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Linear solvation energy relationships in micellar liquid chromatography and micellar electrokinetic capillary chromatography

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Abstract

Linear solvation energy relationships (LSERs) were used to evaluate and characterize chemical interactions that influence retention behavior in micellar liquid chromatography (MLC) and micellar electrokinetic capillary chromatography (MEKC). High correlations were found between solutes' capacity factors in MLC and in MEKC, as well as binding constants to micelles and their solvatochromic parameters using two anionic surfactants, sodium dodecyl sulfate (SDS) and sodium cholate (SC), and one cationic surfactant, tetradecyltrimethylammonium bromide (C_{14}TAB). Surprisingly, in the C_{14}TAB MLC system capacity factor (k') vs. solvatochromic parameters gives better correlation than log k' vs. solvatochromic parameters, which is an opposite behavior to that observed in the SDS MLC system. The capacity factors in the C_{14}TAB MLC system were characterized using LSERs with and without organic modifiers. It was found that the addition of a small amount of short-chain alcohols (e.g., 7% 2-propanol or 5% butanol) does not significantly change the high correlations between k' vs. solvatochromic parameters. The changes in the coefficients with the volume fraction of organic solvents were explained by comparing the differences in chemical natures between mobile phase and stationary phase. Stationary phase shows a significant effect on the chemical interactions in MLC through LSER study using a diphenyl column and a C_8 column.

LSERs were also used to characterize retention behavior in MEKC. High correlations between the logarithm of solutes' capacity factors and their solvatochromic parameters were observed for a group of 25 uncharged substituted aromatic compounds and polycyclic aromatic hydrocarbons with SDS and SC micelles. It was found that solutes' size and basicity are the two dominant factors that influence the migration behavior in MEKC.

1. Introduction

In micellar liquid chromatography (MLC) and micellar electrokinetic capillary chromatography (MEKC), the amphiphilic nature of micelles provides both hydrophobic and polar (or electrostatic) sites of interactions with solutes. In MLC [1–4], solutes partition from the bulk mobile phase into micelles and into the stationary phases. Solutes' retention behavior depends on various chemical interactions (e.g., hydrophobic, dipolar, and hydrogen bonding) in these parti-

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tioning processes. The exact nature of these interactions depends upon the chemical nature of solutes as well as the compositions of the mobile phase, and the stationary phase. MEKC is a mode of capillary electrophoresis (CE) for the separation of uncharged compounds [5–7]. In MEKC, separation of uncharged molecules is solely due to the extent and differences of their interactions with the micelles. In other words, chemical interactions in the partitioning processes control the separations of solutes in these two micellar-mediated chromatographic techniques. A study of the chemical interactions in these systems should provide a better understanding of solutes' retention behavior and selectivity pattern in MLC and MEKC.

Attempts to achieve a better understanding of the retention process in MLC have been mostly qualitative in nature and have been based on the observed changes in retention behavior as a function of the composition of the micellar eluents, the stationary phase, as well as solutes structural properties [8–11]. Quantitative structure–retention relationships (QSRRs) can play an important role in achieving a better understanding of the role of different factors that influence retention behavior in MLC and MEKC. Recently, linear solvation energy relationships (LSERs) [12–18] have been successfully applied for the evaluation of retention behaviors in RPLC with hydro–organic eluents, stationary phase effect in RPLC and for the characterization of partitioning process between *n*-octanol and water for non-electrolytes. In LSERs, solvent-related properties of solutes, SP, can be described in terms of the solvatochromic parameters in the following general form:

$$SP = SP_0 + mV/100 + s\pi^* + b\beta + a\alpha \quad (1)$$

where SP is the solutes' property that depends on solute–solvent interactions, SP_0 is the regression constant, V is the molar volume of solutes, π^* is a measure of solutes' ability to engage in dipolarity/polarizability interactions with the solvent, β is the solutes' basicity and α is the solutes' acidity. Coefficients (m, s, b and a) are related to the chemical nature of the solvent systems.

The term $mV/100$ represents the disfavorable endoergic cavity formation process of separating the solvent molecules in order to provide a suitably sized cavity for solutes; $V/100$ instead of V is used to adjust the magnitude of the cavity term within a same range as the other independent variables in Eq. 1. The term $s\pi^*$ represents the dipolarity/polarizability term that measures the favorable exoergic effects of solute–solvent, dipole–dipole and dipole–induced dipole interactions. Exoergic hydrogen bonding terms, $b\beta$ and $a\alpha$, measure the effects of specific associations involving hydrogen bond acceptor (HBA) basic solutes and hydrogen bond donor (HBD) acidic solvents ($b\beta$ term) as well as the interactions between HBA basic solvents and HBD acidic solutes ($a\alpha$ term).

In order to express the net interactive properties of the aqueous and organic phases in different partitioning processes (e.g., micelle–water or *n*-octanol–water), the following relationships can be written [13,18]:

$$m = M(\delta_A^2 - \delta_B^2) \quad (2)$$

$$s = S(\pi_B^* - \pi_A^*) \quad (3)$$

$$b = C(\alpha_B - \alpha_A) \quad (4)$$

$$a = D(\beta_B - \beta_A) \quad (5)$$

where M, S, C and D are constants, δ is the Hildebrand solubility parameter (which is a measure of the cohesiveness of a phase). π^*, β and α in Eqs. 3–5 are the solvent's dipolarity/polarizability, basicity and acidity. The subscript B corresponds to *n*-octanol, micelle or stationary phase and the subscript A denotes the bulk aqueous phase or HPLC mobile phase. The significance of the chemical interactions in MLC and MEKC can be evaluated through a comparative study of the coefficients obtained from the different terms in the LSER models.

In this work, capacity factors in MLC and in MEKC as well as solute–micelle binding constants are quantitatively evaluated by LSER modeling and compared to the LSER models involving capacity factors in RPLC with hydro–

organic eluents and *n*-octanol–water partition coefficients.

2. Experimental

2.1. Chromatographic system

The MLC data were obtained from Ref. [19]. The MLC system has been described previously [11]. In MEKC, all the experiments were carried out on a laboratory-built CE system, which comprised a 0–30-kV high-voltage power supply (Series EH; Glassman High Voltage, Whitehouse Station, NJ, USA) and a 50 μm I.D. × 375 μm o.d. fused-silica capillary tubing (Polymicro Technologies, Phoenix, AZ, USA). The total length of the capillary was 62 cm and detection was performed at 50 cm downstream. The samples were introduced into the anodic end of the capillary by gravity, 10 cm height for 8 s. Positive voltage of 20 kV was applied throughout the experiment. A variable-wavelength UV detector (Model 200; Linear Instruments, Reno, NV, USA) was used with the wavelength at 210 nm for sodium dodecyl sulfate (SDS) buffers and 254 nm for sodium cholate (SC) buffer. The electropherograms were recorded using an integrator (Model SP 4200; Spectra-Physics, San Jose, CA, USA).

2.2. Reagents

The stock solutions of SDS (Sigma, St. Louis, MO, USA), and SC (Aldrich, Milwaukee, WI, USA) were prepared by dissolving the required amount of surfactant in doubly distilled deionized water and were filtered through a 0.45 μm nylon-66 membrane filter (Rainin, Woburn, MA, USA). All the test solutes were purchased from Aldrich. Test solutes in MLC and their solvatochromic parameters are listed in Table 1. The reported solvatochromic parameters values have been at room temperature [14], while the operating temperature for the MLC was 38°C. It has been found that temperature effect on these values is negligible [18]. In MEKC, buffer solutions were kept at pH 7.00 and 0.05 *M* phosphate (ionic strength) for both SDS and SC. Room temperature was maintained throughout the experiment. The void time (i.e., t_{eo}) of the system was measured from the time of injection of methanol to the first deviation from the baseline. Dodecaphenone was used to determine

Table 1
Test solutes in MLC and their solvatochromic parameters

Compound	$V/100$	π^*	β	α
(1) Benzylamine	0.665	0.35	0.59	0.06
(2) Benzyl alcohol	0.634	0.99	0.52	0.39
(3) Acetanilide	0.776	0.86	0.90	0.56
(4) Phenol	0.536	0.72	0.33	0.61
(5) Benzaldehyde	0.606	0.92	0.44	0
(6) Benzonitrile	0.590	0.90	0.37	0
(7) Acetophenone	0.690	0.90	0.49	0.04
(8) Nitrobenzene	0.631	1.01	0.30	0
(9) Benzoic acid	0.650	0.74	0.40	0.59
(10) Anisol	0.639	0.73	0.32	0
(11) Benzene	0.491	0.59	0.10	0
(12) Propiophenone	0.788	0.88	0.49	0
(13) Butyrophenone	0.886	0.86	0.49	0
(14) Chlorobenzene	0.581	0.71	0.07	0
(15) Naphthalene	0.753	0.70	0.15	0
(16) Anthrancene	1.015	0.80	0.20	0

Solvatochromic data are from Ref. [14].

t_{mc}, the migration time of micelles in both SDS and SC buffer systems.

3. Results and discussion

3.1. Retention behavior in MLC

In this study, the effects of organic solvent type and concentration as well as stationary phase on the retention behavior in MLC are examined. Capacity factors in MLC and solute–micelle binding constants are evaluated using LSER.

The results of the LSER models between capacity factor (k' and log k') in MLC, solute–micelle binding constant (K_{mw}), as well as capacity factor (log k') in RPLC with hydro–organic eluents and the solvatochromic parameters for a group of 16 aromatic compounds are shown in Table 2. The LSER modeling was originally developed for non-electrolytes and the solvatochromic polarity parameters have been measured for a wide range of solutes under non-ionizable conditions [12,16]. Apparently, the presence of a partially charged solute (e.g., benzoic acid) among the 16 test solutes in this study does not have a significant impact on the LSER models.

One common factor among all of the LSER models in Table 2 is that the cavity term is the most important factor. In all of the reported LSER studies [12–18], the SP term in Eq. 1 represents the logarithm of a solvent related

Table 2
LSER regression for retention behavior in MLC and solute–micelle binding

SP	SP_0	m	s	b	a	$-b/m$	n	r	S.E.
Solute–micelle binding constant									
Log K_{mw} (C_{14}TAB + 3% 2-PrOH)	0.97	2.67 (0.14)[a]	−0.88 (0.10)	−1.44 (0.10)	0.32 (0.08)	0.54	16	0.9703	0.118
Log K_{mw} (SDS + 3% 2-PrOH)	0.34	2.81 (0.18)	−0.29 (0.14)	−1.36 (0.13)	−0.35 (0.11)	0.48	16	0.9585	0.160
Retention in MLC									
Log k' (0.08 M SDS + 3% 2-PrOH)	1.27	1.52 (0.14)	−0.92 (0.11)	−0.78 (0.10)	−0.92 (0.08)	0.51	16	0.9702	0.120
k' (0.08 M SDS + 3% 2-PrOH)	−5.52	121.90 (9.04)	−40.42 (6.93)	−59.94 (6.40)	−8.63[b] (5.36)	0.49	16	0.9485	7.81
Log k' (0.08 M C_{14}TAB + 3% 2-PrOH)	1.02	1.01 (0.09)	−0.23[b] (0.13)	−0.76 (0.06)	−0.02[b] (0.01)	0.75	16	0.9434	0.078
k' (0.08 M C_{14}TAB + 3% 2-PrOH)	0.53	53.89 (2.67)	−8.22 (2.04)	−32.46 (1.89)	1.36[b] (1.58)	0.60	16	0.9746	2.304
Retention in RPLC with hydro–organic eluents									
Log k' (40% MeOH)	−0.33	3.22 (0.08)	−0.32 (0.06)	−1.73 (0.06)	−0.23 (0.05)	0.54	16	0.9938	0.068
Log k' (40% 2-PrOH)	−0.16	1.84 (0.11)	−0.31 (0.09)	−1.43 (0.08)	−0.22 (0.07)	0.78	16	0.9764	0.097

n = Number of test solutes; r = correlation coefficient of linear regression; S.E. = standard error of the y estimate.
[a] 95% confidence level of the coefficient.
[b] Values are not statistically significant at the 95% confidence level.

property such as capacity factor (log k') in RPLC with hydro–organic eluents, n-octanol–water partition coefficient (log P_{ow}), or aqueous solubility (log S_w). This is because the logarithms of these solvent related properties represent the free energy of transfer of solutes from one phase (e.g., mobile phase or aqueous phase) to another phase (e.g., stationary phase or n-octanol phase). Surprisingly, in the C_{14}TAB MLC system k' vs. solvatochromic parameters gives a better correlation ($r = 0.9746$) than log k' vs. solvatochromic parameters ($r = 0.9434$) as shown in Fig. 1. A similar observation has been previously reported for the relationship between k' in MLC and log P_{ow} for the same group of compounds [11] as well as for the relation between k' and the carbon number of homologous series [9,20]. A clear curvature has been observed in the log k' vs. log P_{ow} and log k' vs. number of carbons in homologous series (N_c) plots. However, an opposite behavior is observed for the LSER model in SDS MLC system, i.e., log k' vs. solvatochromic parameters gives better correlation than k' vs. solvatochromic parameters. In the conventional RPLC with hydro–organic solvents and n-octanol–water partitioning process, solutes' size ($V/100$) and basicity (β) are the two predominant terms [14–16]. However, this was not the case for the retention (log k') in MLC with SDS micelles. It was also seen that the significance of the chemical interactions is quite different for the solute–micelle binding constant (log K_{mw}) in these two micellar systems (SDS and C_{14}TAB), which is evident from the different regression coefficients (m, s, b and a). For example, the $a\alpha$ term is a positive value for the solutes binding to C_{14}TAB micelles while it is a negative value for the SDS system. This result suggests that the C_{14}TAB micellar phase provides more basic environment for the binding of acidic solutes than the SDS micellar phase. It was also found that C_{14}TAB micelles have less dipolar environment (more negative s value) for solutes than SDS micelles (less negative s value). This indicates that the type of surfactant has a significant impact on the chemical interactions in the partitioning processes in MLC, which in turn affects the retention behavior dramatically. Further study is needed to explain the remarkable differences in these two micellar systems.

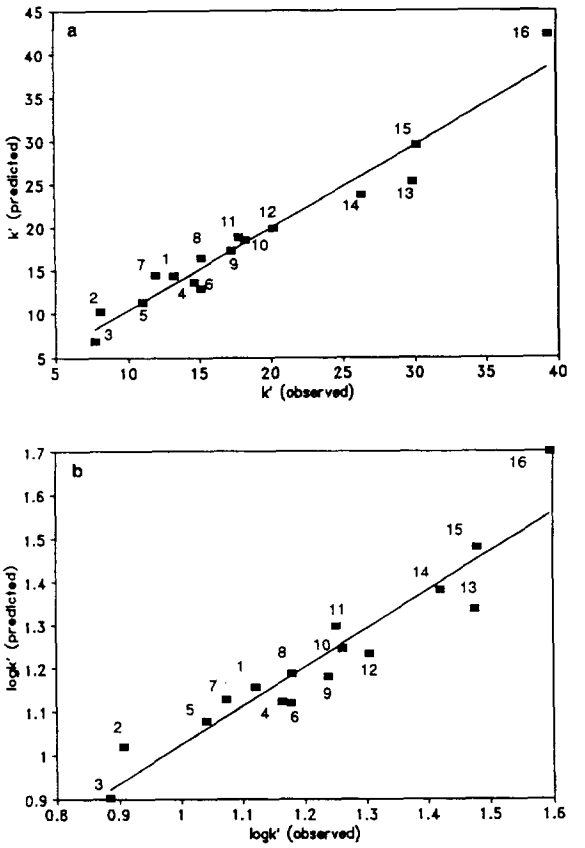

Fig. 1. (a) The plot of the capacity factors predicted by LSER vs. the capacity factors observed in MLC with 0.08 M C_{14}TAB and 3% 2-propanol. The LSER model is $k' = 0.53 + 53.89V/100 - 8.22\pi^* - 32.46\beta + 1.36\alpha$ ($n = 16$, $r = 0.9746$, S.E. = 2.304). (b) The plot of the logarithm of capacity factors predicted by LSER vs. the logarithm of capacity factors observed in MLC with 0.08 M C_{14}TAB and 3% 2-propanol. The LSER model is $\log k' = 1.02 + 1.01V/100 - 0.23\pi^* - 0.76\beta - 0.02\alpha$ ($n = 16$, $r = 0.9434$, S.E. = 0.078).

3.2. Effect of organic solvents on retention behavior in MLC

Organic solvents (mainly short-chain alcohols) have been widely used in MLC systems to enhance column efficiency [21], to influence eluents' strength, and to improve the overall separations [8,22–25]. The addition of organic solvents in micellar eluents may change the

micelle structure and the extent of adsorption of surfactant monomers on the stationary phase, thus influencing the retention behavior and selectivity in MLC [8,20,22–24]. The results of the LSER study in a C_{14}TAB MLC system with and without organic solvents are shown in Table 3. The magnitude of coefficient m reflects the difference in the solubility parameters between the stationary phase and the micellar mobile phase as shown in Eq. 2. Solubility parameter value of the mobile phase (δ_A) decreases with the increase of volume fraction of organic solvents because they are less cohesive (e.g., $\delta = 11.5$ for 2-propanol) than water ($\delta = 23.4$). However, solubility parameter value of the stationary phase (δ_B) increases with the increase of volume fraction of organic solvents. The combined effect of mobile phase and stationary phase is that m values decrease with an increase in volume fraction of organic solvents. The solvent property complementary to solutes' dipolarity/polarizability (π^*) is solvent's dipolarity/polarizability (π_1^*) as shown in Eq. 3. Alcohols are less dipolar (e.g., $\pi_1^* = 0.48$ for 2-propanol) than water ($\pi_1^* = 1.09$), therefore, the dipolarity of the mobile phase (π_A^*) decreases with the increase of volume fraction of short-chain alcohols. The dipolarity of the stationary phase (π_B^*) increases with the increase of volume fraction of short-chain alcohols. The overall effect contributed from the mobile phase and the stationary phase makes the coefficient s become less negative with the increase of volume fraction of short-chain alcohols. Coefficient b denotes the difference in hydrogen bond donor ability (α_1) between the stationary phase and the mobile phase. As shown in Table 3, the b values increase (less negative) with the increase of volume fraction of short-chain alcohols. Alcohols are less acidic (e.g., $\alpha_1 = 0.76$ for 2-propanol) than water ($\alpha_1 = 1.17$), therefore, the acidity of the mobile phase (α_A) decreases with the increase of volume fraction of short-chain alcohols, while the acidity of the stationary phase (α_B) may increase with the increase of volume fraction of short-chain alcohols. However, the a-coefficient value that represents solvent's basicity (β_1) decreases with the increase of volume fraction of short-chain alcohols because alcohols are stronger base (e.g., $\beta_1 = 0.68$ for 2-propanol) than water ($\beta_1 = 0.18$)

Table 3
Effect of organic solvent on retention behavior in MLC

Condition[a] (k')	SP_0	m	s	b	a	$-b/m$	n	r	S.E.
0% 2-PrOH	−41.43	238.90	−22.33	−136.09	26.59	0.57	16	0.9858	6.945
(or butanol)		(8.04)	(6.16)	(5.69)	(4.77)				
1% 2-PrOH	−24.16	141.23	−14.21	−79.15	11.47	0.56	16	0.9833	4.409
		(5.22)	(4.00)	(3.69)	(3.10)				
3% 2-PrOH	−14.72	108.54	−13.06	−64.53	9.11	0.59	16	0.9817	3.731
		(4.32)	(3.31)	(3.06)	(2.56)				
5% 2-PrOH	−14.68	100.91	−12.01	−59.63	7.21	0.59	16	0.9822	3.437
		(3.98)	(3.05)	(2.82)	(2.36)				
7% 2-PrOH	−13.80	94.47	−10.76	−57.63	7.27	0.61	16	0.9828	3.202
		(3.70)	(2.84)	(2.62)	(2.20)				
2% butanol	−7.55	81.36	−11.13	−51.69	5.50	0.64	16	0.9723	3.629
		(4.20)	(3.22)	(2.97)	(2.49)				
3% butanol	−4.38	67.65	−9.90	−45.76	6.25	0.68	16	0.9666	3.394
		(3.95)	(3.01)	(2.78)	(2.33)				
5% butanol	−3.33	56.72	−9.22	−38.81	4.83	0.68	16	0.9633	3.032
		(3.51)	(2.69)	(2.48)	(2.08)				

See Table 2 for the definitions of n, r and S.E.
[a] With 0.04 M C_{14}TAB.

(with two exceptions). The basicities of both the mobile phase (β_A) and the stationary phase (β_B) increase with the increase in volume fraction of short-chain alcohols. The same strategy can also be used to explain the different results at the same volume fraction of 2-propanol and butanol. For example, butanol is less cohesive and less acidic solvent than 2-propanol, the combined effect of the mobile phase and the stationary phase makes the m value in the butanol MLC system smaller than that in the 2-propanol MLC system and the b value less negative in the butanol MLC system than in the 2-propanol MLC system. A similar trend was observed for the retention behavior (log k') with the change of volume fraction of methanol in the conventional RPLC [15].

It was also found that the addition of a small amount of short-chain alcohols (up to 7% 2-propanol or 5% butanol) does not significantly change the ratio of $-b/m$ and the high correlations between k' and solvatochromic parameters. Carr et. al. [18] have reported that the ratio of $-b/m$ is quite consistent from column to column as the amount of mobile phase modifier is varied and it is about +1.3 to +1.4 in acetonitrile–water mixtures, +1.3 for methanol–water and +1.75 for tetrahydrofuran (THF)–water. Kamlet et al. [15] obtained different $-b/m$ values (0.65–0.92) for a group of substituted aromatic compounds in the methanol–water RPLC system which are more similar to the $-b/m$ value observed in this work [0.54 for methanol–water (40:60)] as shown in Table 2. The high correlation for k' vs. solvatochromic parameters is a unique situation in the C_{14}TAB MLC system, however, the exact reason is not known yet.

3.3. Stationary phase effect in MLC

Not surprisingly, the stationary phase is an important factor in retention behavior and separation as well as for the determination of log P_{ow} by MLC [11,20,25]. Table 4 shows the regression results for the same group of 16 compounds on a C_8 column and a diphenyl column in MLC at the same mobile phase conditions (0.040 M C_{14}TAB, 3% 2-propanol, pH 7.0). The different LSER models (as represented by the coefficients in Table 4) indicate the large differences in chemical interactions in the two MLC systems with different stationary phases. For instance, on the diphenyl bonded stationary phase the dipolar/polarizability interactions between solutes and the surroundings (mobile and stationary phase) favor solutes' partition into the stationary phase because s has a positive value (+5.18), which is in contrast to all of the other LSER reports [12–18]. In addition, the larger m value for the C_8 phase indicates that it is less cohesive (smaller δ_B) than the diphenyl stationary phase (larger δ_B).

3.4. Migration behavior in MEKC

In MEKC, migration behaviors of uncharged solutes are primarily dependent upon their interactions with micelles and water. The type of surfactant in MEKC has a major effect on separation of uncharged solutes. The partitioning process of various solutes can be affected by the chemical property (e.g., hydrophobic moiety/chain length, ionic head group/charge) of a surfactant. In this study, two micelles were investigated; they are (1) SDS (an anionic hydro-

Table 4
Stationary phase effect on retention behavior in MLC (diphenyl vs. C_8)

SP	SP_0	m	s	b	a	$-b/m$	n	r	S.E.
k' (C_8)	−14.72	108.54 (4.32)	−13.06 (3.31)	−64.53 (3.06)	9.11 (2.56)	0.59	16	0.9817	3.73
k' (diphenyl)	−23.34	82.55 (3.15)	5.18 (2.42)	−51.33 (2.23)	8.65 (1.87)	0.62	16	0.9832	2.72

See Table 2 for the definitions of n, r and S.E. Mobile phase conditions: 0.04 M C_{14}TAB, 3% 2-PrOH.

carbon surfactant) and (2) SC (an anionic bile salt surfactant). The test solutes and their solvatochromic parameters for the LSER study in MEKC are listed in Table 5. The set includes substituted aromatic compounds and polycyclic aromatic hydrocarbons (PAHs).

The results of the LSER models for MEKC using two different micellar pseudo-phases (SDS and SC) are listed in Table 6 and compared with that of *n*-octanol–water partitioning process. The correlation coefficients (r) of the regression were quite high for both SDS and SC systems, which suggests that migration behavior in MEKC can be characterized by LSER. Figs. 2 and 3 show high correlations between the experimentally observed log k' and the predicted log k' by LSER for both SDS and SC micellar systems. Concentration of surfactant has a significant effect on migration factors in MEKC, which is due to the change in the phase ratio, however, coefficients (m, s, b and a) are only slightly varied with the change of SDS concentration from 0.020 to 0.040 M as shown in Table 6. It was also found that coefficients (m, s, b and a) in the LSER model for log K_{mw} with SDS micelles are very similar to those obtained in the LSER models using log k' at different concentrations of SDS (0.02 or 0.04 M) as shown in Table 6. This is because k' in MEKC is directly related to K_{mw} as [6,7,26]:

$$k' = K_{mw}([S] - CMC) \quad (6)$$

where [S] is the surfactant concentration and CMC is the critical micelle concentration of the surfactant.

The above-mentioned results suggest that log k' in MEKC can be used for the characterization of chemical interactions in the micelle–water partitioning process. Therefore, in this work log

Table 5
Test solutes in MEKC and their solvatochromic parameters

Compound	$V/100$	π^*	β	α
(1) Benzene	0.491	0.59	0.10	0
(2) Toluene	0.592	0.55	0.11	0
(3) Ethylbenzene	0.668	0.53	0.12	0
(4) Acetophenone	0.690	0.90	0.49	0.04
(5) Propiophenone	0.788	0.88	0.49	0
(6) Benzyladehyde	0.606	0.92	0.44	0
(7) Benzonitrile	0.590	0.90	0.37	0
(8) Nitrobenzene	0.631	1.01	0.30	0
(9) Anisol	0.639	0.73	0.32	0
(10) Methyl benzoate	0.736	0.75	0.39	0
(11) Fluorobenzene	0.520	0.62	0.07	0
(12) Chlorobenzene	0.581	0.71	0.07	0
(13) Bromobenzene	0.624	0.79	0.06	0
(14) Iodobenzene	0.671	0.81	0.05	0
(15) *p*-Dichlorobenzene	0.671	0.70	0.03	0
(16) *o*-Dichlorobenzene	0.671	0.80	0.03	0
(17) 4-Chlorotoluene	0.679	0.67	0.08	0
(18) 4-Chloroanisole	0.720	0.73	0.22	0
(19) Phenol	0.536	0.72	0.33	0.61
(20) 4-Chlorophenol	0.626	0.72	0.23	0.67
(21) 4-Chlorobenzyl alcohol	0.724	1.11	0.42	0.40
(22) 4-Chloroaniline	0.653	0.73	0.40	0.31
(23) Naphthalene	0.753	0.70	0.15	0
(24) 1-Naphthalene	0.851	0.66	0.16	0
(25) Biphenyl	0.920	1.18	0.20	0

Solvatochromic data are from Ref. [14].

Table 6
Effect of micelles on migration behavior in MEKC

SP	SP_0	m	s	b	a	$-b/m$	n	r	S.E.
Log k'	−2.21	4.53	−0.19	−1.84	−0.05[a]	0.41	25	0.9869	0.087
(0.02 M SDS)		(0.09)	(0.06)	(0.06)	(0.04)				
Log k'	−1.88	4.42	−0.15	−1.88	−0.07[a]	0.43	25	0.9885	0.081
(0.04 M SDS)		(0.05)	(0.05)	(0.05)	(0.07)				
Log k'	2.07	4.56	−0.24	−2.84	0.26	0.62	25	0.9903	0.084
(0.06 M SC)		(0.09)	(0.06)	(0.06)	(0.04)				
Log K_{mw}[b]	−0.41	4.33	−0.11	−1.92	−0.09	0.44	25	0.9890	0.079
(0.02–0.04 M SDS)		(0.08)	(0.05)	(0.05)	(0.04)				
Log P_{ow}	0.11	5.49	−0.43	−3.88	0.02[a]	0.71[a]	25	0.9952	0.080
		(0.08)	(0.05)	(0.05)	(0.04)				

See Table 2 for the definitions of n, r and S.E.
[a] Values are not statistically significant at the 95% confidence level.
[b] K_{mw} values are estimated according to Eq. 6 with the two SDS concentrations (0.02 and 0.04 M).

k' values in MEKC were used to build the LSER models for the comparison of chemical interactions in micelle–water and n-octanol–water partitioning processes.

It was also seen that migration behavior of solutes in MEKC with SDS and SC micelles are mainly influenced by their size ($V/100$) and hydrogen bond basicity (β) because the absolute values of m and b are relatively large. However, solutes' dipolarity/polarizability (π^*) and acidity (α) cause smaller changes in the capacity factor than the other two parameters (e.g., size and basicity). This is a similar behavior to the n-octanol–water partitioning process [14] and to the retention behavior in RPLC with hydro-organic solvent [15]. It is, however, different from the retention behavior (log k') in the SDS MLC system as shown in Table 2. The coefficient m reflects the effect of solvents' cohesiveness on solutes' capacity factor or partition constant. It is a large positive value because water is a very cohesive solvent and is not easy to create a cavity for the solute as compared to n-octanol and micelles. Water has a high hydrogen bonding

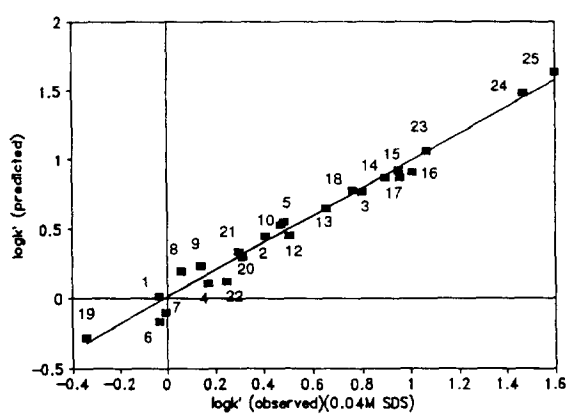

Fig. 2. The plot of the logarithm of capacity factors predicted by LSER vs. the logarithm of capacity factors observed in MEKC with 0.040 M SDS; 20 kV, pH 7.0, 0.050 M phosphate buffer.

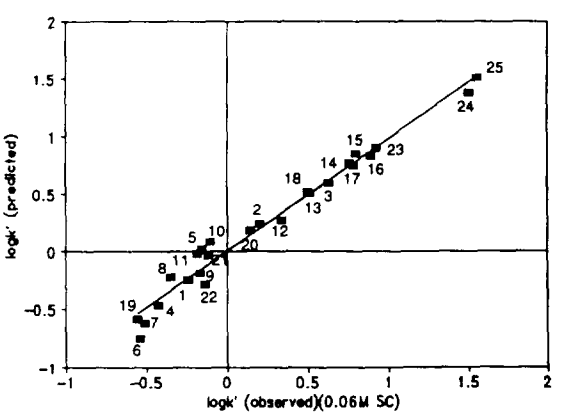

Fig. 3. The plot of the logarithm of capacity factors predicted by LSER vs. the logarithm of capacity factors observed in MEKC with 0.060 M SC; 20 kV, pH 7.0, 0.050 M phosphate buffer.

donor ability ($\alpha = 1.17$), therefore, one can anticipate that solutes' basicity would have a significant impact on the migration behavior in MEKC and in micelle–water partitioning process.

It was found that SC micelles are slightly less cohesive than SDS micelles, but more cohesive than *n*-octanol, which is reflected by the *m* values as shown in Table 6. It was also seen that SC micelles are less acidic than SDS micelles, but are more acidic than *n*-octanol by comparing the *b* values of the different LSER models. The *m* and *b* values as well as the ratio $-b/m$ using SC micelles in MEKC are more similar to those obtained in *n*-octanol–water system and are different from those observed using SDS micelles in MEKC. The reason behind this may be the similarity in environment between *n*-octanol and SC micelles. However, the dissimilarity between *n*-octanol and SC micelles results in the obviously different solute–solvent dipolar interactions and hydrogen bond interaction with solutes playing the role of HBD acids and solvents as HBA bases (the $s\pi^*$ and $a\alpha$ terms). It is also obvious that the difference in chemical selectivity for this group of test solutes with SDS and SC micelles is mainly due to different hydrogen bonding interactions. An extensive study of LSER of migration behavior in MEKC is underway and the results will be reported elsewhere [27].

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