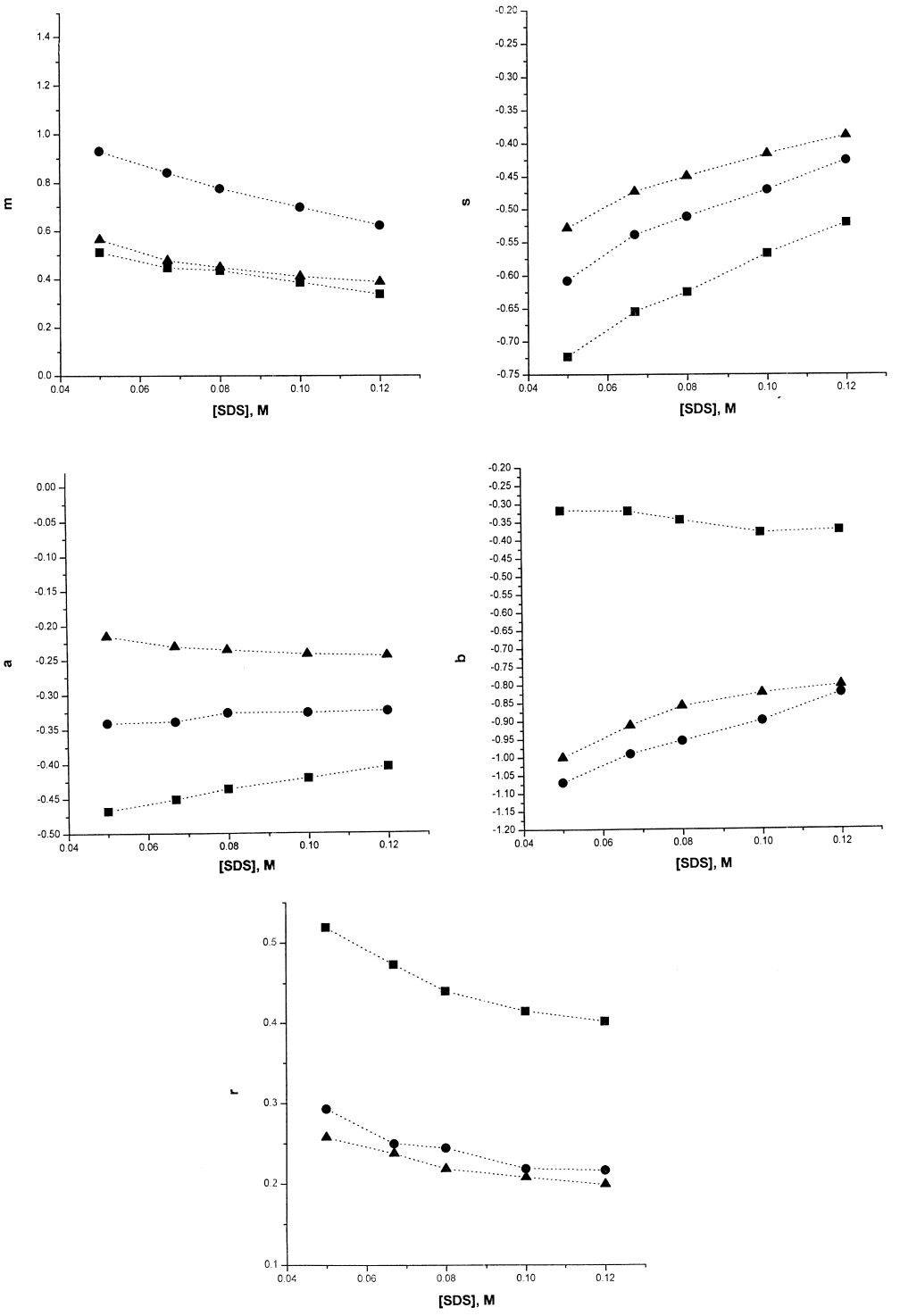

Fig. 1. LSER coefficients as a function of SDS concentration. Modifiers are: ■ 10% methanol, ● 10% *n*-propanol and ▲ 10% *n*-butanol. Error bars have been omitted for clarity. Standard deviations for each coefficient are listed in Table 2.

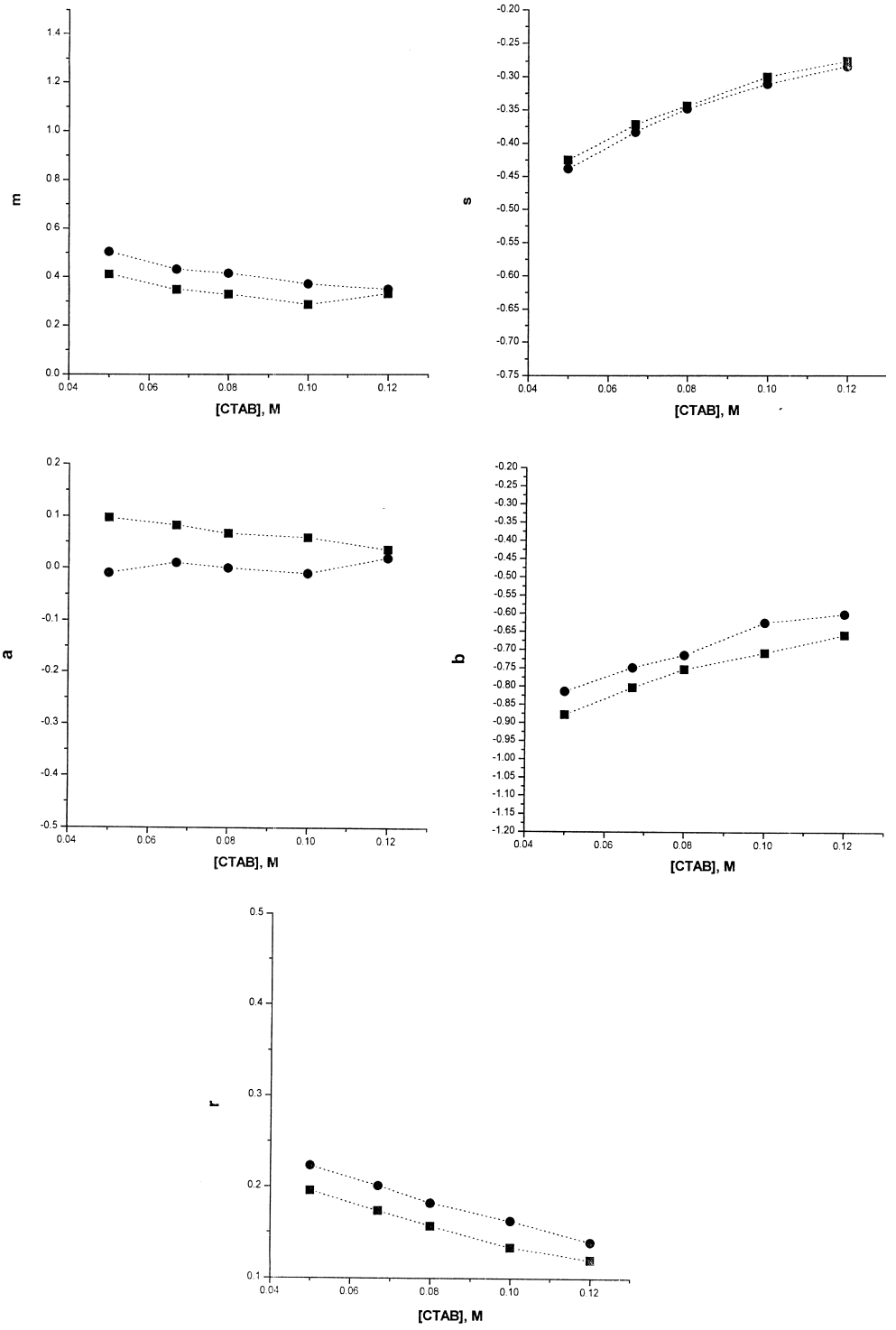

Fig. 2. LSER coefficients as a function of CTAB concentration. Modifiers are: ● 5% *n*-propanol and ■ 5% *n*-butanol. Error bars have been omitted for clarity. Standard deviations for each coefficient are listed in Table 1.

magnitude of *m* and *b* coefficients decreased generally when adding modifiers relative to their values in micellar systems in the absence of alcohol modifiers while the magnitude of *s* and *r* coefficients slightly increased in the same conditions.

In the case of SDS micellar systems, the same trends as for CTAB were generally observed with slight increases for *r* and *s* coefficients and decreases for *m* and *b* coefficients in presence of alcohols modifiers with respect to mobile phases without alcohols. However, in this case, some deviations of the general behavior were observed when methanol was used as modifier. As examples, the increase in *r* and *s* coefficients in the presence of methanol was greater than the increases in presence of the other modifiers, and the decreases observed for *m* and *b* coefficients were also greater in the presence of methanol than in the presence of the other modifiers, except in the case of 10% *n*-butanol for which values for the *m* coefficients were similar to those obtained in the presence of 10% methanol.

With respect to the influence of the percentage of the alcohol modifier, the coefficients are modified when adding the alcohol, but once the modifier has been added, the percentage at which the alcohol is present does not have a great influence on the values of the coefficients, at least in the range studied (from 3 to 10% alcohol). Then, in the presence of alcohols, the decrease observed in the retention of solutes could be explained through the decrease in the term log k_0 with the percentage of the alcohol.

3.3. Residuals of LSER equations for SDS and CTAB systems

Figs. 3A and 4A show the plot of the experimental log *k* values as a function of log *k* values predicted from the LSER equation for 0.120 *M* SDS–3% *n*-butanol and 0.120 *M* CTAB–10% *n*-propanol mobile phases, respectively. The residual values (calculated minus experimental log *k*) for each solute normalized to the standard deviation of the residuals are also shown for both systems (Figs. 3B and 4B). It can be observed that good correlations were obtained for experimental log *k* values versus predicted log *k* values (slopes >0.970), that is, LSERs are able to reproduce approximately the experimental log *k* values for the solutes studied in the different

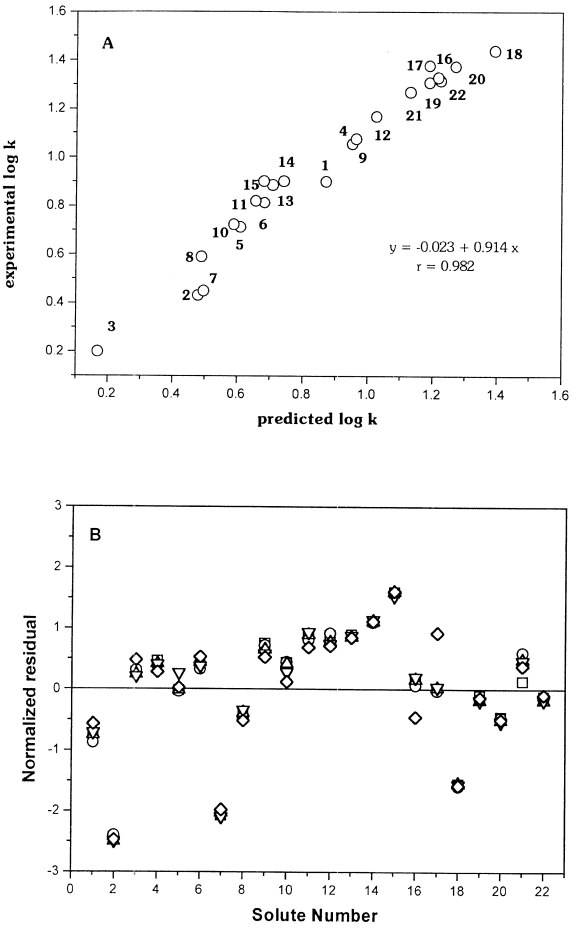

Fig. 3. (a) Experimental versus predicted log *k* values in a 3% *n*-butanol–0.120 *M* SDS mobile phase. (b) Normalized residuals (predicted minus experimental log *k* values) of the LSERs for 3% *n*-butanol–SDS mobile phases. Residuals are normalized to the average standard error of each LSER equation. SDS concentrations (*M*) are 0.050, 0.067, 0.080, 0.100, and 0.120. Solute numbers are as listed in the Experimental section.

mobile phases. In fact, it seems that there may be some systematic nature to the residuals indicating that LSERs are not accounting for all of the energetics in the system as observed for a C_{18} stationary phase [28].

4. Conclusions

The coefficients for the LSER equations were obtained for a group of 22 aromatic solutes in 80

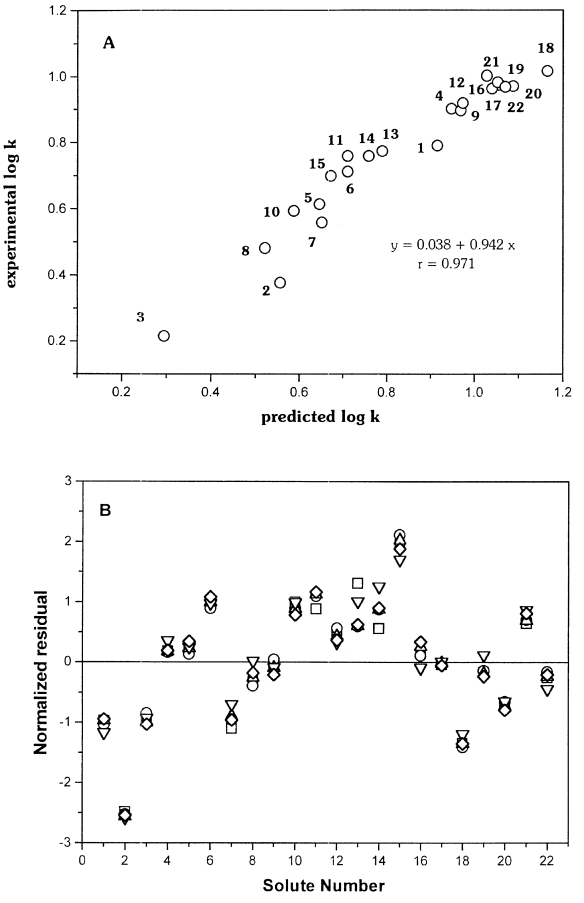

Fig. 4. (a) Experimental versus predicted log k values in a 10% n-propanol–0.120 M CTAB mobile phase. (b) Normalized residuals (predicted minus experimental log k values) of the LSERs for 10% n-propanol–CTAB mobile phases. Residuals are normalized to the average standard error of each LSER equation. CTAB concentrations (M) are 0.050, 0.067, 0.080, 0.100, and 0.120. Solute numbers are as listed in the Experimental section.

different micellar mobile phases in which the nature and concentration of the surfactant (SDS or CTAB) and the alcohol modifier (methanol, n-propanol, or n-butanol) were varied.

Solute volume and HB basicity generally play the largest role in determining the retention of solutes in all the systems studied. Solute dipolarity/polarizability can be also an important factor, especially in the case of CTAB systems for which the coefficients are comparable in magnitude to those of solute volume. Additionally, it was found that the coefficients of π_2^H and $\Sigma\beta_2^H$ were negative, meaning that increases in the solute dipolarity/polarizability and HB basicity decrease the retention of the solute while the coefficients of V_X and R_2 were positive, increasing the retention.

LSER coefficients were little influenced by the nature or the percentage of alcohol, although in general these coefficients presented differences as compared to those obtained with mobile phases in the absence of alcohols.

Finally, although some systematic nature for the residuals was observed indicating that LSERs could not account for all the energetics in the system, LSERs were able to reproduce adequately the experimental retention factors of the solutes studied in the different experimental conditions investigated.

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