Study of Retention in Micellar Liquid Chromatography on a C_{18} Column on the Basis of Linear Solvation Energy Relationships

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In this study, 8 solutes (aniline, caffeine, *p*-cresol, ethyl benzene, methylparaben, phenol, pyridine, and toluene) have been tested in terms of linear solvation energy relationships (LSER). Several micellar liquid chromatography (MLC) systems using cationic surfactant cetyltrimethylammonium bromide (CTAB) and a mixture of water with (methanol, *n*-propanol, and *n*-butanol) modifiers were characterized using the LSER solvation parameter model. The effects of the surfactant and modifier concentration on the retention in MLC were discussed. LSER model had demonstrated high potential to predict retention factors with high squared correlation coefficients ($r^2 > 0.99$). 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. This model is a helpful tool to understand the solute-surfactant interactions and evaluate the retention characteristic of micellar liquid chromatography.

Key Words : Micellar liquid chromatography, Linear solvation energy relationships (LSER), Chromatographic retention, Surfactant, Modifier

Introduction

Since its introduction by Armstrong and Henry in 1980,[1,2] micellar liquid chromatography (MLC) has seen solid growth in its use. The major advantages of MLC over most separation techniques as well as its unique capabilities have been widely investigated, with more than one hundred papers on this subject as well as reviews[3-5] and several books having been published.[6-8] According to reported studies, intermolecular solute-solvent interactions play a major role not only in separation science but also in many other areas of chemistry, as well as synthesis, spectroscopy, and pharmaceuticals. Since retention prediction and selectivity optimization have been very important in the rapid method development of MLC, it is imperative to achieve a better understanding of the factors that control separation efficiency.

For some time, the linear solvation energy relationship (LSER) model has been extensively used for the characterization of the quantitative structure-retention relationship (QSRR) and selectivity in MLC. The fundamental conceptual definition of the LSER model, known as the solvatochromic model, was first introduced by Kamlet and Taft.[9-13] In these pioneer papers they showed that chemical systems involve some properties that are linearly related to the free reaction energy, the free transfer energy, or the activation energy.

Furthermore, properties such as the common logarithm of retention factor ($\log k$) can be correlated with various fundamental molecular characteristics of the solvents and solutes involved in the physicochemical processes. The approach known as the Kamlet-Taft solvatochromic model was initially employed by Chen *et al.*[14] and Yang and Khaledi.[15] In Eq. (1), $\log k$ is correlated to known solute descriptors, V1, π^*, β, and α:

$$\log k = c + m\mathrm{V}_1 + s\pi^* + b\beta + a\alpha \quad (1)$$

The first descriptor, V_1, is the intrinsic volume of the solute and is usually divided by 100 to bring it to scale with the other terms. The solute polarity and polarizability are represented by the π^* term. β and α characterize the solute hydrogen bond accepting and solute hydrogen bond donating abilities, respectively. The system coefficients (*m*, *s*, *b*, and *a*) in Eq. (1) reflect differences in the two bulk phases, the aqueous and the stationary phases, between which the solute is transferring. They are obtained by multivariable, simultaneous, linear regression.[16] Thus, these coefficients provide quantitative information about solute-solute, solute-mobile phase, and solute-stationary phase interactions in MLC. The constant *c* represents the intercept and provides information about the separation phase ratio.[17] The *m* term is a measure of the relative proneness of cavity formation and general dispersion interactions for the solute with the stationary phase and the bulk aqueous phase, respectively. The difference in dipolarity/polarizability between the stationary phase and the bulk aqueous phase is represented by the coefficient *s*. The *b* and *a* terms represent the hydrogen bond donating ability and hydrogen bond accepting ability of the phase, respectively.

Another expression of LSER was introduced by Abraham *et al.* the solvation parameter model[13,18,19] and is a form of the Kamlet-Taft solvatochromic model, but revised as given by Eq. (2):

$$\log k = c + m\mathrm{V}_\mathrm{x} + s\pi^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^0 + r\mathrm{R}_2 \quad (2)$$

In the solvation parameter model (Eq. (2)), V_x represents the

McGowan solute characteristic volume[20] and R_2 represents the excess molar refraction of the solute[18] The subscript 2 denotes that these parameters are solute properties. The system coefficients *m*, *a*, and *b* for this model contain the same information as for the solvatochromic model, *i.e.*, Eq. (1).

It is important to note that the Kamlet-Taft solvatochromic model (Eq. (1)) does not contain the excess molar refraction solute descriptor, R2. In addition, the solvatochromic model uses the intrinsic volume (V_I) of the solute instead of the McGowan characteristic volume (V_X). Notwithstanding the numerical differences in the values for the two models, discrepancies in overall trends predicted by both approaches are quite rare. However, exact agreement in quantitative aspects cannot be expected.

In this study, 8 solutes (aniline, caffeine, *p*-cresol, ethyl benzene, methylparaben, phenol, pyridine, and toluene) have been in terms of LSER. Several MLC systems using cationic surfactant cetyltrimethylammonium bromide (CTAB) as well as a mixture of CTAB/methanol/water, CTAB/*n*-propanol/water, and CTAB/*n*-butanol/water as mobile phases were characterized using the previously mentioned solvation parameter LSER model.

Experimental Section

Instruments. All MLC experiments were performed on a Younglin M930 (Korea) equipped with a spectrophotometer (M 7200 Absorbance Detector, Young-In Scientific Co., Korea), and a Rheodyne injector (Hamilton Company, USA) valve with a 20 μL sample loop. The software Chromate (Ver. 3.0 Interface Eng., Korea) was used for system control and data handling. The detector was operated at 254 nm for LSER test solutes. Experiments were performed with a commercially available C_{18} column (Optimapak, Korea, 4.6 × 150 mm, 5 μm). An injection volume of 3 μL was applied throughout the experiments. All procedures were carried out at 298 K.

Materials. All of the LSER test solutes and the surfactant cetyltrimethylammonium bromide (CTAB) were purchased from Daejung (Korea). The mobile phase modifiers (methanol, *n*-propanol, and *n*-buthanol) were purchased from Duksan (Korea). Sodium nitrite was obtained from Daejung (Korea). Deionized water was obtained *via* a water purification system from Millipore Corp. (Milford, MA).

Preparation of Mobile Phases and Standard Solutions. The solutions of CTAB were prepared by first dissolving 0.1 gram of surfactant in 5.0 mL of deionized water. The final volume was adjusted to 100.0 mL with deionized water. The same sequence was followed for the preparation of mixed mobile phases. The corresponding molar concentrations of the surfactant were 0.03 M, 0.06 M, and 0.09 M. The mixed mobile phase contained 5, 7, and 10% (v/v) alcohol modifiers for the surfactant mixture. After thorough mixing in a sonicator for 30 minutes, the final running eluents were filtered through a syringe filter (HA-0.45, Division of Millipore, Waters, USA) and then sonicated for 20 more minutes prior to the MLC experiments. A mobile phase was refrigerated after each use. All stock solute solutions were prepared at concentrations of 1000 ppm each. Caffeine, phenol, and pyridine were dissolved in water; aniline, *p*-cresol, ethyl benzene, methylparaben, and toluene were dissolved in methanol. It should be emphasized that the working solutions were re-prepared every 3 days so as to avoid potential errors arising from decomposition.

Calculations

Retention Factor Estimation. The retention factor, *k*, of each solute was measured according to the following formula (3):

$$k = (t_R - t_M)/t_M \quad (3)$$

where t_R and t_M are the retention times of the retained analyte and the retention times of the unretained analyte (also known as dead time), respectively. Sodium nitrite was used as a t_M marker and was measured from the time of injection to the first deviation from the baseline following a 5 μL injection of 1% sodium nitrite solution. The retention factors reported in this study are the averages of at least three determinations. Evaluation of the results of the chromatographic experiments was carried out using mathematical statistic techniques. The relative error of a single measurement did not exceed 5%.

Linear Solvation Energy Relationship Estimations. Retention factors were determined for the 8 compounds used in this study, and the system constants were calculated by multiple linear regressions using Origin Pro 8.0 software (Microcal Software Inc., MA, USA.).[21] The statistical validity of the LSER models was evaluated through a F test, squared correlation coefficient (r^2), and root mean square error in the estimate (SD). The differences in LSER coefficients indicate the variations in the types of interactions between stationary phases and solutes. Solute interactions with the micellar systems occur through a variety of mechanisms such as surface adsorption, coaggregation, or partitioning into the hydrophobic core of the micelles. Due to these different mechanisms, the LSER constants for different kinds of solutes are not identical.

Results and Discussion

The retention behaviors of the 8 test solutes (aniline, caffeine, *p*-cresol, ethyl benzene, methylparaben, phenol, pyridine, and toluene) in each MLC system were examined and compared using the solvation parameter LSER model, *i.e.*, model described in Eq. (2). The test solutes and their descriptors used in this study are given in Table 1. We have selected eight compounds to illustrate the effect of the solute nature on the retention process in MLC.

Some recommendations for selecting an appropriate set of solutes have been gathered from a survey of the literature: 1) mathematically, a minimum number of seven solutes is needed to solve a multiple linear regression equation for six

Table 1. Test solutes and their descriptors for the solvation parameter model

Solute	Descriptor				
	V_X ($cm^3/mol^{-1}/100$)	π^H	α_2^H	β_2^0	R_2 ($cm^3/10$)
Aniline	0.955	0.96	0.26	0.50	0.8162
Caffeine	1.50	1.60	0.00	1.35	1.3630
p-Cresol	0.82	0.87	0.57	0.31	0.9160
Ethyl benzene	0.613	0.51	0.00	0.15	0.9982
Methylparaben	0.90	1.37	0.69	0.45	1.131
Phenol	0.805	0.89	0.60	0.30	0.7751
Pyridine	0.631	0.84	0.00	0.52	0.6753
Toluene	0.601	0.52	0.00	0.14	0.8573

Table 2. Squared correlation coefficients of cross-correlation matrix for the solvation parameters

	V_X	π^H	α_2^H	β_2^0	R_2
V_X	1.0000				
π^H	0.7765	1.0000			
α_2^H	0.0003	0.0735	1.0000		
β_2^0	0.8536	0.7154	0.0511	1.0000	
R_2	0.5786	0.4841	0.0011	0.4347	1.0000

unknowns (five system constants and the intercept); 2) there should be an absence of significant cross-correlation among the descriptors, and the clustering of individual descriptor values should be avoided (the cross-correlation matrix for descriptors with respect to one another is listed in Table 2); 3) since the used detection method in this work is UV absorption, the solutes should have a reasonable absorbance, between 200 and 250 nm, for convenient detection; and 4) solutes should be quite stable in the used solutions. The LSER constants and the data for all of the MLC phases using the solvation parameter model (Eq. (2)) are listed in Table 3 (I-III).

Positive *m* values indicate that retention in MLC increases with the size of the solute. Furthermore, a quite small positive *m* value shows that the endoergic cavity formation term does not have the most important effect on retention. According to Eq. (2), a positive sign of *m* indicates that the solute will preferentially transfer from the aqueous phase to the surfactant phase. Small *m* values also suggest that retention is not influenced by the size of the solute. From Table 3-III, when *n*-butanol as a modifier, it is found that *m* (0.09 M CTAB) > *m* (0.06 M CTAB) > *m* (0.03 M CTAB). Therefore, surfactant and modifier enriched mobile phases provide more viscosity (more polar) than the water eluent (more apolar). The quite large *m* values (1.04, 1.39, and 1.59) obtained for *n*-butanol and 0.09 M CTAB indicate that water is a solvent with high viscosity and that is not easy to create a cavity for the solute as compared to the employed MLC phase systems.

The difference in dipolarity/polarizability is represented by the coefficient *s*. A negative sign for this coefficient indicates that the solutes experience a microenvironment that has less dipolar/polarizable characteristics than the aqueous phase. On the contrary, positive *s* values indicate that the solutes find a more dipolar microenvironment in the MLC phases. As shown in Table 3 (I-III), the *s* values are negative for all studied MLC systems, with the exception of the positive value for 0.09 M CTAB with 5% methanol (0.01) and *n*-butanol (0.0026), and with 7% *n*-butanol (0.024). The small positive coefficient *s* indicates that these two surfactant systems are slightly more dipolar. However, it should be noted that none of the *s* values for the systems are statistically insignificant.

The coefficient *a* is one of the important factors in the solvatochromic model in the surfactant systems studied here. This coefficient represents the difference in the hydrogen bond accepting basicity of the MLC phase and that of the aqueous phase. A positive coefficient means that the hydrogen bond accepting ability of the MLC phase is greater. The coefficient *a* is small as compared to the *r* coefficient. The

Table 3-I. Constants for the micellar liquid chromatography systems using solvation parameter model (modifier-methanol)*

Surfactant concentration, M		0.03	0.06	0.09
Modifier concentration, % v/v			5	
Constants	*c*	0.88 (0.08)	0.80 (0.05)	0.68 (0.10)
	m	0.55 (0.19)	0.50 (0.12)	0.45 (0.23)
	s	−0.34 (0.17)	−0.09 (0.11)	0.01 (0.21)
	a	0.30 (0.13)	0.16 (0.08)	0.09 (0.16)
	b	−2.02 (0.23)	−1.91 (0.15)	−1.77 (0.29)
	r	1.05 (0.11)	0.70 (0.07)	0.63 (0.14)
Statistics	r^2	0.99931	0.99964	0.99822
	SD	0.0316	0.0200	0.0394
	F	577.48	1110.23	224.81
Modifier concentration, % v/v			7	
Constants	*c*	0.51 (0.08)	0.54 (0.09)	0.48 (0.12)
	m	0.74 (0.17)	0.87 (0.19)	0.68 (0.27)
	s	−0.30 (0.15)	−0.01 (0.17)	−0.01 (0.25)
	a	0.35 (0.12)	0.16 (0.13)	0.15 (0.18)
	b	−2.29 (0.21)	−2.22 (0.23)	−1.90 (0.33)
	r	1.32 (0.10)	0.70 (0.12)	0.66 (0.16)
Statistics	r^2	0.99948	0.99911	0.99768
	SD	0.0286	0.0321	0.0455
	F	744.45	450.84	171.71
Modifier concentration, % v/v			10	
Constants	*c*	0.43 (0.14)	0.41 (0.17)	0.30 (0.12)
	m	0.69 (0.32)	0.73 (0.38)	0.79 (0.26)
	s	−0.49 (0.29)	−0.19 (0.35)	−0.03 (0.24)
	a	0.63 (0.22)	0.44 (0.26)	0.37 (0.18)
	b	−2.01 (0.39)	−1.95 (0.47)	−1.87 (0.32)
	r	1.38 (0.19)	0.89 (0.23)	0.62 (0.16)
Statistics	r^2	0.99812	0.99634	0.99781
	SD	0.0539	0.0652	0.0444
	F	212.57	108.93	182.23

*Standard deviations for each coefficient are shown in parentheses

Table 3-II. Constants for the micellar liquid chromatography systems using solvation parameter model (modifier-*n*-propanol)

Surfactant concentration, M		0.03	0.06	0.09
Modifier concentration, % v/v			5	
Constants	*c*	0.49 (0.07)	0.42 (0.12)	0.40 (0.34)
	m	0.43 (0.16)	0.73 (0.27)	0.53 (0.74)
	s	−0.39 (0.15)	−0.06 (0.25)	−0.04 (0.68)
	a	0.68 (0.11)	0.38 (0.18)	0.32 (0.51)
	b	−1.83 (0.20)	−1.98 (0.33)	−1.71 (0.92)
	r	1.29 (0.10)	0.72 (0.16)	0.60 (0.46)
Statistics	r^2	0.99947	0.99812	0.98224
	SD	0.0278	0.0454	0.1268
	F	753.26	211.86	22.12
Modifier concentration, % v/v			7	
Constants	*c*	0.31 (0.24)	0.30 (0.24)	0.40 (0.28)
	m	0.54 (0.53)	0.70 (0.53)	0.53 (0.61)
	s	−0.53 (0.48)	−0.22 (0.49)	−0.08 (0.56)
	a	0.80 (0.36)	0.50 (0.37)	0.41 (0.42)
	b	−1.85 (0.65)	−1.83 (0.66)	−1.70 (0.75)
	r	1.44 (0.32)	0.88 (0.33)	0.56 (0.37)
Statistics	r^2	0.99494	0.99247	0.98889
	SD	0.0895	0.0907	0.1034
	F	78.69	52.72	35.59
Modifier concentration, % v/v			10	
Constants	*c*	0.39 (0.41)	0.31 (0.45)	0.39 (0.22)
	m	0.26 (0.90)	0.43 (0.98)	0.60 (0.49)
	s	−0.81 (0.82)	−0.46 (0.90)	−0.04 (0.45)
	a	1.09 (0.62)	0.79 (0.68)	0.53 (0.34)
	b	−1.34 (1.11)	−1.34 (1.21)	−1.61 (0.60)
	r	1.50 (0.55)	0.96 (0.60)	0.33 (0.30)
Statistics	r^2	0.98471	0.97314	0.99260
	SD	0.1526	0.1673	0.0832
	F	25.76	14.49	53.62

*Standard deviations for each coefficient are shown in parentheses

Table 3-III. Constants for the micellar liquid chromatography systems using solvation parameter model (modifier-*n*-butanol)*

Surfactant concentration, M		0.03	0.06	0.09
Modifier concentration, % v/v			5	
Constants	c	0.34 (0.08)	0.23 (0.13)	0.14 (0.40)
	m	0.62 (0.18)	1.00 (0.28)	1.04 (0.87)
	s	−0.25 (0.17)	−0.18 (0.26)	0.003 (0.80)
	a	0.63 (0.13)	0.43 (0.19)	0.15 (0.60)
	b	−2.08 (0.23)	−2.06 (0.35)	−2.09 (1.08)
	r	1.21 (0.11)	0.77 (0.17)	0.54 (0.53)
Statistics	r^2	0.99937	0.99798	0.97547
	SD	0.0310	0.0476	0.1487
	F	638.78	197.20	15.90
Modifier concentration, % v/v			7	
Constants	c	0.08 (0.22)	−0.02 (0.15)	−0.11 (0.26)
	m	0.75 (0.49)	0.97 (0.32)	1.39 (0.57)
	s	−0.54 (0.45)	−0.39 (0.30)	0.02 (0.52)
	a	0.82 (0.34)	0.60 (0.22)	0.14 (0.39)
	b	−1.97 (0.60)	−1.91 (0.40)	−2.4 (0.70)
	r	1.48 (0.30)	1.08 (0.20)	0.56 (0.35)
Statistics	r^2	0.99574	0.99736	0.99065
	SD	0.0828	0.0551	0.0970
	F	93.44	151.15	42.37
Modifier concentration, % v/v			10	
Constants	c	0.15 (0.39)	−0.01 (0.24)	−0.20 (0.18)
	m	0.49 (0.85)	0.63 (0.53)	1.59 (0.40)
	s	−0.89 (0.78)	−0.70 (0.48)	−0.04 (0.37)
	a	1.16 (0.59)	0.95 (0.36)	0.38 (0.28)
	b	−1.39 (1.05)	−1.34 (0.65)	−2.29 (0.49)
	r	1.56 (0.52)	1.24 (0.32)	0.32 (0.24)
Statistics	r^2	0.98621	0.99270	0.99531
	SD	0.1452	0.0897	0.0681
	F	28.60	54.37	84.81

*Standard deviations for each coefficient are shown in parentheses

regression constant *a* is positive and not overly large for all of the eluents studied. As seen in Table 3 (I-III), 0.03 M CTAB systems have the largest coefficient *a* values; thus they are the most basic among all the surfactant systems studied. It should be noted that the coefficients *a* are quite small (0.09-1.16) and statistically insignificant. This means that the solute's hydrogen-bond-donating acidity has a small or no effect on retention. In other words, the smaller values of coefficient *a* for these three different concentrations of surfactants indicate that their hydrogen bond accepting strength is not significantly different from the mobile phase without additives. A comparison of the coefficient *a* values provides the following order of acidity for all the assessed surfactant systems: 0.03 M CTAB < 0.06 M CTAB < 0.09 M CTAB.

The coefficient *b* is the second most important factor in the LSER solvation parameter model in the MLC systems used in this study. A comparison of the coefficients for each concentration of surfactant reveals that *b* and *r* have the largest absolute values among all coefficients for all concentrations presented here. The *b* coefficients in Table 3 (I-III) reveal play the most important roles in MLC retention. The regression constant *b* is large and negative for all of the mobile phases studied. The *b* coefficient is proportional to the difference in the hydrogen bond donating ability of the MLC phase and that of the aqueous phase. The larger (or less negative) *b* coefficient is, the higher the hydrogen bond donating ability strength of the MLC phase. The relative hydrogen bond donating strength of the methanol contained phases used in this study can be ordered as 0.09 M CTAB > 0.06 M CTAB > 0.03 M CTAB. The opposite tendency has been observed with *n*-butanol enriched MLC systems. On the whole, the negative values of the *b* coefficients decrease with surfactant concentration. In other words, the MLC phases with larger *b* values provide stronger hydrogen bond donating sites for solute interaction. The *n*-butanol adjusted

Table 4. The calculated (cal) and experimental (exp) log$k$ for surfactant system with 7% v/v of modifier, using Eq. (2) (ε is the relative error, %)

	log$k$	Aniline	Caffeine	*p*-Cresol	Ethyl benzene	Methyl paraben	Phenol	Pyridine	Toluene
		Solute							
		0.03 M CTAB							
	exp	0.96	−0.15	1.58	1.77	1.47	1.36	0.43	1.62
	cal	0.95	−0.15	1.55	1.78	1.47	1.38	0.43	1.61
	ε	1	0	2	1	0	1	0	1
		0.06 M CTAB							
Methanol	exp	0.88	−0.23	1.30	1.45	1.21	1.18	0.40	1.32
	cal	0.86	−0.21	1.29	1.43	1.21	1.20	0.40	1.35
	ε	2	9	1	1	0	2	0	2
		0.09 M CTAB							
	exp	0.77	−0.20	1.14	1.29	1.07	1.02	0.36	1.14
	cal	0.75	−0.18	1.13	1.27	1.07	1.05	0.36	1.18
	ε	3	1	1	2	0	3	0	4
		0.03 M CTAB							
	exp	0.83	−0.28	1.53	1.57	1.42	1.25	0.23	1.26
	cal	0.78	−0.26	1.49	1.53	1.42	1.31	0.22	1.33
	ε	6	7	3	3	0	5	4	6
		0.06 M CTAB							
n-Propanol	exp	0.74	−0.30	1.25	1.25	1.14	1.02	0.21	1.04
	cal	0.69	−0.27	1.21	1.22	1.15	1.10	0.20	1.10
	ε	7	10	3	2	1	8	5	6
		0.09 M CTAB							
	exp	0.60	−0.46	0.97	1.08	0.93	0.93	0.18	0.82
	cal	0.54	−0.46	0.98	0.99	0.92	0.93	0.16	0.92
	ε	10	0	1	8	1	0	11	12
		0.03 M CTAB							
	exp	0.78	−0.30	1.50	1.49	1.39	1.20	0.10	1.20
	cal	0.72	−0.29	1.44	1.45	1.38	1.26	0.08	1.25
	ε	8	3	4	3	1	5	2	4
		0.06 M CTAB							
n-Butanol	exp	0.64	−0.31	1.21	1.17	1.09	0.98	0.003	0.99
	cal	0.61	−0.30	1.17	1.16	1.09	1.03	0.004	1.01
	ε	5	3	3	1	0	5	3	2
		0.09 M CTAB							
	exp	0.57	−0.49	0.87	1.03	0.82	0.83	−0.08	0.78
	cal	0.53	−0.46	0.9	0.95	0.82	0.83	−0.08	0.88
	ε	7	6	3	8	0	0	0	13

mobile phases with 0.09 M CTAB showed the least acidity whereas 0.03 M CTAB had the least acidity among all the methanol systems. The pH of *n*-propanol systems is between the *n*-butanol and methanol systems.

As discussed earlier,[18] the r coefficient represents the excess molar refraction of the solute. All MLC phases have a positive coefficient r (Table 3 (I-III)). The coefficient r is statistically significant for all MLC systems. According to the data, the polarity of MLC phases is ranked as: 0.03 M CTAB > 0.06 M CTAB >0.09 M CTAB.

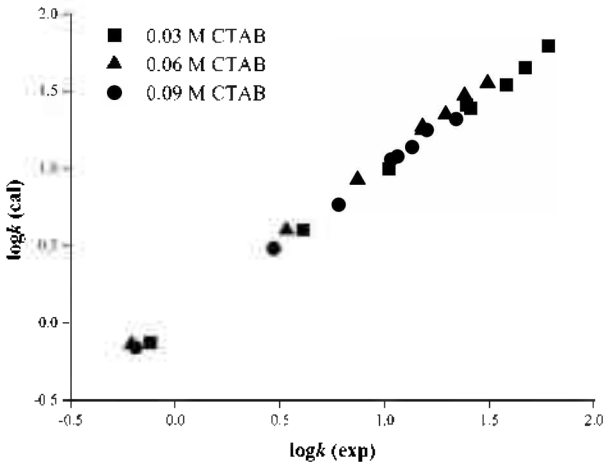

Figure 1. The correlation between experimental (exp) and calculated (cal) log$k$ (mobile phases composed from methanol 5% (v/v) with different concentrations of CTAB).

Estimation of LSER Equations. We have selected eight benzene derivatives to illustrate the effect of solute structure on the retention process in MLC: two nonpolar compounds (toluene and ethyl benzene), two acidic compounds (*p*-cresol and methylparaben), two basic compounds (caffeine and pyridine), and two amphoteric compounds (aniline and phenol). The coefficients in Table 3-III show that the surfactant systems with large absolute values of coefficients a and b (*e.g.*, 0.03 M CTAB with 7 and 10% v/v *n*-propanol) could be employed to conveniently separate mixtures of solutes with dissimilar hydrogen-bond acidity. Among all MLC phases, 0.03 M CTAB with 10% v/v *n*-propanol and 0.03 and 0.06 M CTAB with 10% v/v *n*-butanol, which have relatively large absolute coefficient s values (0.81, 0.89, and 0.70 respectively), would be comparatively better systems of choice to separate compounds by their polarity. Similarly, 7 and 10% v/v of *n*-propanol and *n*-butanol with 0.03 M CTAB would be convenient systems to separate solutes by excess molar refraction (coefficient r). The surfactant systems based on the methanol modifier show similar capacity to separate compounds according to their size, as all systems have similar coefficient m values. A change in the nature of the mobile phase modifier leads to a change in the discriminating ability of the MLC systems. In the cases of *n*-propanol and *n*-butanol, better selectivity can be expected. Calculated (or predicted) log$k$ values of the test solutes were computed for each MLC system using Eq. (2). The calculated (cal) and experimental (exp) log$k$ and relative error (ε, %) for some surfactant systems are given in Table 4.

The solvation parameter model is found to provide statistically and chemically results. This is evident when comparing the statistics (*i.e.*, r^2, SD, and F values) of the solvation parameter model results in Table 3 (I-III) with the results of prediction in Table 4. The correlation between experimental (exp) and calculated (cal) log$k$ (mobile phases composed from methanol 5% (v/v) with different concentrations of CTAB) demonstrated in Figure 1. Also, good

correlations were obtained for the experimental log k values versus predicted log k values for other MLC systems (data not shown); that is, LSERs are able to approximately reproduce the experimental log k values for the solutes studied in the different mobile phases.

Conclusion

Cationic surfactant (cetyltrimethylammonium bromide) systems with alcohol modifiers (methanol, *n*-propanol, and *n*-butanol) were applied as MLC mobile phases. The LSER model, *i.e.*, the solvation parameter model, was successfully applied to investigate the effect of the surfactant and modifiers concentrations on retention in MLC. The results obtained from the solvation parameter model provide comparable information, for example, coefficient b and coefficient r play the most important role in retention behavior in all MLC systems. It is worth noting that, using the obtained LSER models, it is possible to predict retention factors with high correlation coefficients ($r^2 > 0.99$). It is evident from the results of the LSER model that hydrophobicity plays an important role in the solute-surfactant interaction; however, the excess molar refraction and hydrogen bond accepting or donating ability have dominant effects. This model is a helpful tool to understand the solute-surfactant interactions and evaluate the retention characteristic of micellar liquid chromatography.

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