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Monomeric and polymeric anionic gemini surfactants and mixed surfactant systems in micellar electrokinetic chromatography.

Part II: Characterization of chemical selectivity using two linear solvation energy relationship models

Sodium di(undecenyl) tartarate monomer (SDUT), a vesicle-forming amphiphilic compound possessing two hydrophilic carboxylate headgroups and two hydrophobic undecenyl chains, was prepared and polymerized to form a polymeric vesicle (*i.e.*, poly-SDUT). The anionic surfactants of SDUT and poly-SDUT (carboxylate head group) and sodium dodecyl sulfate, SDS (sulfate head groups) as well as mixed surfactant systems (SDS/SDUT, SDS/poly-SDUT, and SDUT/poly-SDUT) were applied as pseudostationary phases in micellar electrokinetic chromatography (MEKC). Two linear solvation energy relationship (LSER) models, *i.e.*, solvatochromic and solvation parameter models, were successfully applied to investigate the effect of the type and composition of pseudostationary phases on the retention mechanism and selectivity in MEKC. The solvatochromic and solvation parameter models were used to help understand the fundamental nature of the solute-pseudostationary phase interactions and to characterize the properties of the pseudostationary phases (*e.g.*, solute size and hydrogen bond-accepting ability for all pseudostationary phases). The solute types were found to have a significant effect on the LSER system coefficients and on the predicted retention factors. Although both LSER models provide the same information, the solvation parameter model is found to provide much better results both statistically and chemically than the solvatochromic model.

Keywords: Gemini surfactants / Linear solvation energy relationships / Micellar electrokinetic chromatography / Polymeric surfactants
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1 Introduction

Since its introduction by Terabe [1], micellar electrokinetic chromatography (MEKC) has been extensively used for the separation of both charged and neutral solutes. A major advantage of MEKC over most of the separation techniques is the feasibility of changing the chemical composition of the MEKC buffer system by simply rinsing the capillary with a solution of a new pseudostationary phase. Thus, the selectivity of the technique can easily be manipulated and controlled by proper selection of the

surfactant type or addition of modifiers, such as organic solvents or cyclodextrins [2, 3]. In MEKC, neutral solutes are separated based on their differential partitioning into the pseudostationary phase and aqueous phase. A major driving force behind the solute retention is hydrophobic interaction between solutes and the pseudostationary phase. However, some other types of interactions between solutes and the pseudostationary phase also influence solute retention and selectivity. Therefore, understanding the nature of the interactions is necessary to rapidly optimize the separation method in MEKC.

In the last several years, the linear solvation energy relationship (LSER) model has been given a significant attention for the characterization of retention and selectivity differences between different pseudostationary phases in MEKC [2–13]. The solvatochromic model, the basic concept of the LSER model, was first developed by Kamlet, Taft, and their co-workers [14, 15]. The Kamlet-Taft solvatochromic model was first employed by Chen *et al.* [4] and Yang and Khaledi [5] to determine the selectivity of a

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Abbreviations: HBA, hydrogen bond acceptor; HBD, hydrogen bond donor; LSER, linear solvation energy relationships; NHB, nonhydrogen bond donor; SDUT, sodium di(10-undecenyl) tartarate; poly-SDUT, poly sodium di(10-undecenyl) tartrate

number of pseudostationary phases in MEKC. They have shown that the logarithmic retention factor ($\log k'$) can be correlated with various molecular properties of the solvents or solutes involved in the chemical process. In Eq. (1), $\log k'$ is correlated to known solute descriptors, V_1 , π^* , β , and α :

$$\log k' = c + mV_1 + s\pi^* + b\beta + a\alpha \quad (1)$$

The descriptor V_1 is the intrinsic volume of the solute and is 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 represent the solute hydrogen bond-accepting and solute hydrogen bond-donating abilities, respectively. The system coefficients (c , m , s , b , and a) reflect differences in the two bulk phases, *i.e.*, the aqueous and the pseudostationary phase, between which the solute is transferring. The constant c represents the intercept and includes information about the separation phase ratio, *i.e.*, the volume of pseudostationary phase divided by the volume of the aqueous mobile phase ($V_{\text{psp}}/V_{\text{aq}}$). The m term is a measure of the relative ease of cavity formation in the pseudostationary phase or aqueous phase. In other words, the coefficient m is directly related to the difference in the cohesive energies of the aqueous phase and the pseudostationary phase. The coefficient s represents the difference in dipolarity/polarizability between the pseudostationary phase and the bulk aqueous phase. The coefficients b and a represent the hydrogen bond-donating and hydrogen bond-accepting ability of the pseudostationary phase, respectively.

Another LSER model is the solvation parameter model, which was introduced by Abraham *et al.* [16–18] and is a revised form of Kamlet-Taft's solvatochromic model:

$$\log k' = c + mV_2 + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^0 \quad (2)$$

In this model, V_2 and R_2 represent the McGowan solute characteristic volume ($\text{cm}^3/\text{mol}^{-1}$) [19] and the excess molar refraction (cm^3), respectively. In order to obtain a rough scaling with the other descriptors, V_2 and R_2 are divided by 100 and 10, respectively. The subscript 2 denotes that these parameters are solute properties. The m , b , and a coefficients and their descriptors for the solvation parameter model contain the same information as in the solvatochromic model. The coefficient r verifies the difference in ability of pseudostationary phase and separation buffer to interact with solute n - or π -electrons. The dipolarity/polarizability differences between pseudostationary phase and separation buffer is represented by the coefficient s . Previous MEKC studies have shown that the solute retention is predominately influenced by the solute size [7, 13]. The second contributor towards solute retention is the solute hydrogen bond-accepting ability, which is also the largest contributor to the selec-

tivity differences of different pseudostationary phases. In addition, the pseudostationary phase head group and the counterion may influence the MEKC solute retention and selectivity as demonstrated by spectroscopic and electrophoretic studies that solutes interact with micellar palisade and Stern layers [20–22].

In this second part of our study six surfactant systems, *i.e.*, sodium dodecyl sulfate (SDS), sodium di(undecenyl) tartrate (SDUT), and poly sodium di(undecenyl) tartrate (poly-SDUT) as well as the mixed surfactant systems SDS/SDUT, SDS/poly-SDUT, and SDUT/poly-SDUT were characterized using the aforementioned two LSER models.

2 Materials and methods

2.1 Instrumentation and materials

Same as in Part I of this study [23].

2.2 Synthesis and characterization of SDUT and CE

Synthesis and characterization of the surfactants as well as the CE procedure are detailed in the first part of this study [23].

2.3 Preparation of separation buffers and standard solutions

Details of buffer and standard solution preparation are given in Part I [23]. Test solutes and their descriptors used in this study are listed in Table 1. Based on their hydrogen bond formation abilities, the solutes are grouped as non-hydrogen bond donors (NHBs) (solutes 1–12, $\beta \leq 0.20$), hydrogen bond acceptors (HBAs) (solutes 13–24, $\beta \geq 0.22$), and hydrogen bond donors (HBDs) (solutes 25–36, $\alpha \geq \beta$). The NHB solutes that include alkyl- and halo-substituted benzenes and polyaromatic hydrocarbons do not have any hydrogen-bonding functional groups. However, due to the aromatic ring(s), they are weak hydrogen bond acceptors ($\beta \leq 0.2$). The HBA solutes possess hydrogen bond-accepting functional groups on the aromatic ring, whereas HBD solutes have hydrogen bond-donating functional groups.

2.4 Calculations

The retention factors, k' , of the neutral solutes were measured using the equation given in Part I of this study [23]. System coefficients (m , r , s , a , and b) in Eqs. (1) and (2) were determined by multiple linear regression using SAS software (SAS Institute, Cary, NC, USA).

Table 1. Test solutes and their solvation descriptors^{a)} for solvatochromic and solvation parameter models

	Solvatochromic model				Solvation parameter model				
	V_1	π^*	β	α	V_2	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^0$
Nonhydrogen bond donors (NHBs)									
1 Benzene	0.491	0.59	0.10	0	0.716	0.610	0.52	0	0.14
2 Toluene	0.592	0.55	0.11	0	0.857	0.601	0.52	0	0.14
3 Ethylbenzene	0.668	0.53	0.12	0	0.998	0.613	0.51	0	0.15
4 Propylbenzene	0.769	0.51	0.12	0	1.139	0.604	0.50	0	0.15
5 <i>p</i> -Xylene	0.668	0.51	0.12	0	0.998	0.613	0.52	0	0.16
6 Chlorobenzene	0.581	0.71	0.07	0	0.839	0.718	0.65	0	0.07
7 Bromobenzene	0.624	0.79	0.06	0	0.891	0.882	0.73	0	0.09
8 Iodobenzene	0.671	0.81	0.05	0	0.975	1.188	0.83	0	0.12
9 4-Chlorotoluene	0.679	0.67	0.08	0	0.980	0.705	0.67	0	0.07
10 Biphenyl	0.920	1.18	0.20	0	1.324	1.360	0.99	0	0.22
11 Naphthalene	0.753	0.70	0.15	0	1.085	1.360	0.92	0	0.20
12 1-Methylnaphthalene	0.851	0.66	0.16	0	1.226	1.344	0.90	0	0.20
Hydrogen bond acceptors (HBAs)									
13 Acetophenone	0.690	0.90	0.49	0.04	1.014	0.818	1.01	0	0.48
14 Benzonitrile	0.590	0.90	0.37	0.00	0.871	0.742	1.11	0	0.33
15 Nitrobenzene	0.631	1.01	0.30	0.00	0.891	0.871	1.11	0	0.28
16 Methyl benzoate	0.736	0.75	0.39	0.00	1.073	0.733	0.85	0	0.46
17 Ethyl benzoate	0.834	0.74	0.41	0.00	1.214	0.689	0.85	0	0.46
18 4-Chloroanisole	0.720	0.73	0.22	0.00	1.038	0.838	0.86	0	0.24
19 4-Nitrotoluene	0.729	0.97	0.31	0.00	1.032	0.870	1.11	0	0.28
20 4-Chloroacetophenone	0.780	0.90	0.45	0.06	1.136	0.955	1.09	0	0.44
21 Methyl 2-methylbenzoate	0.834	0.71	0.40	0.00	1.214	0.772	0.87	0	0.43
22 Phenyl acetate	0.736	1.14	0.52	0.00	1.073	0.661	1.13	0	0.54
23 3-Methylbenzyl alcohol	0.732	0.95	0.53	0.39	1.057	0.815	0.90	0.33	0.59
24 Phenethyl alcohol	0.732	0.97	0.55	0.33	1.057	0.784	0.83	0.30	0.66
Hydrogen bond donors (HBDs)									
25 Benzyl alcohol	0.634	0.99	0.52	0.39	0.916	0.803	0.87	0.33	0.56
26 Phenol	0.536	0.72	0.33	0.61	0.775	0.805	0.89	0.60	0.30
27 4-Methylphenol	0.634	0.68	0.34	0.58	0.916	0.820	0.87	0.57	0.31
28 4-Ethylphenol	0.732	0.66	0.35	0.58	1.057	0.800	0.90	0.55	0.36
29 4-Fluorophenol	0.562	0.73	0.28	0.65	0.793	0.670	0.97	0.63	0.23
30 4-Chlorophenol	0.626	0.72	0.23	0.67	0.898	0.915	1.08	0.67	0.20
31 4-Bromophenol	0.669	0.79	0.23	0.67	0.950	1.080	1.17	0.67	0.20
32 4-Chloroaniline	0.653	0.73	0.40	0.31	0.939	1.060	1.13	0.30	0.31
33 3-Chlorophenol	0.626	0.77	0.23	0.69	0.898	0.909	1.06	0.69	0.15
34 3-Methylphenol	0.634	0.68	0.34	0.58	0.916	0.822	0.88	0.57	0.34
35 3-Bromophenol	0.669	0.84	0.23	0.69	0.950	1.060	1.15	0.70	0.16
36 3,5-Dimethylphenol	0.732	0.64	0.35	0.56	1.057	0.820	0.84	0.57	0.36

a) Solute solvation descriptors from [7]

3 Results and discussion

The retention behavior of 36 test solutes in each pseudostationary phase was examined and compared using the aforementioned two LSER models. The results of the two LSER models are discussed below.

3.1 Solvatochromic model

The LSER constants and the statistics of the pseudostationary phases using the solvatochromic model, Eq. (1), are listed in Table 2. As discussed earlier, the *c* constant is related to the phase ratio of the separation system, *i.e.*,

Table 2. System constants for the six pseudostationary phases in MEKC using the solvatochromic model

	Pseudostationary phases					
	SDS	SDUT	Poly-SDUT	SDS/SDUT	SDS/ Poly-SDUT	SDUT/ Poly-SDUT
System constants						
<i>c</i>	-1.89±0.19	-2.88±0.44	-2.69±0.20	-2.79±0.27	-2.63±0.20	-2.68±0.25
<i>m</i>	4.55±0.25	4.79±0.59	4.59±0.27	5.60±0.36	5.09±0.27	4.26±0.33
<i>s</i>	-0.34±0.15	<u>0.24±0.36</u>	<u>0.21±0.16</u>	<u>0.10±0.22</u>	<u>0.03±0.17</u>	<u>-0.09±0.20</u>
<i>b</i>	-2.04±0.18	-3.44±0.42	-3.11±0.19	-3.23±0.25	-2.80±0.19	-2.37±0.23
<i>a</i>	-0.01±0.08	0.74±0.20	0.23±0.09	<u>0.04±0.12</u>	<u>0.08±0.09</u>	0.49±0.11
Statistics						
<i>n</i>	36	36	36	36	36	36
<i>R</i>	0.97	0.89	0.97	0.97	0.98	0.92
SE	0.12	0.29	0.13	0.17	0.13	0.16
Recalculated system constants after excluding the outlier solutes						
System constants						
<i>c</i>	-2.01±0.11	-2.48±0.28	-2.76±0.18	-2.28±0.28	-2.75±0.16	-2.79±0.16
<i>m</i>	4.51±0.15	5.09±0.37	4.65±0.24	5.00±0.33	5.08±0.21	4.34±0.22
<i>s</i>	<u>-0.13±0.10</u>	<u>-0.34±0.24</u>	<u>0.27±0.15</u>	<u>-0.18±0.22</u>	<u>0.21±0.13</u>	<u>0.02±0.13</u>
<i>b</i>	-2.01±0.11	-3.65±0.25	-3.22±0.17	-2.74±0.24	-2.80±0.15	-2.71±0.16
<i>a</i>	-0.07±0.05	0.58±0.12	0.24±0.08	<u>-0.08±0.10</u>	<u>0.04±0.07</u>	0.61±0.07
Statistics						
<i>n</i>	34	32	35	34	34	32
<i>R</i>	0.99	0.97	0.98	0.97	0.99	0.98
SE	0.07	0.17	0.12	0.14	0.10	0.10

n = number of test solutes

R = correlation coefficient of linear regression

SE = standard error of the *y*-estimate

Underlined values are not statistically significant at the 95% confidence level.

$V_{\text{psp}}/V_{\text{aq}}$. Thus, the phase ratio is related to the molar volume of pseudostationary phase. The *c* values of the six pseudostationary phases suggest that the molar volumes of poly-SDUT, SDS/poly-SDUT, and SDUT/poly-SDUT are 1.4-fold, while SDUT and SDS/SDUT are 1.5-fold of that of SDS. This indicates that gemini surfactants and their binary mixtures with SDS form larger aggregates than SDS micelles. In all pseudostationary phases, the coefficient *m* is positive indicating that the MEKC retention increases with an increase in the size of solutes (Table 2). Larger *m* values indicate smaller cohesive energy of the pseudostationary phase. A positive sign of the coefficient *m* indicates that solutes prefer to transfer from more cohesive aqueous phase to less cohesive pseudostationary phase. The *m* values in Table 2 show that SDUT/poly-SDUT provides the most cohesive (more polar, *m* = 4.26) environment and the SDS/SDUT has the least cohesive (more apolar, *m* = 5.60) media.

The coefficient *b* is proportional to the difference in hydrogen bond-donating ability (HBD acidity) of the pseudostationary phase and that of the aqueous phase. The negative sign of coefficient *b* indicates that all pseudostationary phases are less acidic than the aqueous buffer phase. The pseudostationary phases with larger (or less negative) *b* values provide stronger HBD sites for solute interaction. Therefore, SDS (*b* = -2.04) has the strongest whereas SDUT (*b* = -3.44) has the weakest HBD character.

The coefficient *a* represents the difference in hydrogen bond-accepting ability (HBA basicity) of the pseudostationary phase and that of the aqueous phase. A positive *a* coefficient means that the HBA ability of the pseudostationary phase is greater than that of the aqueous phase. The HBA strength of the pseudostationary phases are as follows: SDUT (*a* = 0.74) > SDUT/poly-SDUT (*a* = 0.49) > poly-SDUT (*a* = 0.23). The coefficient *a* values of SDS,

SDS/SDUT, and SDS/poly-SDUT systems are statistically insignificant. In other words, the hydrogen bond-accepting strength of these three pseudostationary phases is not much different from the hydrogen bond-accepting strength of the aqueous phase. It is interesting to note that all the pseudostationary phases with sulfate head groups (SDS, SDS/SDUT, and SDS/poly-SDUT) have statistically insignificant α coefficients, whereas the pseudostationary phases with carboxylate head groups (*i.e.*, SDUT, poly-SDUT, and SDUT/poly-SDUT) have statistically significant coefficient α values. Thus, pseudostationary phases with a carboxylate head group display better hydrogen bond-accepting characteristics than the pseudostationary phases with sulfate head groups, which is in a good agreement with previous findings [8].

The difference in polarizability of the pseudostationary phase and the aqueous phase is represented by the coefficient s . As shown in Table 2, only SDS provides a statistically significant s value ($s = -0.34$). The negative sign indicates that the solutes experience a less dipolar/polarizable microenvironment in SDS micelles than in aqueous phase.

Expressions for $\log k'$ were developed for each pseudostationary phase by substituting the coefficient values listed in Table 2 into Eq. (1). Shown below in Eq. (3) is the $\log k'$ expression for the SDS system. Other expressions for the remaining surfactant systems are obtained in a similar way.

$$\log k' = -1.89(\pm 0.19) + 4.55(\pm 0.25)V_1 - 0.34(\pm 0.15)\pi^* - 2.04(\pm 0.18)\beta \quad (3)$$

It should be noted that the descriptor α is excluded from Eq. (3) due to its insignificant coefficient. The calculated (or predicted) $\log k'$ values of 36 test solutes were computed using these expressions or were obtained directly from the SAS software for each pseudostationary phase. Next, the experimental and calculated $\log k'$ values of the 36 solutes were compared. Experimental $\log k'$ versus calculated $\log k'$ of 36 solutes in each pseudostationary phase resulted in regression fits with correlation coefficient (R) ranging from 0.889 (SDUT, Fig. 1B) to 0.975 (SDS/poly-SDUT, Fig. 1E). However, when the calculated $\log k'$ values of each subset solutes (*i.e.*, NHB, HBA, and HBD) are graphically compared with their experimental $\log k'$ values, NHB solutes provided R values ranging from 0.985 (SDS/SDUT, Fig. 1, inset D1) to 0.995 (SDS/poly-SDUT, Fig. 1, inset E1) for all pseudostationary phases (except for SDUT) as compared to HBA and HBD solutes.

Relatively poor correlations between the experimental $\log k'$ and calculated $\log k'$ values (especially for the SDUT system) are caused primarily by a few outlying solutes. The outliers for each pseudostationary phase were de-

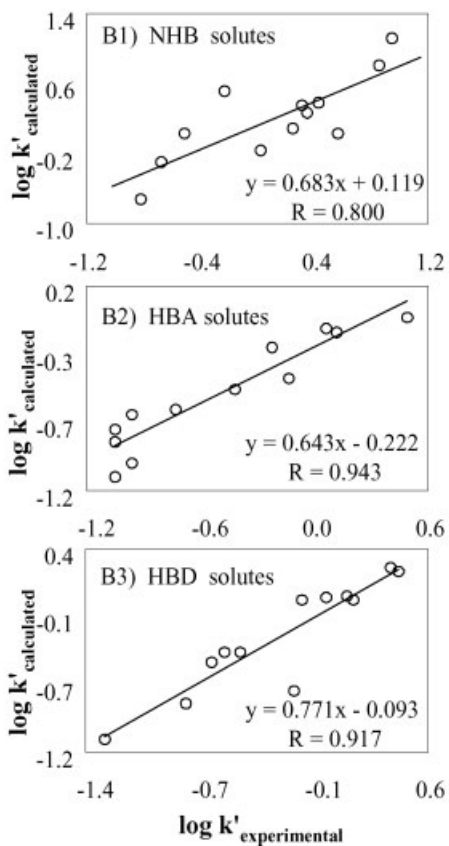
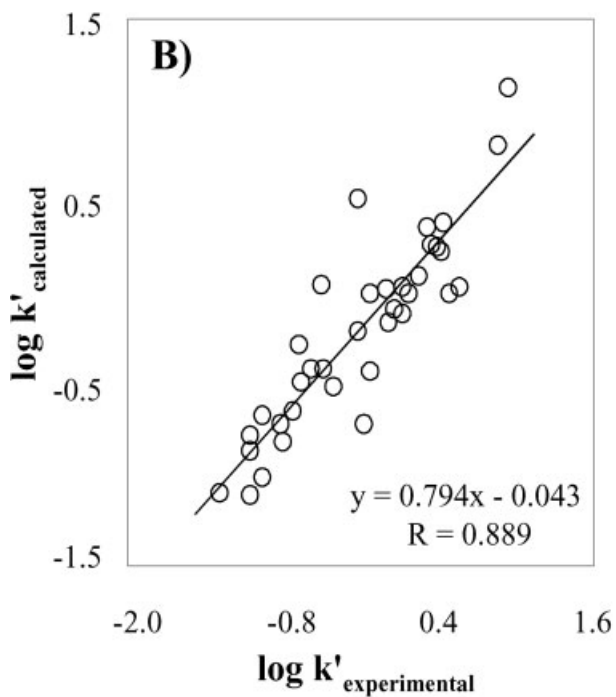
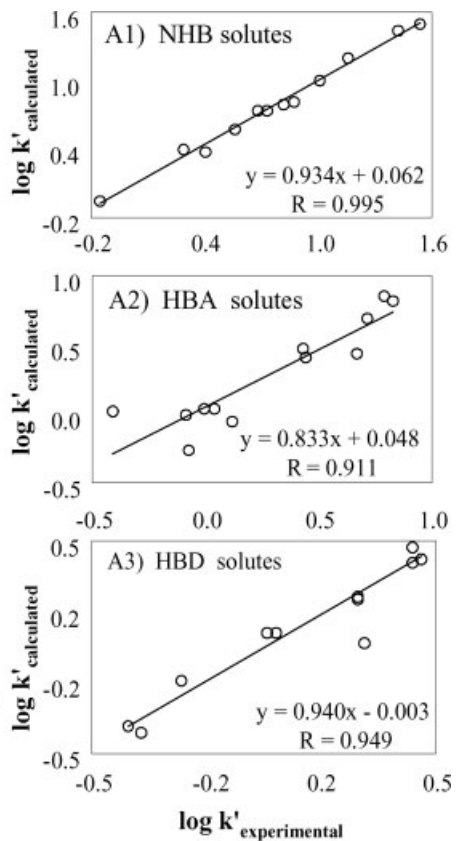
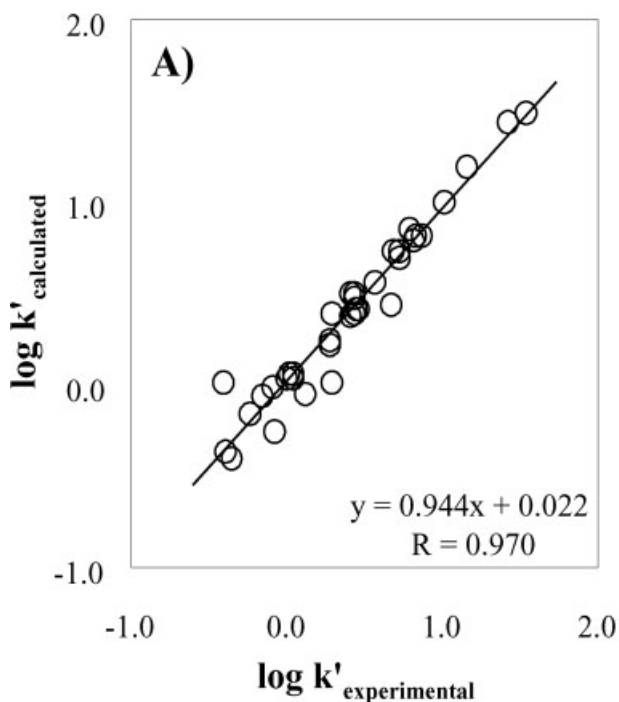
termined by: (i) calculating the residual values (experimental $\log k'$ minus calculated $\log k'$) for each solute, (ii) normalizing residual values (dividing residual value by the standard deviation of the residual) for each pseudostationary system, and (iii) plotting the normalized residual values against solute number (Fig. 2). As can be seen in Fig. 2, solutes 22 (phenyl acetate, HBA) and 32 (4-chloroaniline, HBD) are the major outliers for most of the pseudostationary phases. The best correlation between experimental $\log k'$ and calculated $\log k'$ values can be obtained when the normalized residuals are zero or close to zero but the normalized residual range of +2 to -2 is reasonable for statistically sound correlations.

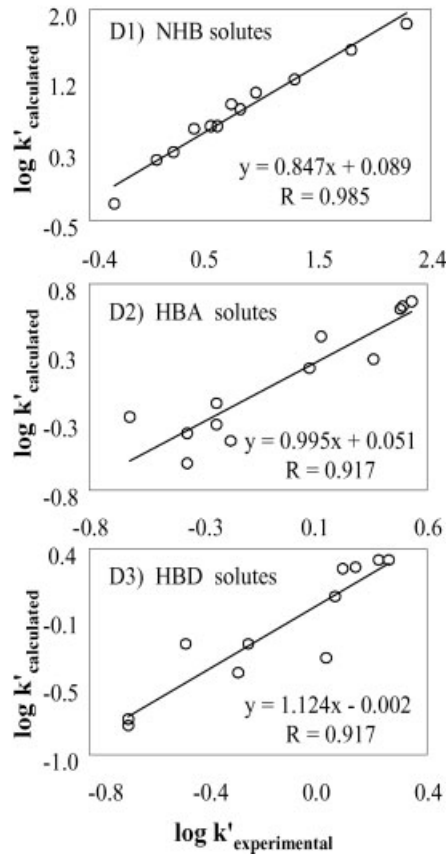
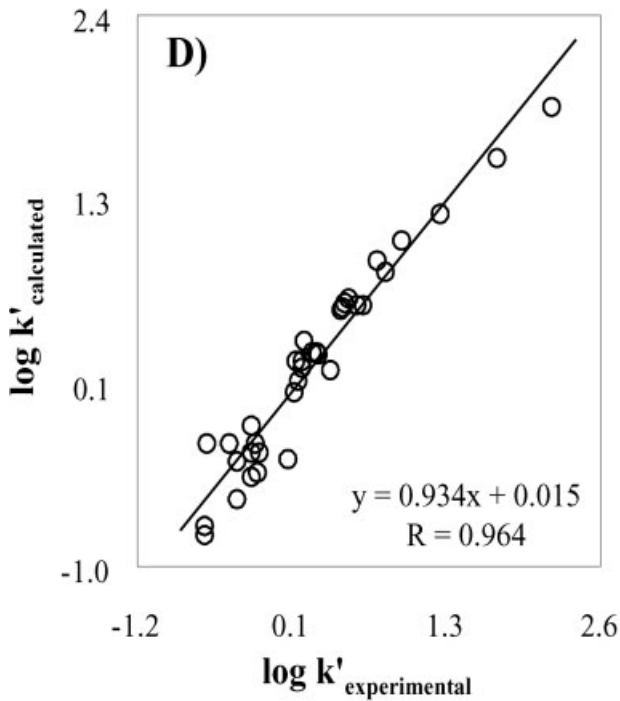
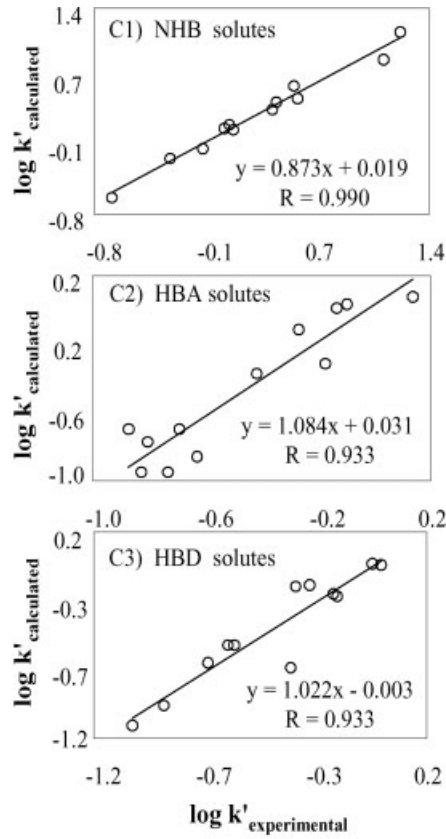
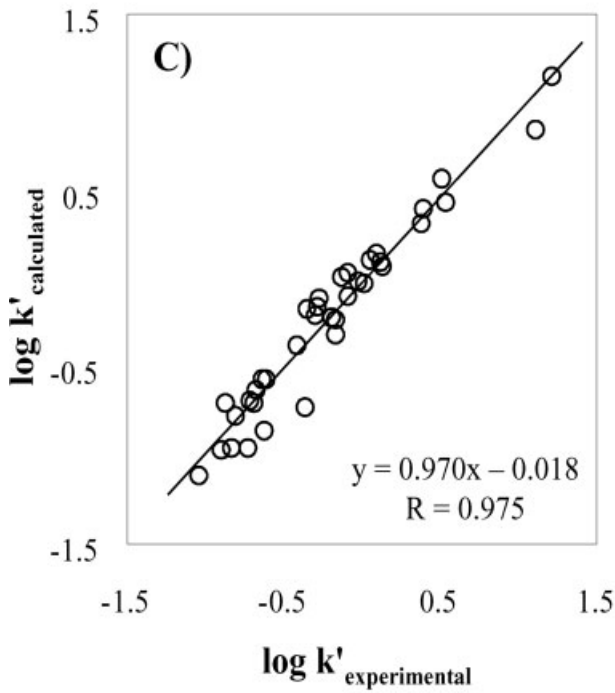
The LSER coefficients for all pseudostationary phases were recalculated using the solvatochromic model (Eq. 1) after excluding the outliers. The new coefficients are listed in Table 2 (bottom portion). Using the new coefficients, new fits were obtained for each pseudostationary phase (data not shown). Removing the outliers improved the correlations significantly resulting in relatively small standard deviations in the system constants and in the y estimate, and provided higher R values. For example, excluding four outliers (solutes 2, 3, 4, and 32) from the SDUT system improved R from 0.89 to 0.97 (Table 2). Notice also that the magnitudes of the new system coefficients are generally slightly different than that of the original coefficients (*i.e.*, those obtained with 36 solutes). In addition, coefficient s in the SDS system became statistically insignificant upon eliminating two outliers.

The $\log k'$ values were recalculated using new system constants, and new calculated $\log k'$ values were then plotted against experimental $\log k'$ values. The R , slope, and the intercept values of the new correlation lines for all pseudostationary phases are listed in Table 3. Comparing the R , slope, and intercept values listed in Table 3 with those in Fig. 1 clearly shows that eliminating a few outliers improved the correlation significantly. For instance, eliminating phenyl acetate and 4-chloroaniline from the SDS system improved the R from 0.970 to 0.989. Similar improvements in R values are observed in all pseudostationary phases.

3.2 Solvation parameter model

The solvation parameter model, Eq. (2), is similar to the solvatochromic model, Eq. (1), but contains a new term, which accounts for the solutes excess molar refraction (R_2). The LSER constants and the statistics for all pseudostationary phases using the solvation parameter model are listed in Table 4. Based on the coefficient m values (Table 4), the pseudostationary phases can be ordered as: SDS/SDUT (3.52) > SDS/poly-SDUT (3.19) > SDUT (3.03)





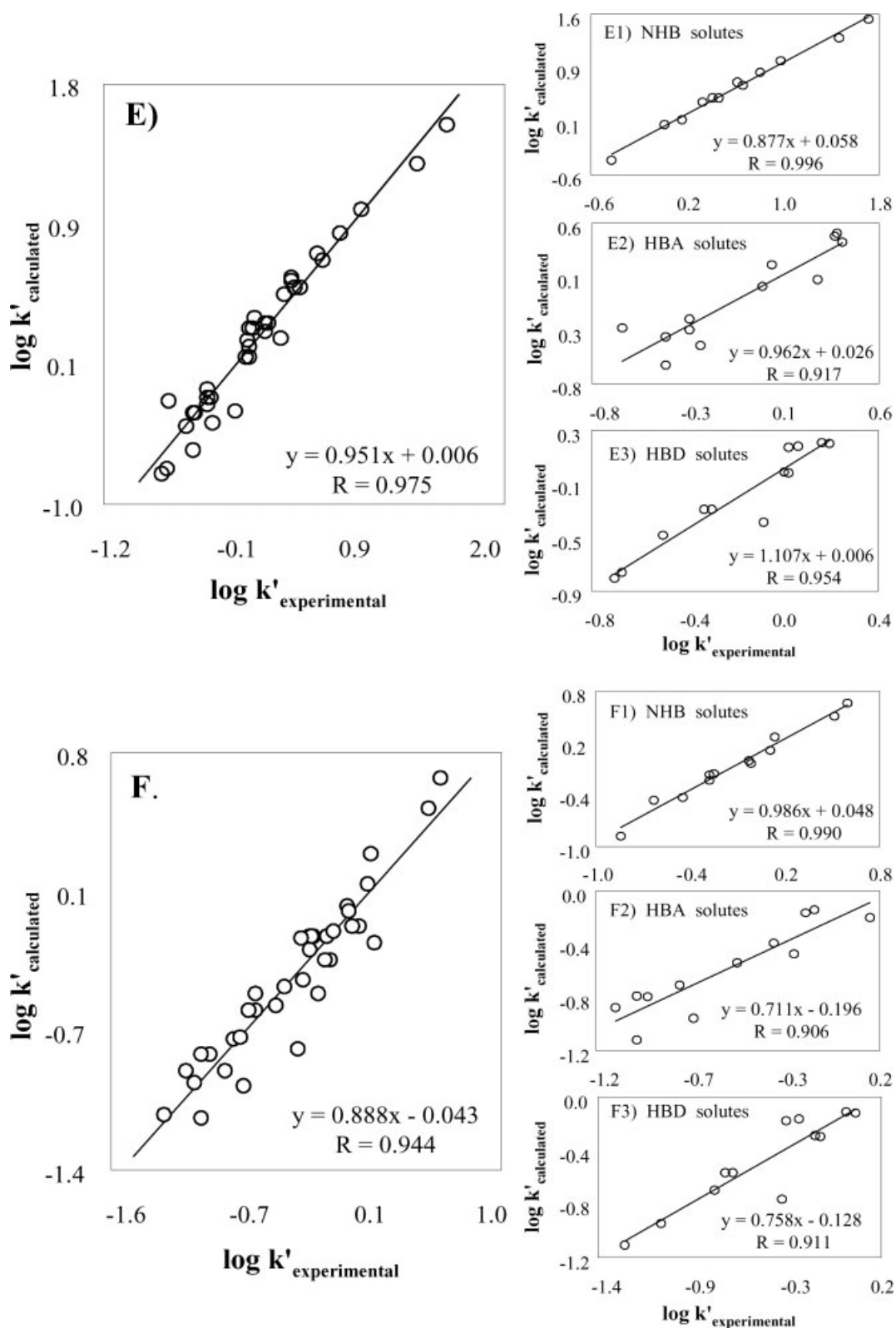


Figure 1. Predicted *versus* experimental $\log k'$ values in (A) SDS, (B) SDUT, (C) poly-SDUT, (D) SDS/SDUT, (E) SDS/poly-SDUT, and (F) SDUT/poly-SDUT using the solvatochromic model and parameters. Plots (insets) on the right of each figure represent calculated *versus* experimental $\log k'$ values of NHB, HBA, and HBD solutes.

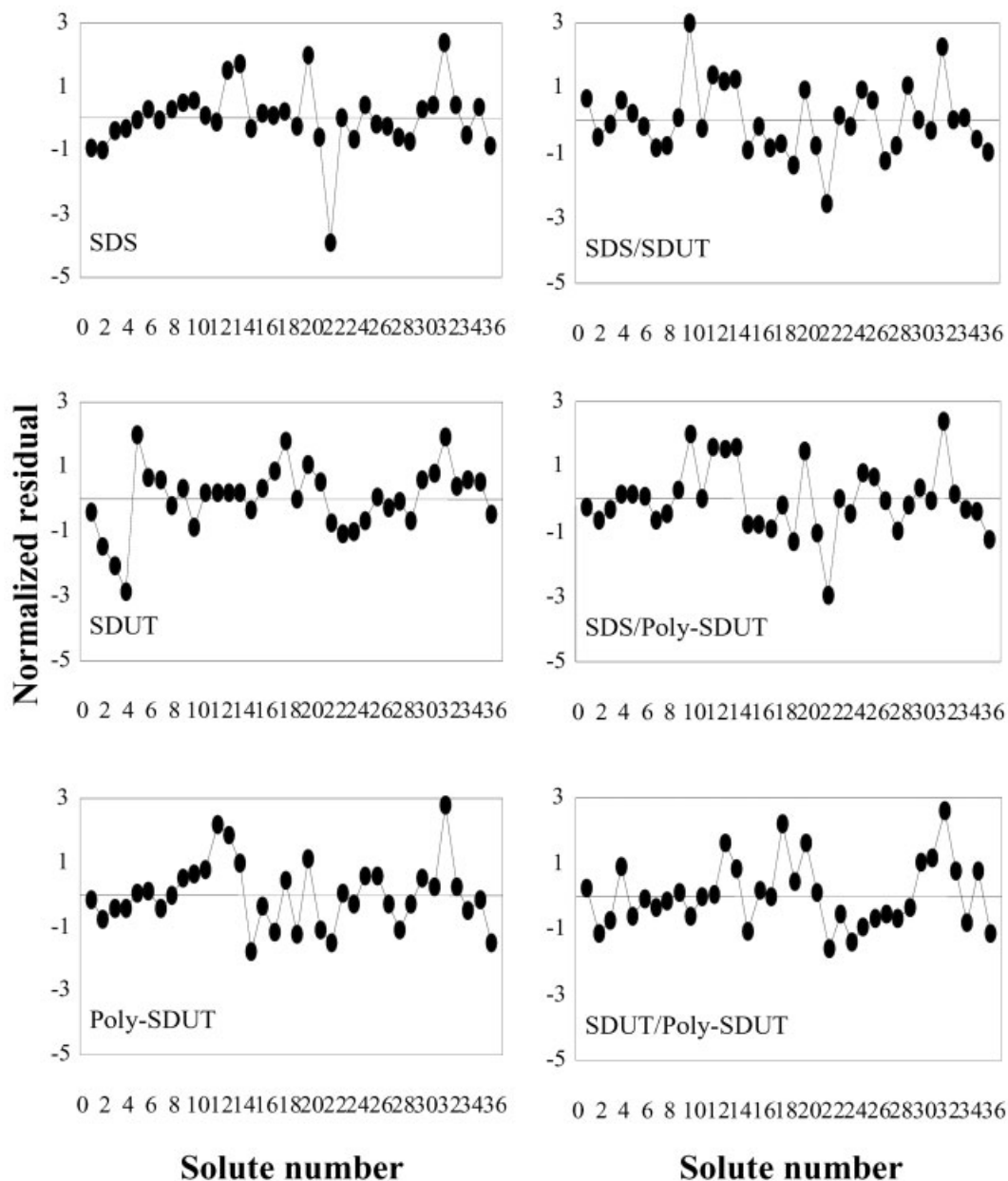


Figure 2. Normalized residuals versus solute number in six pseudostationary phases using the solvatochromic model. Solute numbers are same as listed in Table 1.

\approx SDS (2.99) > SDUT/poly-SDUT (2.84) > poly-SDUT (2.75). The order of the first three pseudostationary phases is the same in both LSER models. However, in the solvatochromic model (Table 2), poly-SDUT has a larger m value than SDS and SDUT/poly-SDUT.

The acidity (coefficient b) of the pseudostationary phases can be ranked from the most acidic to the least acidic as follows: SDS (−1.85) > SDS/poly-SDUT (−2.16) \approx SDUT/

poly-SDUT (−2.24) > poly-SDUT (−2.30) > SDS/SDUT (−2.43) > SDUT (−2.99). Although the absolute values for the coefficient b are different in both LSER models, the order of pseudostationary phases (based on the constant b values) are almost the same except that in the solvatochromic model the order of SDUT/poly-SDUT and poly-SDUT is reversed. Comparing the values of coefficient a provides the following order of basicity of the pseudostationary phases: SDUT > SDUT/poly-SDUT. Coefficient a

Table 3. Correlation coefficient (*R*), slope, and intercept values of the calculated log *k'* versus experimental log *k'* plots for each surfactant system using recalculated system constants listed in Table 2

Pseudostationary phase	Solutes	<i>R</i>	Slope	Intercept	<i>n</i>	Excluded solutes
SDS	All	0.989	0.979	0.009	34	22, 32
	NHB	0.996	0.963	0.035	12	–
	HBA	0.959	0.965	0.008	11	22
	HBD	0.990	0.947	0.003	11	32
SDUT	All	0.966	0.934	–0.011	32	2, 3, 4, 32
	NHB	0.951	0.920	0.096	9	2, 3, 4
	HBA	0.968	0.811	–0.14	12	–
	HBD	0.962	0.834	–0.046	11	32
Poly-SDUT	All	0.980	0.960	–0.008	35	32
	NHB	0.989	0.893	0.015	12	–
	HBA	0.920	1.000	0.013	12	–
	HBD	0.979	1.067	0.034	11	32
SDS/SDUT	All	0.971	0.943	0.011	34	10, 22
	NHB	0.987	0.874	0.102	11	10
	HBA	0.965	1.105	0.030	11	22
	HBD	0.917	0.989	–0.013	12	–
SDS/poly-SDUT	All	0.985	0.971	0.004	34	22, 32
	NHB	0.995	0.904	0.038	12	–
	HBA	0.948	1.074	0.026	11	22
	HBD	0.989	1.113	0.017	11	32
SDUT/Poly-SDUT	All	0.978	0.957	–0.017	32	13,18,20,32
	NHB	0.990	1.011	0.030	12	–
	HBA	0.950	0.810	–0.168	9	13, 18, 20
	HBD	0.981	0.850	–0.069	11	32

for the remaining pseudostationary phases is not statistically significant. The order of the first two pseudostationary phases is the same in both LSER models. It should be mentioned that coefficient *a* for poly-SDUT is statistically significant using the solvatochromic model whereas it is insignificant using the solvation parameter model. All pseudostationary phases except SDUT and SDS/poly-SDUT have statistically significant negative coefficient *s* values (Table 4). Thus, except these two surfactant systems, all pseudostationary phases are less dipolar than the aqueous mobile phase. The dipolarity of SDUT and SDS/poly-SDUT is, however, similar to that of the aqueous phase. Four out of six surfactant systems provided statistically significant coefficient *s* values using the solvation parameter model, whereas the coefficient *s* value of only one surfactant system (*i.e.*, SDS) was statistically significant employing the solvatochromic model.

As discussed earlier, *r* represents the ability of the pseudostationary phase to interact with *n*- and π -electron pairs of solute and hence become polarized. According to the coefficient *r* values in Table 4, the polarizability of surfactant systems upon interacting with solute *n*- and/or

π -electrons is ordered as: poly-SDUT (0.80) \approx SDS/SDUT (0.79) > SDS/poly-SDUT (0.69) > SDS (0.40). The coefficient *r* is statistically insignificant for SDUT and SDUT/poly-SDUT systems.

Upon substituting the coefficient values listed in Table 4 (upper portion) into Eq. (2), expressions for log *k'* were developed for each pseudostationary phase. For example, below is the log *k'* expression for SDS using the solvation parameter model:

$$\log k' = -2.01(\pm 0.16) + 2.99(\pm 0.18)V_2 + 0.40(\pm 0.13)R_2 - 0.40(\pm 0.13)\pi_2^H - 1.85(\pm 0.15)\Sigma\beta_2^0 \quad (4)$$

Due to its insignificant coefficient, descriptor $\Sigma\alpha_2^H$ is omitted from Eq. (4). By solving the expressions for each pseudostationary phase, the calculated log *k'* values of 36 test solutes were computed. Then, the experimental log *k'* versus the calculated log *k'* values were compared, and the regression results are shown in Fig. 3. The *R* values in Fig. 3 range from 0.911 (SDUT) to 0.990 (SDS/poly-SDUT). These values are better than those obtained with the solvatochromic model (Fig. 1), as seen in the insets of Fig. 3, when the calculated log *k'* values of each solute

Table 4. System constants for the six pseudostationary phases in MEKC using the solvation parameter model

	Pseudostationary phases					
	SDS	SDUT	Poly-SDUT	SDS/SDUT	SDS/ Poly-SDUT	SDUT/ Poly-SDUT
System constants						
<i>c</i>	-2.01±0.16	-2.97±0.40	-2.52±0.13	-2.60±0.21	-2.53±0.13	-2.88±0.20
<i>m</i>	2.99±0.18	3.03±0.45	2.75±0.14	3.52±0.23	3.19±0.15	2.84±0.22
<i>r</i>	0.40±0.13	0.50±0.31	0.80±0.10	0.79±0.16	0.69±0.10	0.28±0.16
<i>s</i>	-0.40±0.13	0.13±0.32	-0.51±0.10	-0.69±0.17	-0.55±0.10	0.01±0.16
<i>a</i>	-0.06±0.08	0.41±0.19	0.02±0.06	-0.10±0.10	-0.06±0.06	0.33±0.09
<i>b</i>	-1.85±0.15	-2.99±0.38	-2.30±0.12	-2.43±0.20	-2.16±0.12	-2.24±0.19
Statistics						
<i>n</i>	36	36	36	36	36	36
<i>R</i>	0.98	0.91	0.99	0.98	0.99	0.96
SE	0.11	0.26	0.08	0.14	0.08	0.13
Recalculated system constants after excluding the outlier solutes						
System constants						
<i>c</i>	-2.100±0.09	-3.06±0.25	-2.49±0.12	-2.33±0.18	-2.58±0.11	-2.88±0.13
<i>m</i>	3.06±0.10	3.52±0.31	2.69±0.14	3.31±0.19	3.24±0.12	2.76±0.15
<i>r</i>	0.22±0.08	0.27±0.21	0.79±0.10	0.71±0.13	0.60±0.09	0.17±0.11
<i>s</i>	-0.18±0.08	-0.04±0.20	-0.45±0.10	-0.73±0.13	-0.43±0.09	0.24±0.12
<i>a</i>	-0.13±0.04	0.52±0.12	-0.02±0.06	-0.05±0.08	-0.10±0.05	0.23±0.07
<i>b</i>	-1.83±0.09	-3.24±0.25	-2.31±0.11	-2.34±0.16	-2.15±0.10	-2.20±0.13
Statistics						
<i>n</i>	35	32	35	34	35	33
<i>R</i>	0.99	0.97	0.99	0.98	0.99	0.98
SE	0.06	0.16	0.08	0.11	0.07	0.09

Explanation as in Table 2

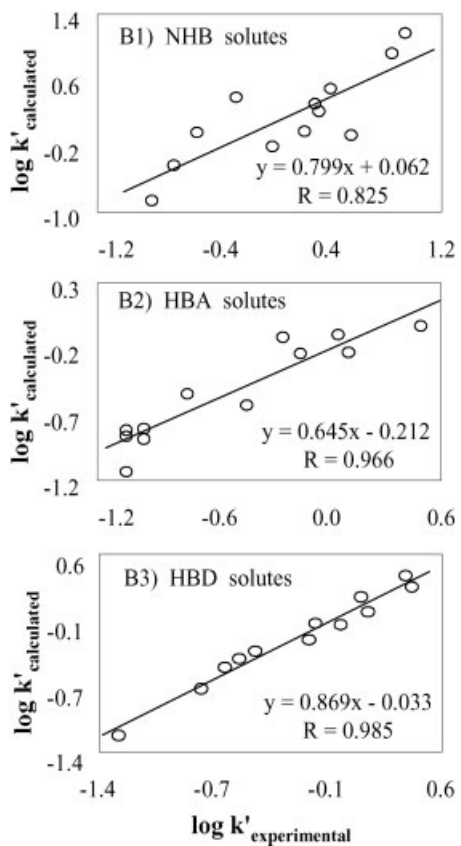
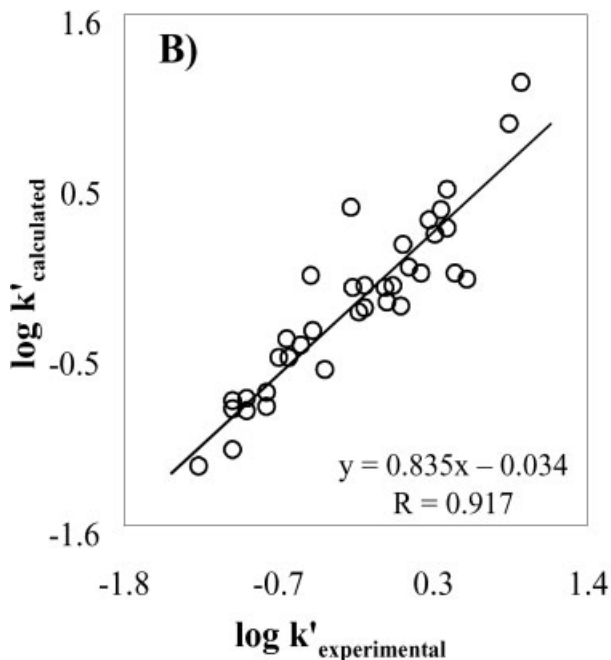
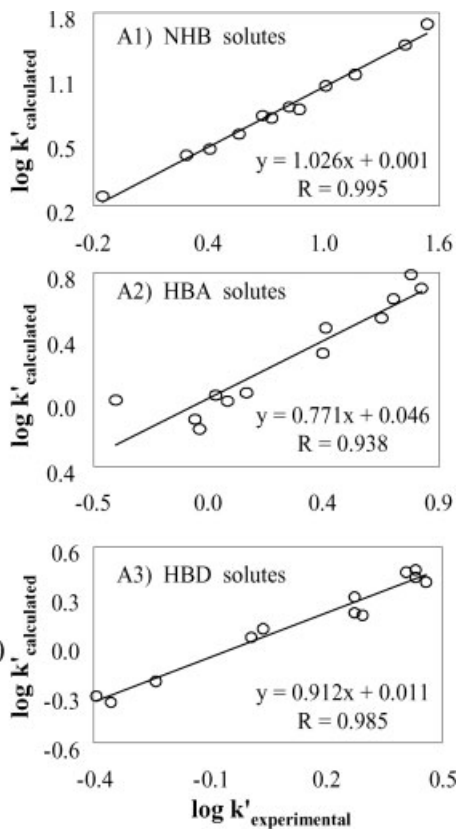
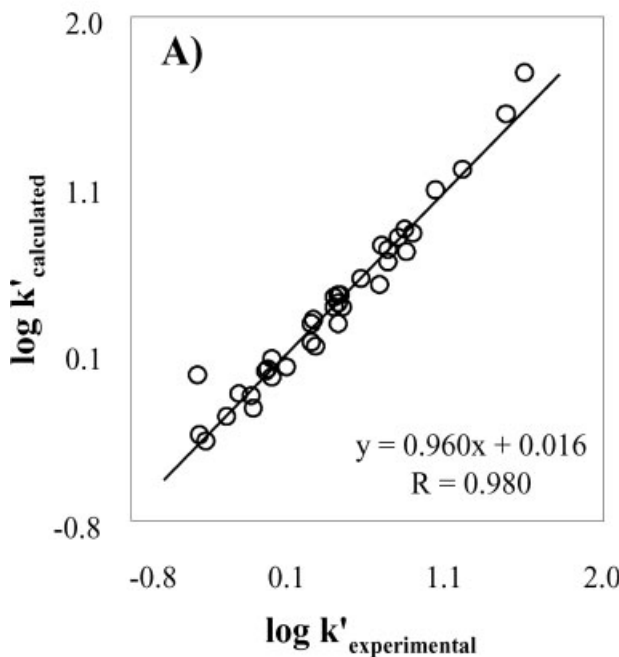
subset (*i.e.*, NHB, HBA, and HBD) were plotted against their experimental $\log k'$ values. Some solute subsets provide better correlations as compared to the whole set of 36 solutes. For example, the *R* values for the NHB solute subset (Figs. 3A1–F1) ranged from 0.825 for SDUT to 0.995 for SDS.

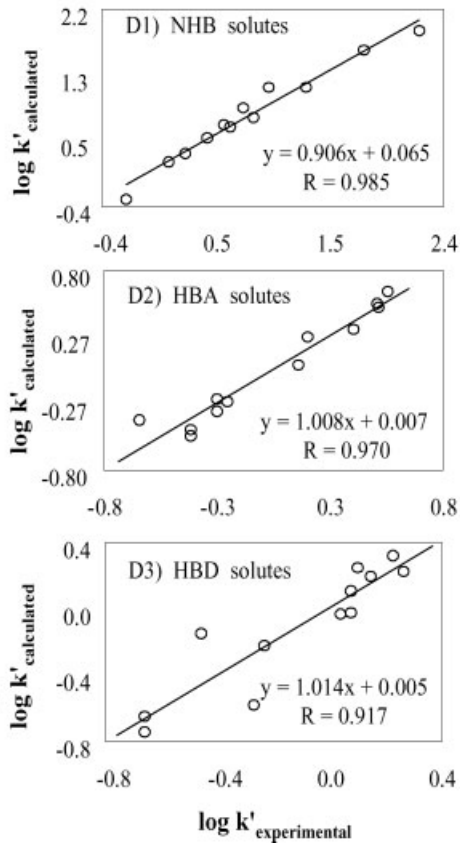
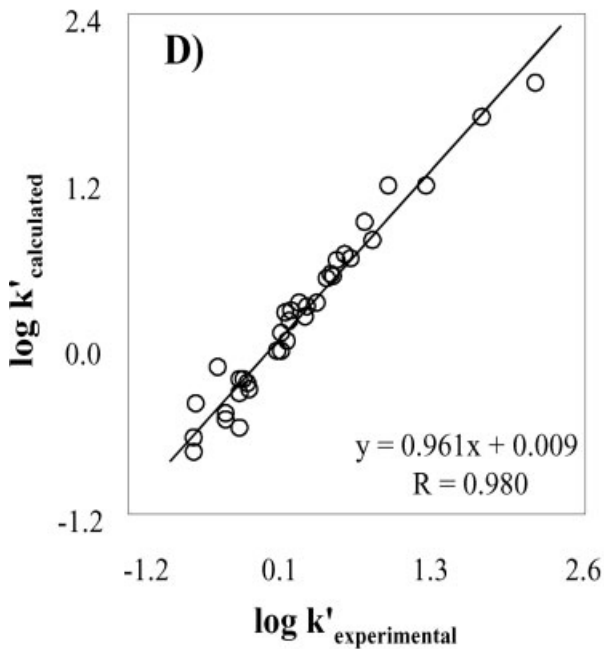
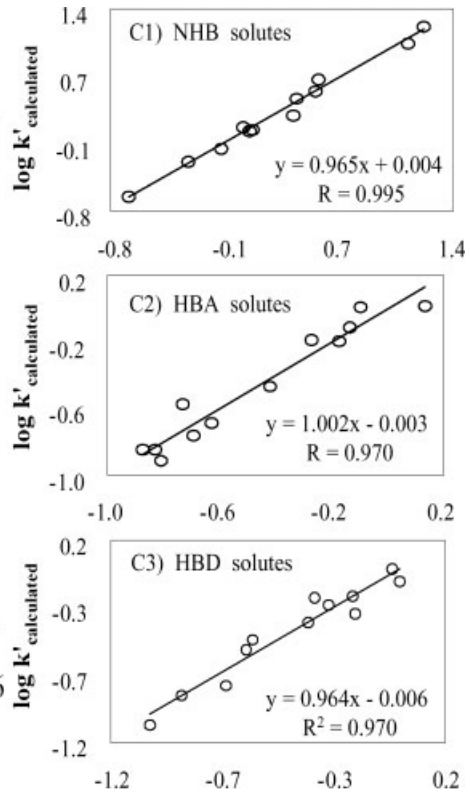
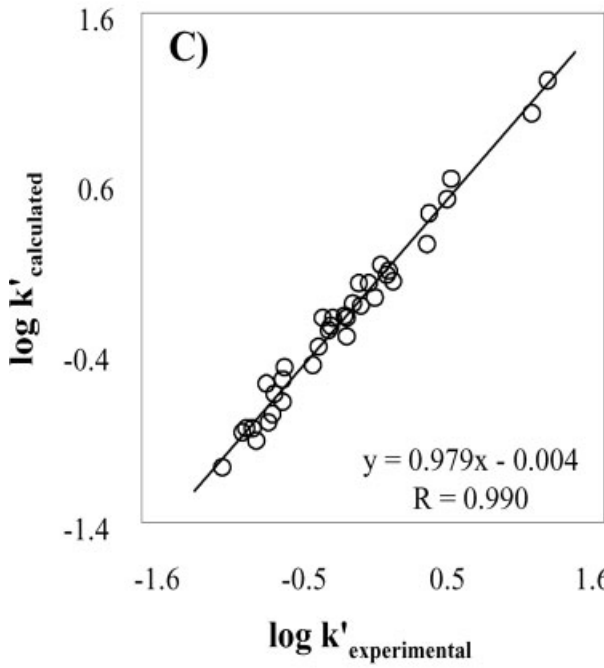
The outliers for each pseudostationary phase were determined through Fig. 4. Five out of six pseudostationary phases have at least one HBA outlier. For example, SDS (solute 22), SDUT (solute 18), poly-SDUT (solute 15), and SDS/poly-SDUT (solute 22) have one HBA outlier, while SDUT/poly-SDUT has three HBA outliers (solutes 15, 18, and 22). Only SDS/SDUT had an HBD outlier (solute 27). SDUT (solutes 3, 4, and 5) and SDS/SDUT (solute 10) had NHB solutes as outliers.

After eliminating outliers, the system coefficients were recalculated by multiple linear regression using the solvation parameter model. The new coefficients are listed in

Table 4 (lower portion). Comparing the system constant and recalculated system constant in Table 4 reveals that the standard errors in the system constants and *y* estimate and *R* values are statistically better in recalculated system constants. It is worth noting that removing phenyl acetate from the solute set increased the absolute value of coefficient *a* in SDS system and hence made it statistically significant.

Recalculated $\log k'$ values were then plotted against experimental $\log k'$ values (figure not shown). The *R*, slope, and the intercept values of the new correlation lines for all pseudostationary phases are listed in Table 5. Comparing the *R*, slope, and the intercept values listed in Table 5 with those in Fig. 3 clearly show that eliminating a few outliers improved the correlation significantly for each pseudostationary phase. For example, eliminating phenyl acetate from the SDS system improved *R* of calculated $\log k'$ versus experimental $\log k'$ plot for 35 solutes from 0.980 (Fig. 3A) to 0.993 (Table 5).





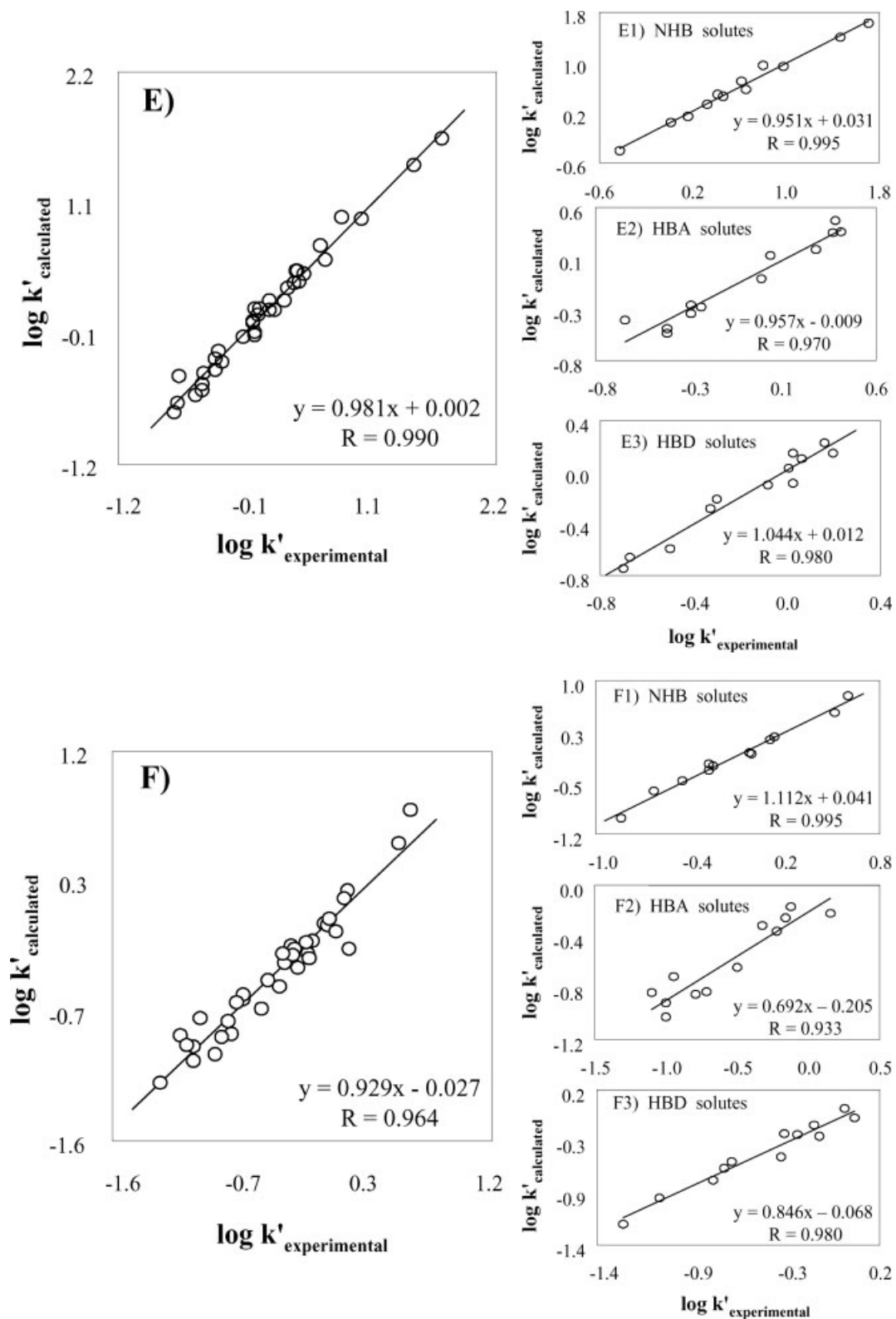


Figure 3. Predicted *versus* experimental $\log k'$ values in (A) SDS, (B) SDUT, (C) poly-SDUT, (D) SDS/SDUT, (E) SDS/poly-SDUT, and (F) SDUT/poly-SDUT using the solvation parameter model and parameters. Plots (insets) on the right of each figure represent calculated *versus* experimental $\log k'$ values of NHB, HBA, and HBD solutes.

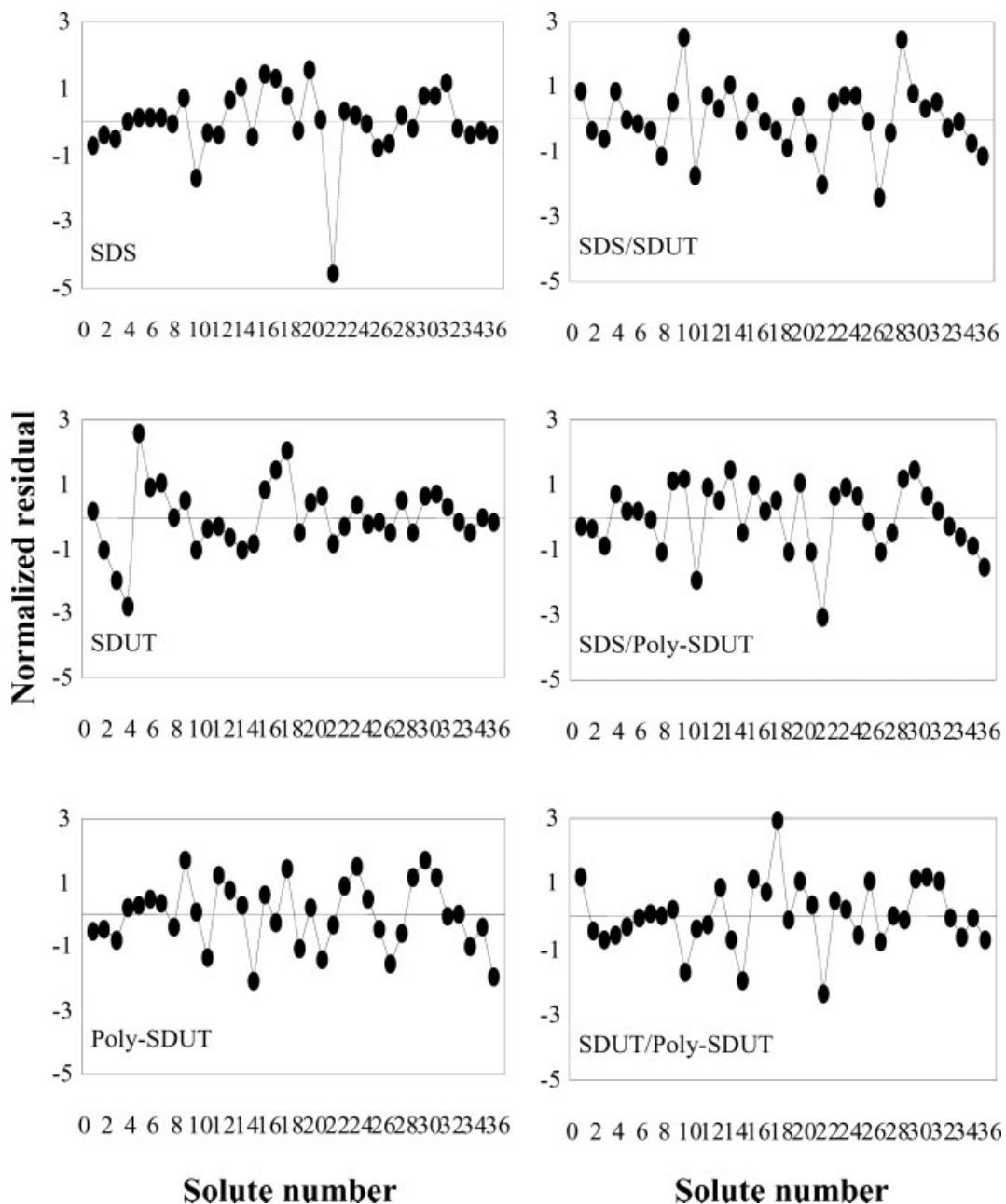


Figure 4. Normalized residuals versus solute number for the six pseudostationary phases using the solvation parameter model. Solute numbers are the same as listed in Table 1.

3.3 Determination of system coefficients using NHB, HBA, and HBD subset solutes

It is intended here to show that the number and the type of the test solutes have a significant effect on the magnitude of the system coefficients. The system coefficients obtained from NHB, HBA, and HBD solute subsets are listed in Tables 6–8, respectively. Each table contains system coefficients obtained by both the sol-

vatochromic model and the solvation parameter model. The phase ratio (coefficient c) obtained from the NHB solutes is similar to that obtained from the complete solute set (36 solutes) (Tables 2 and 4) and more negative than the c coefficient obtained from HBA (Table 7) and HBD (Table 8) solutes. This indicates that the distribution of solutes of each subset between pseudostationary phase and the mobile phase (*i.e.*, buffer solution) is not identical.

Table 5. The correlation coefficient (R), slope, and intercept values of the calculated $\log k'$ versus experimental $\log k'$ plots for each surfactant system using recalculated system constants listed in Table 4

Pseudostationary phase	Solutes	R	Slope	Intercept	n	Excluded solutes
SDS	All	0.993	0.986	0.006	35	22
	NHB	0.995	1.024	-0.017	12	-
	HBA	0.984	0.938	0.022	11	22
	HBD	0.989	0.911	0.010	12	-
SDUT	All	0.971	0.942	-0.014	32	2, 3, 4, 18
	NHB	0.956	1.005	0.016	9	2, 3, 4
	HBA	0.964	0.800	-0.127	11	18
	HBD	0.973	0.893	-0.030	12	-
Poly-SDUT	All	0.991	0.982	-0.004	35	15
	NHB	0.994	0.957	0.008	12	-
	HBA	0.979	1.032	0.007	11	15
	HBD	0.971	0.966	-0.004	12	-
SDS/SDUT	All	0.983	0.967	0.006	34	10, 27
	NHB	0.985	0.900	0.069	11	10
	HBA	0.973	0.957	-0.001	12	-
	HBD	0.954	1.048	0.005	11	27
SDS/Poly-SDUT	All	0.993	0.986	0.002	35	22
	NHB	0.995	0.950	0.021	12	-
	HBA	0.985	1.062	0.007	11	22
	HBD	0.981	1.044	0.012	12	-
SDUT/Poly-SDUT	All	0.983	0.966	-0.011	32	15, 18, 22
	NHB	0.993	1.089	0.013	12	-
	HBA	0.967	0.902	-0.062	9	15, 18, 22
	HBD	0.986	0.839	-0.069	12	-

The m constant obtained from NHB subset solutes is larger than those obtained from the complete solute subset, HBA solutes, and HBD solutes. It is obvious from Tables 6–8 that the order of the pseudostationary phases for each coefficient is not exactly the same for any solute set. This indicates that the number and type of the solutes have a significant influence on the magnitude of the system constants. Comparing the m values for the NHB subset reveals that SDS/SDUT ($m = 5.61$) provides a somewhat less cohesive microenvironment for NHB solutes. Coefficient m values obtained from HBA solutes are smaller than those obtained from NHB, HBD, and the main set. Thus, HBA solutes interact with the relatively polar regions of the pseudostationary phases. Coefficient m values of HBD acids are larger than those obtained from HBA bases but smaller than those obtained from NHB or the complete solute set. This indicates that the HBD acids are located in a slightly more nonpolar environment in the pseudostationary phases than HBA bases; however, NHB solutes experience a relatively more nonpolar environment in the pseudostationary phases than HBD solutes.

The b coefficients obtained with HBA solutes are less negative as compared to those obtained with NHB solutes, HBD solutes, and the main set solutes using the solvatochromic model. Thus, the interaction between solutes and the pseudostationary phases increase with an increase in HBA strength of the solutes as evidenced by the negative b coefficients. In general, HBD solutes provide less negative b values. It should be mentioned that the coefficient b trend in the solvation parameter model and solvatochromic model is not identical. However, both models provide comparable s coefficients obtained from NHB, HBA, and HBD solute subsets. Having positive coefficient s values, the HBD solutes experience a more dipolar/polarizable environment in pseudostationary phases than in the aqueous buffer solution (Table 8).

Coefficient a is zero for all surfactant systems using NHB solutes (Table 6) due to zero α and $\Sigma\alpha_2^H$ and values (Table 1) whereas it is not statistically significant using HBA solutes (Table 7). The solvation parameter model provides only one positive coefficient a value that is statistically signifi-

Table 6. Comparison of system coefficients obtained from the two LSER models using NHB solutes

	SDS	SDUT	Poly-SDUT	SDS/SDUT	SDS/ Poly-SDUT	SDUT/ Poly-SDUT
Solvatochromic model						
System constants						
<i>c</i>	-2.13±0.07	-2.83±0.76	-3.02±0.17	-3.14±0.19	-2.99±0.11	-2.74±0.14
<i>m</i>	4.93±0.16	4.26±1.66	5.13±0.36	5.61±0.41	5.47±0.24	4.18±0.30
<i>s</i>	-0.23±0.07	0.76±0.74	0.17±0.16	0.25±0.18	0.08±0.11	0.05±0.13
<i>a</i> ^{a)}	–	–	–	–	–	–
<i>b</i>	-2.97±0.39	-4.51±4.05	-3.12±0.89	-0.79±1.01	-2.13±0.59	-2.59±0.74
Statistics						
<i>n</i>	12	12	12	12	12	12
<i>R</i>	1.00	0.82	0.99	0.99	1.00	0.99
SE	0.04	0.39	0.09	0.10	0.06	0.07
Solvation parameter model						
System constants						
<i>c</i>	-1.85±0.11	-2.85±0.99	-2.72±0.15	-3.40±0.30	-2.94±0.16	-2.46±0.15
<i>m</i>	3.14±0.11	1.93±1.03	3.03±0.16	3.77±0.32	3.51±0.17	2.49±0.16
<i>r</i>	0.73±0.23	-0.78±2.15	0.57±0.33	-0.72±0.66	0.06±0.34	0.59±0.33
<i>s</i>	-1.00±0.39	3.02±3.66	-0.14±0.56	1.64±1.12	0.40±0.59	-0.43±0.56
<i>a</i> ^{a)}	–	–	–	–	–	–
<i>b</i>	-3.30±0.46	-2.45±4.31	-3.17±0.66	-0.40±1.32	-2.10±0.69	-2.72±0.66
Statistics						
<i>n</i>	12	12	12	12	12	12
<i>R</i>	1.00	0.87	1.00	0.99	1.00	1.00
SE	0.04	0.36	0.06	0.11	0.06	0.06

Explanation as in Table 2

a) Coefficient *a* could not be determined, because α and $\Sigma\alpha_2^H$ values for this set of solutes are 0 (Table 1)

cant with poly-SDUT system using HBD solutes (Table 8). The solvatochromic model, however, provides statistically significant negative coefficient *a* values for all pseudostationary phases (Table 8).

Predicted $\log k'$ values of 36 solutes were determined by substituting the system constants given in Tables 6–8 into Eqs. (1) and (2). The predicted $\log k'$ values obtained from the solvatochromic model and the solvation parameter model were plotted against the experimental $\log k'$ values (plots not shown). As expected, higher correlation values were obtained, for example, for NHB solutes, when the system constants listed in Table 6 are used. However, the same system constants generated poor correlations for HBA and HBD solutes. This is not surprising, since NHB solutes do not represent all the solutes (*i.e.*, HBA and HBD). These results show that system constants obtained from NHB solutes cannot provide accurate predicted $\log k'$ values for HBA and HBD solutes. It is interesting to note that using only 12 NHB or HBA solutes, it was possible to predict retention factors of all 36 solutes

with an *R* of 0.980 (slope = 1.088, *y*-intercept = -0.030) or 0.975 (slope = 0.969, *y*-intercept = -0.001), respectively, using solvation parameter model with poly-SDUT. In general, the solvation parameter model provided better correlations between predicted and experimental retention factors as compared to the solvatochromic model.

4 Concluding remarks

Anionic pseudostationary phases with carboxylate (SDUT and poly-SDUT) and sulfate (SDS) head groups as well as binary mixed pseudostationary phases (SDS/SDUT, SDS/poly-SDUT, and SDUT/poly-SDUT) were applied as pseudostationary phases in MEKC. Two LSER models, *i.e.*, solvatochromic and solvation parameter models were successfully applied to investigate the effect of the type and composition of pseudostationary phases on the retention mechanism and selectivity in MEKC. These two LSER models are helpful tools to understand the fundamental nature of the solute-surfactant interactions and to characterize the pseudostationary phases. The results

Table 7. Comparison of system coefficients obtained from two LSER models using HBA solutes

	SDS	SDUT	Poly-SDUT	SDS/SDUT	SDS/ Poly-SDUT	SDUT/ Poly-SDUT
Solvatochromic model						
System constants						
<i>c</i>	-0.08 ± 0.83	-2.08 ± 0.76	-1.30 ± 0.70	-0.67 ± 0.74	-0.71 ± 0.72	-1.38 ± 0.92
<i>m</i>	3.13 ± 0.86	5.18 ± 0.79	3.11 ± 0.73	3.44 ± 0.77	3.22 ± 0.75	3.61 ± 0.96
<i>s</i>	-1.36 ± 0.49	-0.60 ± 0.50	-0.61 ± 0.41	-1.14 ± 0.43	-1.02 ± 0.42	-0.90 ± 0.55
<i>a</i>	0.10 ± 0.45	0.20 ± 0.41	0.18 ± 0.38	0.10 ± 0.40	0.11 ± 0.39	0.27 ± 0.50
<i>b</i>	-1.72 ± 0.72	-4.05 ± 0.67	-2.19 ± 0.61	-2.01 ± 0.64	-1.97 ± 0.63	-2.50 ± 0.81
Statistics						
<i>n</i>	12	12	12	12	12	12
<i>R</i>	0.95	0.98	0.95	0.96	0.96	0.94
SE	0.16	0.15	0.13	0.14	0.14	0.18
Solvation parameter model						
System constants						
<i>c</i>	-1.36 ± 0.89	-2.21 ± 0.85	-1.96 ± 0.57	-1.85 ± 0.63	-1.81 ± 0.58	-2.35 ± 0.81
<i>m</i>	2.47 ± 0.61	3.77 ± 0.58	2.33 ± 0.39	2.71 ± 0.43	2.50 ± 0.39	2.79 ± 0.55
<i>r</i>	1.57 ± 0.64	0.82 ± 0.60	1.04 ± 0.41	1.43 ± 0.45	1.39 ± 0.41	1.32 ± 0.58
<i>s</i>	-1.51 ± 0.49	-1.37 ± 0.47	-0.97 ± 0.32	-1.33 ± 0.35	-1.24 ± 0.32	-1.25 ± 0.45
<i>a</i>	-0.67 ± 0.68	0.11 ± 0.64	-0.14 ± 0.43	-0.46 ± 0.48	-0.45 ± 0.44	-0.16 ± 0.62
<i>b</i>	-1.62 ± 0.64	-3.66 ± 0.61	-1.91 ± 0.41	-1.90 ± 0.46	-1.78 ± 0.41	-2.27 ± 0.58
Statistics						
<i>n</i>	12	12	12	12	12	12
<i>R</i>	0.97	0.99	0.98	0.99	0.99	0.98
SE	0.14	0.13	0.09	0.10	0.09	0.12

Explanation as in Table 2

obtained from both LSER models provide very comparable information. For example, in both LSER models the solute size (coefficient *m*) and hydrogen bond-accepting ability (coefficient *b*) play the most important role in MEKC retention for all pseudostationary phases despite the numerical differences in the coefficient *m* values. It was found that omitting the outliers from the solute set improved the statistics (*i.e.*, *R*, and SE) of both LSER models significantly as compared to the original main set solutes. It is worth mentioning that the type of the outlier is varied based on the surfactant system type in both LSER models.

The type and the number of the solutes have a significant effect on the system coefficients and on the predicted $\log k'$ values obtained from these coefficients in both LSER models. Although both LSER models provide the same information, the solvation parameter model is found to provide much better results both statistically and chemically. This is evident when comparing the statistics (*i.e.*, *R*, and SE values) for the solvation parameter model results with those for the solvatochromic model results.

Similar superiority of the solvation parameter model is seen in the results obtained from NHB, HBA, and HBD solutes subsets. A better *R* for each pseudostationary phase is obtained with the solvation parameter model when experimental $\log k'$ values are plotted against predicted $\log k'$ values as compared to the solvatochromic model. The solute subsets (*i.e.*, NHB, HBA, and HBD) were also examined for prediction of $\log k'$ values of the subset solutes and the main set solutes. It was found that higher correlations were always observed when a given type of solute subset (*e.g.*, NHB) was used for the prediction of retention factors of the same type of solute subset (*e.g.*, NHB). Thus, in LSER methodology, it is critical to choose an appropriate solute set that represents a wide range of solutes for better results.

The determined system coefficients show that the pseudostationary phases with large absolute values for the coefficients *a* and *b* (*e.g.*, SDUT) would be able to separate mixtures of solutes with dissimilar hydrogen-bond acidity. Among all pseudostationary phases, SDS/SDUT (Table 4) would be a comparatively better system of

Table 8. Comparison of system coefficients obtained from two LSER models using HBD solutes

	SDS	SDUT	Poly-SDUT	SDS/SDUT	SDS/ Poly-SDUT	SDUT/ Poly-SDUT
Solvatochromic model						
System constants						
<i>c</i>	-0.65±0.23	0.01±0.67	-0.58±0.27	-0.38±0.61	-0.82±0.24	-0.28±0.25
<i>m</i>	4.43±0.18	5.00±0.53	3.61±0.22	3.99±0.48	4.07±0.19	4.25±0.20
<i>s</i>	0.09±0.12	0.63±0.33	0.62±0.14	0.38±0.30	0.30±0.12	0.47±0.13
<i>a</i>	-1.55±0.18	-2.42±0.51	-1.70±0.21	-1.82±0.46	-1.46±0.18	-2.13±0.19
<i>b</i>	-3.84±0.24	-7.94±0.70	-5.20±0.29	-4.79±0.64	-4.23±0.25	-6.35±0.26
Statistics						
<i>n</i>	12	12	12	12	12	12
<i>R</i>	1.00	0.99	1.00	0.98	1.00	1.00
SE	0.03	0.10	0.04	0.09	0.04	0.04
Solvation parameter model						
System constants						
<i>c</i>	-2.58±0.33	-4.51±0.81	-3.72±0.35	-3.66±0.77	-3.21±0.36	-3.92±0.50
<i>m</i>	3.25±0.16	3.52±0.40	2.50±0.17	3.26±0.38	2.93±0.18	3.21±0.25
<i>r</i>	0.13±0.20	0.37±0.49	0.08±0.21	-0.94±0.47	0.07±0.22	-0.15±0.30
<i>s</i>	0.26±0.25	1.05±0.62	1.03±0.27	1.79±0.60	0.63±0.28	1.14±0.38
<i>a</i>	-0.26±0.18	0.65±0.44	0.43±0.19	-0.02±0.42	0.14±0.20	0.21±0.27
<i>b</i>	-1.75±0.29	-2.45±0.71	-1.27±0.31	-1.31±0.67	-1.43±0.32	-2.11±0.44
Statistics						
<i>n</i>	12	12	12	12	12	12
<i>R</i>	1.00	0.99	1.00	0.98	1.00	1.00
SE	0.04	0.09	0.04	0.09	0.04	0.06

Explanation as in Table 2

choice to separate compounds by their polarity because of the relatively larger absolute coefficient *s* value. Similarly, poly-SDUT would be a convenient system to separate solutes by their polarizability (coefficient *r*).

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