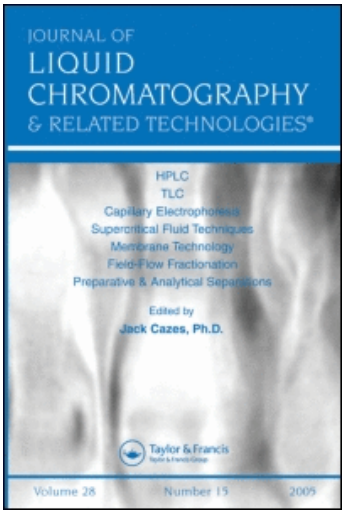

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Retention Factor in Micellar Liquid Chromatography on the Basis of Linear Solvation Energy Relationships

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Abstract: Linear solvation energy relationships (LSERs) are used to investigate the fundamental chemical interactions governing on a C_{18} column. The micellar liquid chromatographic (MLC) systems using sodium lauryl sulfate (SDS) and a mixture of water with (methanol, *n*-propanol, and *n*-butyl alcohol) modifiers were characterized using the LSER model. The ability of the LSERs to account for the chemical interactions underlying solute retention is shown and the effects of the surfactant and modifier concentration on the retention in MLC were discussed. 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 characteristics of micellar liquid chromatography.

Keywords: Linear solvation energy relationships (LSER), Micellar liquid chromatography, Modifier, Retention, Surfactant

INTRODUCTION

Since its introduction by Armstrong and Henry in 1980,[1,2] micellar liquid chromatography (MLC) has seen solid growth in its use. MLC techniques present some advantages over RPLC techniques such as: (1)

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it is possible to separate cationic, anionic, and neutral species simultaneously;[3,4] (2) 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 surfactant in the stationary phase remains constant, and little column reequilibration time is required before a new separation is started;[6,7] (3) luminescence detection can be improved for some solutes when they are incorporated into the micelles, and more typically because of the complex phase transfer phenomenon occurring within the column; and (4) biological fluids can be directly injected into the chromatographic system because of the solubilization of proteins by surfactants.[8,9] An important drawback of MLC, however, is the decrease in chromatographic efficiency observed, as compared to that obtained in RPLC,[10] 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, which in addition to improving the efficiency of MLC separations, can also increase chromatographic selectivity and reduce analysis time.

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.[11–15] 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.[16] and Yang and Khaledi.[17] In Equation (1), *Log k* is correlated to known solute descriptors, V_1, π^*, β and α as follows:

$$LogK = c + mV_1 + s\pi^* + b\beta + a\alpha \tag{1}$$

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 Equation (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.[18] 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.[19] 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,[20,21] and is a form of the Kamlet-Taft solvatochromic model, but revised as given by Equation (2):

$$LogK = c + mV_x + s\pi^H + a\sum \alpha_2^H + b\sum \beta_2^o + \mathbf{r}R_2 \qquad (2)$$

where k is the experimental retention factor. The V_x, π_2^H, $\sum \alpha_2^H$, $\sum \beta_2^H$ and R_2 terms are the solute descriptors, where V_x represents the solute's size/polarizability, π_2^H is the dipolarity/polarizability, $\sum \alpha_2^H$ is the hydrogen bond (HB) donating ability, $\sum \beta_2^H$ 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[22] and are obtained through a multiparameter linear regression. The $Logk_0$ term is simply the intercept of the regression and is comprised of constant contributions from the solutes and the chromatographic system.

It is important to note that the Kamlet-Taft solvatochromic model (Equation (1)) does not contain the excess molar refraction solute descriptor, R_2. In addition, the solvatochromic model uses the intrinsic volume (V_1) 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 can not be expected.

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 (SDS) and organic modifier (methanol, *n*-propanol and *n*-butyl alcohol). For this study, 10 solutes (caffeine, pyridine, aniline, phenol, methyl paraben, *m*-cresol, *o*-cresol, *p*-cresol, acetophenone, and benzene) have been in terms of LSER. Several MLC systems using surfactant SDS, as well as a mixture of SDS/

methanol/water, SDS/*n*-propanol/water, and SDS/*n*-butyl alcohol/water as mobile phases, were characterized using the previously mentioned solvation parameter LSER model.

EXPERIMENTAL

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 30°C.

Materials

All of the LSER test solutes and the SDS were purchased from Daejung (Korea). The mobile phase modifiers (methanol, *n*-propanol, and *n*-butyl alcohol) 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 SDS 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 1.0 mg/mL each. Caffeine, phenol, and pyridine were dissolved in water and the other solutes were dissolved in methanol. It

should be emphasized that the working solutions were reprepared every 3 days so as to avoid potential errors arising from decomposition.

CALCULATION

Retention Factor Estimation

The retention factor k of each solute was measured according to the following formula (3):

$$k = \frac{t_R - t_o}{t_o} \tag{3}$$

where t_R and t_0 are the retention times of the retained analyte and the dead time, respectively. Sodium nitrite was used as a t_0 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 measurements. 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 3%.

Linear Solvation Energy Relationship Estimations

Retention factors were determined for the 10 compounds used in this study, and the system constants were calculated by multiple linear regressions using Origin Pro 6.0 software (Microcal Software Inc., MA, USA). 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 variations in the types of interactions between stationary phases and solutes. Solute interactions with ionic liquid systems occur through a variety of mechanisms such as surface adsorption and co-aggregation. Due to these different mechanisms, the LSER constants for different kinds of solutes are not identical.

RESULTS AND DISCUSSION

The retention behaviors of the 10 test solutes in each MLC system were examined and compared using the LSER model, which was described in Equation (2). The test solutes and their descriptors used in this study are given in Table 1.

Table 1. LSER descriptors of 10 compounds from literatures

Samples	Descriptors				
	$V_X/100$	$(\pi_2)^H$	$(\alpha_2)^H$	$(\beta_2)^H$	R_2
Caffeine	1.50	1.60	0.00	1.35	1.3630
Pyridine	0.631	0.84	0.00	0.52	0.6753
Aniline	0.955	0.96	0.26	0.50	0.8162
Phenol	0.805	0.89	0.60	0.30	0.7751
Methylparaben	0.90	1.37	0.69	0.45	1.131
m-Cresol	0.822	0.88	0.57	0.34	0.9160
p-Cresol	0.82	0.87	0.57	0.31	0.9160
o-Cresol	0.840	0.86	0.52	0.30	0.9160
Acetophenone	0.818	1.01	0.00	0.48	1.0139
Benzene	0.610	0.52	0.00	0.14	0.7164

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 unknowns; (2) there should be an absence of significant cross correlation among the descriptors, and clustering of individual descriptor values should be avoided; (3) since the detection method used 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 employed solutions. The LSER constants and the data for all of the mobile phases are listed in Table 2 (1–3).

Positive m values indicate that retention in the MLC system 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 Equation (2), a positive sign of m indicates that the solute will preferentially transfer from the acqueous phase to the surfactant phase. Small m values also suggest that retention is not influenced by the size of the solute. From Table 2-1, with methanol as a modifier, it is found that m (0.09 M SDS) $> m$ (0.06 M SDS) $> m$ (0.03 M SDS). Therefore, surfactant and modifier enriched mobile phases provide more viscosity (more polar) than the water eluent (more apolar). The quite large m values obtained for methanol and 0.09 M SDS 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 2 (1–3), the *s* values are negative for all studied MLC systems, it 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

Table 2-1. Constants for the MLC systems using LESR model (modifier: methanol, v/v)

Surfactant concentration, M		0.03	0.06	0.09
Type and concentration of modifier		methanol, 5% v/v		
Constants	Log k_0	1.44 (0.16)	1.50 (0.17)	1.67 (0.13)
	m	−0.12 (0.36)	0.024 (0.38)	0.029 (0.29)
	s	−0.84 (0.30)	−1.08 (0.31)	−1.60 (0.24)
	a	−0.20 (0.16)	−0.24 (0.17)	−0.10 (0.13)
	b	−0.62 (0.36)	−0.39 (0.37)	0.10 (0.29)
	r	1.41 (0.33)	1.26 (0.34)	1.25 (0.26)
Statistics	r^2	0.9657	0.9607	0.9793
	SD	0.06745	0.06988	0.05411
	F	22.5066	19.5753	37.9133
Type and concentration of modifier		methanol, 7% v/v		
Constants	Log k_0	1.36 (0.18)	1.15 (0.20)	1.29 (0.27)
	m	−0.34 (0.41)	−0.15 (0.45)	−0.11 (0.60)
	s	−0.79 (0.33)	−0.84 (0.40)	−1.01 (0.49)
	a	−0.29 (0.18)	−0.46 (0.20)	−0.28 (0.27)
	b	−0.58 (0.40)	−0.84 (0.45)	−0.47 (0.59)
	r	1.56 (0.36)	1.45 (0.40)	1.40 (0.54)
Statistics	r^2	0.9578	0.9516	0.9131
	SD	0.07551	0.08374	0.1115
	F	18.1586	15.7331	8.4053
Type and concentration of modifier		methanol, 10% v/v		
Constants	Log k_0	1.15 (0.20)	1.07 (0.24)	1.13 (0.30)
	m	0.012 (0.45)	0.066 (0.53)	0.11 (0.68)
	s	−0.39 (0.37)	−0.43 (0.43)	−0.51 (0.56)
	a	−0.55 (0.20)	−0.59 (0.24)	−0.49 (0.30)
	b	−1.13 (0.44)	−1.04 (0.52)	−0.83 (0.67)
	r	1.18 (0.40)	1.25 (0.47)	1.01 (0.61)
Statistics	r^2	0.9525	0.9306	0.8726
	SD	0.08309	0.09812	0.1266
	F	16.0328	10.7302	5.4811

Table 2-2. Constants for the MLC systems using LESR model (modifier: *n*-propanol, v/v)

Surfactant concentration, M		0.03	0.06	0.09
Type and concentration of modifier		*n*-propanol, 5% v/v		
Constants	Log k_0	1.15 (0.20)	1.29 (0.16)	1.34 (0.13)
	m	0.30 (0.46)	0.033 (0.36)	−0.20 (0.29)
	s	−0.70 (0.37)	−0.82 (0.30)	−0.64 (0.23)
	a	−0.41 (0.20)	−0.17 (0.16)	−0.080 (0.13)
	b	−1.12 (0.45)	−0.68 (0.36)	−0.58 (0.28)
	r	1.41 (0.41)	1.25 (0.33)	1.06 (0.26)
Statistics	r^2	0.9568	0.9669	0.9784
	SD	0.08473	0.06736	0.05305
	F	17.6996	23.3977	36.2250
Type and concentration of modifier		*n*-propanol, 7% v/v		
Constants	Log k_0	1.12 (0.25)	1.15 (0.22)	1.12 (0.23)
	m	−0.093 (0.57)	−0.052 (0.49)	0.064 (0.51)
	s	−0.70 (0.47)	−0.69 (0.40)	−0.54 (0.42)
	a	−0.42 (0.25)	−0.35 (0.22)	−0.38 (0.23)
	b	−0.98 (0.56)	−0.78 (0.48)	−0.89 (0.51)
	r	1.60 (0.51)	1.31 (0.44)	1.07 (0.46)
Statistics	r^2	0.9384	0.9415	0.9348
	SD	0.1060	0.09102	0.09542
	F	12.1932	12.8837	11.4662
Type and concentration of modifier		*n*-propanol, 10% v/v		
Constants	Log k_0	1.00 (0.31)	0.91 (0.22)	1.01 (0.33)
	m	0.13 (0.69)	0.40 (0.50)	0.023 (0.73)
	s	−0.47 (0.57)	−0.50 (0.41)	−0.59 (0.60)
	a	−0.49 (0.31)	−0.48 (0.23)	−0.36 (0.33)
	b	−1.20 (0.68)	−1.20 (0.50)	−0.87 (0.72)
	r	1.34 (0.62)	1.10 (0.45)	1.17 (0.65)
Statistics	r^2	0.9089	0.9419	0.8802
	SD	0.1281	0.09369	0.1356
	F	7.9828	12.9637	5.8770

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 regression constant a is positive and not overly large for all of the eluents studied. As seen in Table 2 (1–3), 0.09 M SDS 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 (from −0.59 to −0.08) and

Table 2-3. Constants for the MLC systems using LESR model (modifier: *n*-butyl alcohol, v/v)

Surfactant concentration, M		0.03	0.06	0.09
Type and concentration of modifier		*n*-butyl alcohol, 5% v/v		
Constants	Log k_0	1.17 (0.14)	1.30 (0.15)	1.25 (0.16)
	m	0.42 (0.32)	0.29 (0.33)	0.17 (0.35)
	s	−0.83 (0.27)	−0.86 (0.27)	−0.78 (0.29)
	a	−0.38 (0.14)	−0.27 (0.15)	−0.22 (0.16)
	b	−1.01 (0.32)	−0.80 (0.33)	−0.73 (0.35)
	r	1.27 (0.29)	1.06 (0.30)	1.05 (0.32)
Statistics	r^2	0.9768	0.9747	0.9689
	SD	0.0601	0.06219	0.0667
	F	33.6992	30.7928	25.0020
Type and concentration of modifier		*n*-butyl alcohol, 7% v/v		
Constants	Log k_0	1.16 (0.22)	1.18 (0.23)	1.06 (0.27)
	m	−0.086 (0.50)	−0.12 (0.51)	−0.092 (0.59)
	s	−0.69 (0.41)	−0.70 (0.42)	−0.67 (0.48)
	a	−0.45 (0.22)	−0.35 (0.23)	−0.27 (0.26)
	b	−1.03 (0.49)	−0.85 (0.50)	−0.73 (0.58)
	r	1.52 (0.45)	1.35 (0.45)	1.26 (0.53)
Statistics	r^2	0.9571	0.9492	0.9143
	SD	0.09348	0.09413	0.1095
	F	17.8434	14.9337	8.5349
Type and concentration of modifier		*n*-butyl alcohol, 10% v/v		
Constants	Log k_0	1.05 (0.23)	1.05 (0.25)	1.03 (0.34)
	m	0.24 (0.52)	0.19 (0.55)	0.16 (0.76)
	s	−0.26 (0.43)	−0.45 (0.45)	−0.27 (0.62)
	a	−0.57 (0.23)	−0.45 (0.25)	−0.51 (0.34)
	b	−1.30 (0.51)	−1.06 (0.55)	−0.99 (0.75)
	r	0.98 (0.47)	0.99 (0.50)	0.73 (0.68)
Statistics	r^2	0.9442	0.9328	0.8561
	SD	0.09659	0.1027	0.1412
	F	13.5438	11.1016	4.7602

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 SDS >0.06 M SDS >0.09 M SDS.

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 2 (1–3) 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 SDS >0.06 M SDS >0.03 M SDS. The opposite tendency has been observed with *n*-butyl alcohol 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*-butyl alcohol adjusted mobile phases with 0.09 M SDS showed the least acidity, whereas 0.03 M SDS had the least acidity among all the methanol systems. The pH of *n*-propanol systems is between the *n*-butyl alcohol and methanol systems.

As discussed earlier,[20] the *r* coefficient represents the excess molar refraction of the solute. All MLC phases have a positive coefficient *r* (Table 2 (1–3)). 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 SDS >0.06 M SDS >0.09 M SDS.

Estimation of LSER Equations

We have selected 10 compounds to illustrate the effect of solute structure on the retention process: 6 benzene derivatives (benzene, acetophenone, *m*-cresol, *p*-cresol, *o*-cresol, and methylparaben), two basic compounds (caffeine and pyridine), and two amphoteric compounds (aniline and phenol). The coefficients in Table 2 (1–3) show that the surfactant systems with large absolute values of coefficients *a* and *b* (e.g., 0.09 M SDS with 5% v/v methanol and *n*-propanol) could be employed to conveniently separate mixtures of solutes with dissimilar hydrogen-bond acidity. Among all MLC phases, 0.03 M SDS with 10% (v/v) methanol, *n*-propanol, and *n*-butyl alcohol, which have relatively large absolute coefficient *s* values (−0.39, −0.47, and −0.26, respectively), would be comparatively better systems of choice to separate compounds by their polarity. Similarly, 7% (v/v) of methanol, *n*-propanol, and *n*-butyl alcohol with 0.03 M SDS would be convenient systems to separate solutes by excess molar refraction

Table 3. The calculated (cal) and experimental (exp) *Log k* for surfactant system with 7% v/v of modifiers (ε is the relative error, %)

		Solutes									
Log *k*		Caffeine	Pyridine	Aniline	Phenol	Methyl paraben	*m*-Cresol	*p*-Cresol	*o*-Cresol	Acetophenone	Benzene
Methanol						0.03 M SDS					
	exp.	0.95	1.23	1.18	1.22	1.33	1.49	1.44	1.46	1.50	1.86
	cal.	0.93	1.23	1.18	1.24	1.27	1.45	1.48	1.50	1.59	1.78
	ε	2	1	0	2	4	3	3	3	6	4
						0.06 M SDS					
	exp.	0.90	1.08	1.11	1.11	1.14	1.32	1.33	1.35	1.39	1.83
	cal.	0.82	0.99	1.06	1.00	1.10	1.20	1.20	1.24	1.25	1.64
	ε	9	8	4	10	4	9	9	8	10	10
						0.09 M SDS					
	exp.	0.82	1.07	1.02	1.06	1.06	1.29	1.25	1.28	1.24	1.77
	cal.	0.78	1.07	1.05	1.08	0.99	1.27	1.30	1.32	1.37	1.63
	ε	4	0	3	2	7	1	4	4	11	7
n-Propanol						0.03 M SDS					
	exp.	0.74	1.04	1.05	1.09	1.21	1.40	1.23	1.38	1.39	1.80
	cal.	0.72	1.04	1.08	1.12	1.16	1.32	1.36	1.39	1.49	1.71
	ε	3	0	2	2	4	5	10	1	7	5

						0.06 M SDS					
	exp.	0.72	1.02	1.02	1.06	1.10	1.32	1.15	1.32	1.30	1.66
	cal.	0.70	1.02	1.03	1.07	1.05	1.24	1.27	1.30	1.36	1.59
	ε	3	0	1	0	5	7	10	2	5	4
						0.09 M SDS					
	exp.	0.63	0.96	0.98	1.01	1.04	1.24	1.08	1.21	1.20	1.60
	cal.	0.61	0.97	0.99	1.03	0.99	1.16	1.19	1.22	1.28	1.52
	ε	3	0	2	1	5	7	10	2	7	5
n-Butyl alcohol						0.03 M SDS					
	exp.	0.64	1.02	1.01	1.08	1.15	1.34	1.21	1.35	1.36	1.79
	cal.	0.61	1.02	1.02	1.08	1.08	1.27	1.31	1.34	1.44	1.69
	ε	6	0	1	0	6	5	8	0	6	5
						0.06 M SDS					
	exp.	0.59	0.99	0.98	1.00	1.06	1.29	1.12	1.30	1.26	1.65
	cal.	0.57	0.99	0.98	1.04	1.02	1.21	1.25	1.28	1.34	1.59
	ε	3	0	0	4	4	6	11	1	6	3
						0.09 M SDS					
	exp.	0.58	0.91	0.95	0.90	1.01	1.26	1.05	1.19	1.15	1.56
	cal.	0.58	0.91	0.92	0.99	0.97	115	1.18	1.20	1.24	1.46
	ε	1	0	3	10	4	9	12	1	7	7

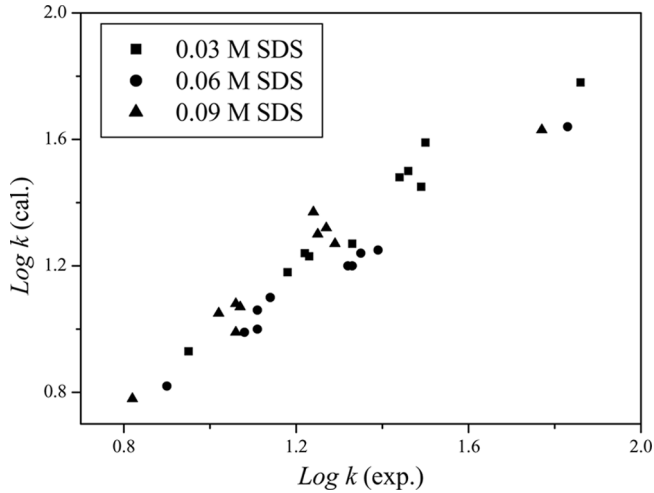

Figure 1. The correlation between experimental and calculated *Log k* from LSER equation for different concentrations of SDS in 7% methanol.

(coefficient *r*, 1.56, 1.60, and 1.52, respectively). The surfactant systems based on the methanol modifier show a 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

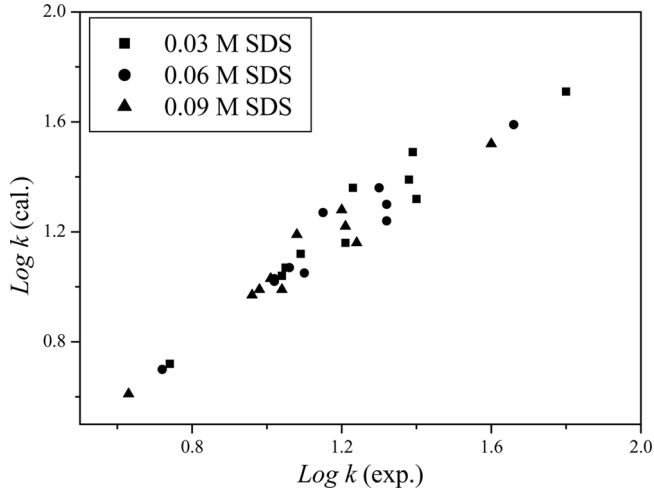

Figure 2. The correlation between experimental and calculated *Log k* from LSER equation for different concentrations of SDS in 7% *n*-propanol.

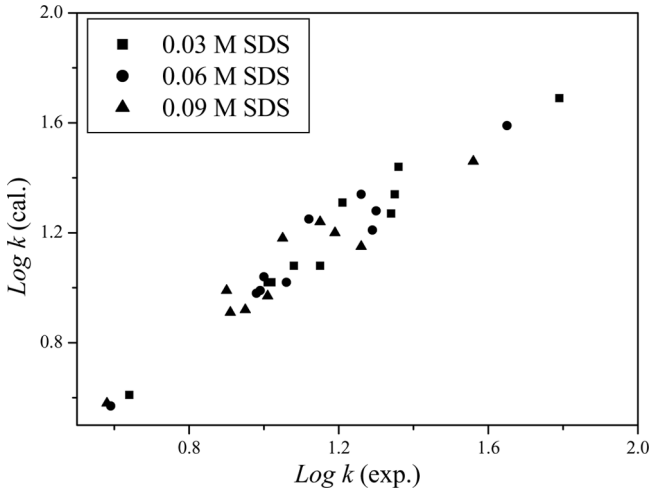

Figure 3. The correlation between experimental and calculated Log k from LSER equation for different concentrations of SDS in 7% *n*-butyl alcohol.

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 Equation (2). The calculated (cal) and experimental (exp) log *k* and relative error (ε, %) for some surfactant systems are given in Table 3.

The solvation parameter model is found to provide statistical and chemical results. This is evident when comparing the statistics (i.e., r^2, *SD*, and *F* values) of the solvation parameter model results in Table 2 (1–3) with the results of prediction in Table 3. The correlation between experimental (exp) and calculated (cal) *Log k* (mobile phases composed from 7% (v/v) methanol, *n*-propanol, and *n*-butyl alcohol with different concentrations of SDS) are demonstrated from Figures 1 to 3. 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.

CONCLUSIONS

SDS systems with alcohol modifiers (methanol, *n*-propanol, and *n*-butyl alcohol) 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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