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Study of chemical selectivity of molecular binary mixed micelles of sodium 10-undecenyl sulfate and sodium N-undecenyl leucinate using linear solvation energy relationships model

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ABSTRACT

Poly(sodium 10-undecenyl sulfate) (poly-SUS), poly(sodium N-undecenyl leucinate) (poly-SUL) and their five molecular binary mixed micelles with varied SUS:SUL composition were prepared and used as pseudostationary phases in micellar electrokinetic chromatography (MEKC). Linear solvation energy relationships (LSERs) model and free energy of transfer studies were used to characterize the retention behavior and the selectivity differences among the seven surfactant systems. System constant differences and regression models for varied benzene derivative compounds are used to establish the selectivity differences of the seven pseudostationary phases. The cavity formation and dispersion interaction (the *v* system constant) and the hydrogen-bonding acidity (the *b* system constant) of the surfactant systems were found to have the most significant influence on selectivity and MEKC retention. The molecular micelle with sulfate head group, poly-SUS, was found to be more hydrogen-bond acidic than the molecular micelle with leucinate head group, poly-SUL. The other system constants (*a*, *s* and *e*) have modest effect on the retention and selectivity of the benzene derivatives. The model intercept coefficients (*c* system constants), which are negative for all surfactant systems have unusually large values. The free energy changes of transfer for the functional groups studied have all negative values except phenol and benzyl alcohol. Selectivity differences between pseudostationary phases were also compared by plotting the log *k* values against each other and were found to agree well with LSER results.

1. Introduction

Since its introduction, micellar electrokinetic chromatography (MEKC), a mode of capillary electrophoresis (CE), has been extensively used for separations of both charged and neutral analytes [1]. Unlike conventional chromatographic techniques, in which a real stationary phase is utilized in separation column, analytes are separated in electrokinetic chromatography according to their relative affinity for an ionic pseudostationary phase, which is dissolved in the background electrolyte. The pseudostationary phase typically migrates in the same direction as the background electrolyte but with a slower velocity. Although sodium dodecyl sulfate (SDS) has been pseudostationary phase of choice since the development of MEKC, a significant amount of effort has been spent on development, characterization, and application of alternative pseudostationary phases [2]. Among the various alternative pseudostationary phases that have been proposed and studied, molecular micelles (or polymeric surfactants) have perhaps received the greatest amount of attention due to their advantages over the conventional surfactants [3–7].

Selection of proper pseudostationary phase for separation of chemicals with diverse physicochemical properties requires an understanding of the nature of solute–micelle interaction. Linear solvation energy relationships (LSERs) model have been introduced as a powerful tool for characterization of the retention and selectivity of pseudostationary phases in MEKC [3,4,8–11]. Initially developed by Kamlet et al. [9,10], this model provides information about the physicochemical properties of the separation systems as well as the magnitude of the different intermolecular interactions between the pseudostationary phases and the solutes. This method

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is considered to be abandoned in favor of the free energy-based solvation parameter model proposed by Abraham and co-workers [12–14]. The model set by Abraham is given in Eq. (1):

$$\log\ k = c + eE + sS + aA + bB + vV \quad (1)$$

The model is composed of product terms representing solute properties (descriptors), indicated by capital letters, and the complementary properties characteristic of the separation system (system constants), indicated by the lower case letters. Each product term defines the relative contribution of a specified interaction to the correlated property, in this case, the capacity factor ($\log k$). The contribution from n- and π-electron pair interactions is defined by eE, interactions of a dipole type by sS, hydrogen-bond interactions by aA and bB, and differences in cavity formation and dispersion interactions in the mobile and pseudostationary phases by vV. Unlike the vV term, which accounts for unfavorable processes, the remaining terms reflect favorable interactions between analyte and solvent molecules or pseudostationary phases. The solute dependent parameters (i.e., E, S, A, B, and V) are defined formally as the excess molar refraction (E), dipolarity/polarizability (S), effective hydrogen-bond acidity (A), effective hydrogen-bond basicity (B), and McGowan's characteristic volume (V). Each parameter is intentionally constructed and deliberately included in the LSER equation to account for a specific intermolecular interaction. Solute descriptors are available for about 4000 compounds with others accessible through calculation and estimation methods [14].

The system coefficients indicate the difference in solvation properties determined by the defined intermolecular interactions for the pseudostationary phase at equilibrium with the aqueous buffer. They are formally defined as the difference in contributions from electron lone pair (n- or π-electrons) interactions (e), dipole-type interactions (s), hydrogen-bond basicity (a: a basic phase will prefer to interact with an acidic solute), hydrogen-bond acidity (b: an acidic phase will tend to interact with a basic solute), and cohesion and dispersion interactions (v) for the solvated pseudostationary phase and the aqueous buffer mobile phase. The c coefficient is the model intercept, which is dominated by the phase ratio when the dependent variable is the capacity factor. The values of the system constants are obtained using multiple linear regression analysis on a number of retention factor determinations for solutes with known descriptors selected to satisfy the statistical and chemical requirements of the model [13–15].

The retention properties of single surfactant micelles can be modified by forming mixed micelles using surfactants with different solvation properties. Mixed surfactant micelles provide a mechanism for expansion of migration time window to increase the peak capacity of separation systems [16,17]. To understand the influence of surfactant composition in binary mixed micelles on electrokinetic separations, a number of reports have been published recently [18–20]. Fuguret et al. analyzed 55 single, mixed and modified surfactant systems reported in the literature from over 200 pseudostationary phases characterized by LSER [18]. Using LSER, the influence of mixed micellar systems of SDS-sodium deoxycholate (SDC) and SDS-sodium cholate (SC) on retention and selectivity in MEKC has been examined by Khaledi et al. [19].

Previously, sodium 10-undecenyl sulfate (SUS), sodium N-undecenyl leucinate (SUL) and their five different mixed micelles at varied percent mole ratios were prepared in our laboratory. These conventional mixed surfactant systems were then evaluated as novel pseudostationary phases in MEKC; LSERs and free energy of transfer studies were applied to predict the selectivity differences between them [20]. Through a comparative study, it was concluded that the cohesiveness and hydrogen bonding interactions were found to have the most significant influence on selectivity and MEKC retention. In addition, the interactive properties of the mixed micelles were found to be different from the constituent individual micelles. It is important to realize that micellization is a dynamic equilibrium and thus conventional micelles have finite lifetimes [21]. Therefore, molecular binary mixed micelles of SUS and SUL were prepared in the present study and LSER was applied for investigation of composition effect on retention and selectivity of the molecular mixed-micellar phases.

2. Materials and methods

2.1. Materials

All benzene derivatives, alkyl phenyl ketone homologues, *N*,*N*′-dicyclohexylcarbodiimide, L-leucine, chlorosulfonic acid, disodium hydrogenphosphate, sodium dihydrogenphosphate, and sodium hydroxide were obtained from Alfa Aesar (Ward Hill, MA, USA). *N*-Hydroxysuccinimide and 10-undecen-1-ol were purchased from TCI America (Wellesley Hills, MA). Undecylenic acid and deionized water were obtained from Acros Organics (Morris Plains, NJ, USA) and a water purification system from Millipore (Milford, MA, USA), respectively. All chemicals were used as received without further purification.

2.1.1. Synthesis of SUS and SUL and their polymerizations

Details of the synthesis of SUS [7] and SUL [20] are available in the literature, thus are not repeated in this report. These two surfactants were polymerized separately to form poly-SUS and poly-SUL and copolymerized at various percent mole fractions to produce five molecular binary mixed micelles possessing both leucinate and sulfate head groups (Fig. 1). Polymerization of SUS and SUL into poly-SUS and poly-SUL was achieved by preparing a 100.0 mM solution of each surfactant in triply deionized water. The molecular binary mixed surfactants were prepared in 100:0; 80:20; 60:40; 50:50; 40:60; 20:80; and 0:100 percent mole ratios of monomeric SUS:SUL surfactants in which the total concentration of both monomers was set at 100.0 mM. Prepared surfactant solutions were exposed to a ^{60}Co γ-radiation source (200 kilograys in total) for polymerization. After polymerization, the molecular micelle solutions were dialyzed against bulk deionized water for at least 24 h using regenerated cellulose membrane with 500 Da molecular weight cutoff (Spectrum Laboratories, Rancho Dominguez, CA, USA). The purified solutions were then freeze-dried to yield the final solid white products.

2.1.2. Preparation of separation buffers and solute solutions

A 1.0 M solution of each of anhydrous NaH_2PO_4 and Na_2HPO_4 was prepared by dissolving appropriate amounts of each compound in deionized water. A mixture of NaH_2PO_4 solution (42.3 mL) and Na_2HPO_4 solution (57.7 mL) provided a stock solution of 1.0 M phosphate buffer with pH of 7.0. Appropriate amount of molecular micelle was added to a given volume of buffer solution; pH value was adjusted to 7.00 using either NaOH or HCl, if necessary, and then the final volume was adjusted with deionized water to produce run buffer with 1.0% (v/w) surfactant concentration in 10 mM phosphate buffer. Each run buffer was sonicated for 2 min, filtered through a 0.45-μm syringe filter (Nalgene, Rochester, NY, USA), and then degassed for one additional min before use in MEKC experiments. All stock test solute solutions were prepared in methanol with a concentration of 20 mg/mL each and were diluted about tenfold before injection.

2.2. Capillary electrophoretic separations

2.2.1. Instrumentation

An Agilent CE system (Agilent Technologies, Palo Alto, CA, USA) equipped with a diode array detector was used for MEKC separations. The system control and data handling were done using

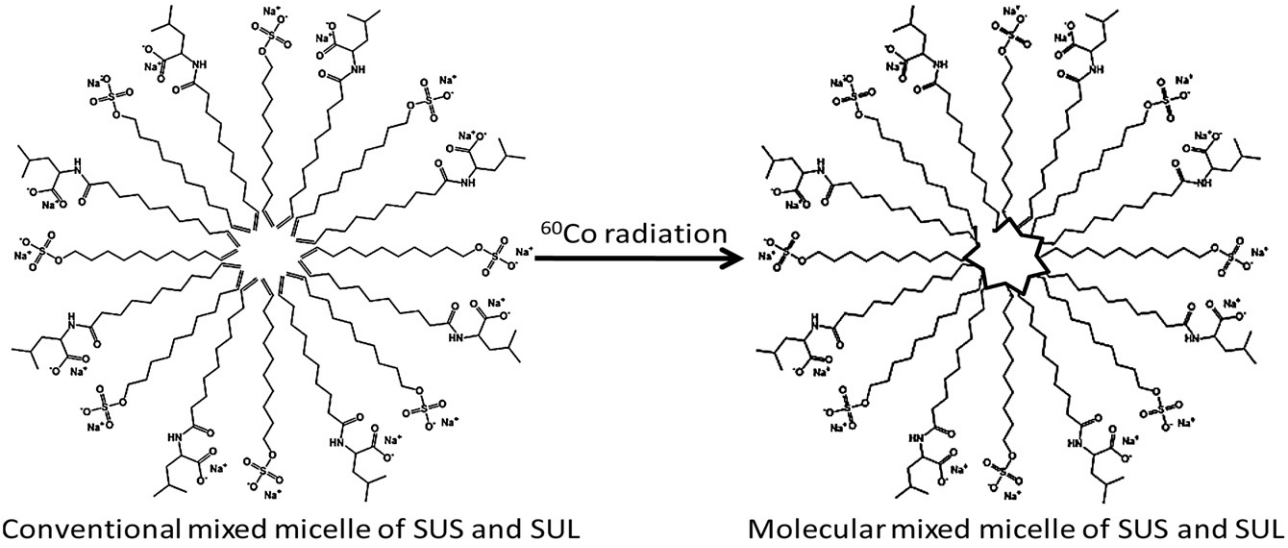

Fig. 1. Representative scheme for polymerization of binary mixed SUS and SUL surfactants. The surfactant monomers are linked to each other via covalent bonds.

3D-CE ChemStation (Rev. B.03.01) software. The MEKC separations were performed in fused-silica capillaries (Polymicro Technologies, Tucson, AZ, USA) with dimensions of 66.0 cm total length (57.5 cm effective length) × 50 μm ID (360 μm OD). Capillaries used in this study were cut from the same capillary bundle and were reactivated thoroughly after each surfactant system using deionized water (10 min) and 1.0 M NaOH (ca. 20 min) to eliminate possible cross contaminations.

2.2.2. Micellar electrokinetic chromatography of benzene derivatives

Each new capillary was activated with 1 M NaOH (30 min at 40 °C) and deionized water (10 min at 25 °C) before use. For a typical MEKC run, the capillary was rinsed for 2 min with triply deionized water and for 2 min 0.1 M NaOH followed by 3 min rinse with separation buffer between injections. Each day, the capillary was reactivated by rinsing with 1 M NaOH (10 min) and triply deionized water (5 min). All MEKC separations were performed at a constant voltage of +30 kV, and the capillary temperature was fixed at 25 °C. Unless otherwise noted, the injection size was 50 mbar for 1 s. Peaks were identified by comparison of their individual UV-spectrum obtained from diode array detector or via spiking when necessary.

2.3. Calculations

The retention factor values, k, of neutral solutes were calculated by use of the following equation [22]:

$$k = \frac{t_R - t_{eof}}{t_{eof}[1 - (t_R/t_{psp})]} \quad (2)$$

where t_R, t_{eof} and t_{psp} are the migration times of solute, EOF, and the pseudostationary phase, respectively. Methanol and undecanophenone were used to measure t_{eof} and t_{psp} markers, respectively. The system coefficients (v, e, s, a, and b) described in Eq. (1) were determined by multiple linear regression using Microsoft Excel.

3. Results and discussion

3.1. LSER results

There are a few important requirements that should be fulfilled for successful application of the LSER for characterization of pseudostationary phases in MEKC [19]: the capacity factors have to be distributed over a wide range without significant clustering; the solute descriptors have to be distributed throughout the descriptor space without significant clustering; cross-correlation of the solute descriptors has to be minimal (a cross-correlation matrix for descriptors with respect to one another is listed in Table 1 and showed no correlation between the analyte descriptors); and the number of solutes included in each model has to be sufficient to ensure that the system constants are adequately defined by statistical tests.

Many analytes, particularly members of the same homologous series, have very similar descriptor values that can result in determination of the system constants with low accuracy. Considering these factors we chose a diverse set of analytes with varied properties and may be grouped as non-hydrogen bond donors (NHB), hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD). The twenty-nine benzene derivatives used in this study and their descriptor values are summarized in Table 2 [23]. Their descriptor values span a wide selectivity range (V 0.716–1.214; E 0.601–1.360; S 0.50–1.170; A 0–0.70; and B 0.070–0.560). The model coefficients were calculated by substituting the experimental log k and the analyte descriptors values into Eq. (1) using multiple linear regression analysis.

In addition, since analytes partition between aqueous buffer phase and pseudostationary phase, the coefficients reflect differences in the two phases. Large coefficients indicate large differences while small or statistically insignificant coefficients indicate similar interaction between the two phases. Furthermore, the sign of the coefficient shows whether the aqueous or the pseudostationary phase interacts more strongly with the analyte [16].

In general, ease of cavity formation and dispersion (v system constant) and electron lone pair (e system constant) interactions have positive signs and favor retention in the pseudostationary phases. Interactions through acidic hydrogen-bonding favor interaction with the aqueous buffer phase (negative b values) in all

Table 1
Cross-correlation matrix for the descriptors of the test analytes.

	V	E	S	A	B
V	1.0000				
E	0.0198	1.0000			
S	0.0038	0.3784	1.0000		
A	0.1233	0.0555	0.2131	1.0000	
B	0.1715	0.0002	0.1658	0.0002	1.0000

Table 2
Solutes and their descriptor values used in LSER model (solute descriptors from [24]).

No	Analytes	Analyte descriptors				
		V	*E*	*S*	*A*	*B*
NHB analytes						
1	Benzene	0.716	0.610	0.52	0.00	0.14
2	Toluene	0.857	0.601	0.52	0.00	0.14
3	Chlorobenzene	0.839	0.718	0.65	0.00	0.07
4	Bromobenzene	0.891	0.882	0.73	0.00	0.09
5	Ethylbenzene	0.998	0.613	0.51	0.00	0.15
6	p-Xylene	0.998	0.613	0.52	0.00	0.16
7	Iodobenzene	0.975	1.188	0.83	0.00	0.12
8	4-Chlorotoluene	0.980	0.705	0.67	0.00	0.07
9	Naphthalene	1.085	1.360	0.92	0.00	0.20
10	Propylbenzene	1.139	0.604	0.50	0.00	0.15
HBA analytes						
11	Benzonitrile	0.8710	0.742	1.11	0.00	0.33
12	Nitrobenzene	0.8910	0.871	1.11	0.00	0.28
13	Acetophenone	1.0140	0.818	1.01	0.00	0.48
14	Methyl benzoate	1.0730	0.733	0.85	0.00	0.46
15	Propiophenone	1.1550	0.800	0.95	0.00	0.51
16	4-Nitrotoluene	1.0320	0.870	1.11	0.00	0.28
17	4-Chloroacetophenone	1.1360	0.955	1.09	0.00	0.44
18	4-Chloroanisole	1.0380	0.838	0.86	0.00	0.24
19	Ethyl benzoate	1.2140	0.689	0.85	0.00	0.46
HBD analytes						
20	Benzyl alcohol	0.9160	0.803	0.87	0.33	0.56
21	Phenol	0.7750	0.805	0.89	0.60	0.30
22	3-Methylphenol	0.9160	0.822	0.88	0.57	0.34
23	4-Flourophenol	0.7930	0.670	0.97	0.63	0.23
24	4-Chloroaniline	0.9390	1.060	1.13	0.30	0.31
25	4-Chlorophenol	0.8980	0.915	1.08	0.67	0.20
26	3-Chlorophenol	0.8980	0.909	1.06	0.69	0.15
27	4-Ethylphenol	1.0570	0.800	0.90	0.55	0.36
28	3-Bromophenol	0.9500	1.060	1.15	0.70	0.16
29	4-Bromophenol	0.9500	1.080	1.17	0.67	0.20

molecular micellar phases. Interactions of dipole-type and basic hydrogen-bonding are not significant, with a few exceptions.

3.1.1. Influence of molecular mixed-micelle composition on system constant *c*

The LSER intercept constant, coefficient *c*, values for the seven pseudostationary phases and their statistical values are listed in Table 3. The values of coefficient *c* are overall smallest (least negative) among all system constants. They decrease (become more negative) as percent mole fraction of SUL is increased in the molecular mixed micelles, except for 80% [poly (20:80)], where the value drops to −2.442. However, interpretation of coefficient *c* is difficult because of its complex nature despite the fact that it contains helpful chemical information [24]. It is important to remember that coefficient *c* influences the retention time but has no effect on selectivity.

3.1.2. Influence of molecular mixed-micelle composition on cavity formation and cohesiveness

As can be seen in Table 3, the coefficient *v* is positive and has the largest values in all the pseudostationary phases; however, no apparent trend is observed between the coefficient *v* and the surfactant composition. The magnitude of the *v* coefficient indicates the greatest influence of cavity formation and dispersion interaction on MEKC retention. In other words, the coefficient *v* is related to the difference in cohesive energies of the aqueous phase and the micellar phase; the larger the *v* value, the lesser cohesive the micelle phase is. The positive sign of the *v* coefficient indicates that the pseudostationary phase is more hydrocarbon-like (less cohesive) than aqueous phase. As a result, solutes prefer to transfer from more cohesive aqueous phase to less cohesive micellar phase. As seen in Table 3, the coefficient *v* values range from 2.747 (poly-SUL) to 3.197 [poly (40:60)], that is, among the pseudostationary phases studied, poly (40:60) and poly-SUL provide the highest and lowest hydrocarbon-like environment, respectively, for the test analytes. Comparison of coefficient *v* values for poly-SUL and poly-SUS reveals that the former is less cohesive than the later. Although the difference in *v* coefficient is not immense, the combination of SUL and SUS in molecular micelles has an effect on the cohesiveness of the molecular micelles. It is worth mentioning that, in general, monomeric SUS:SUL mixed micelles are more hydrocarbon-like [20] than their polymeric (molecular) counterparts (with minor exceptions). The only difference between monomeric mixed micelles and molecular mixed micelles is that the former are formed from free SUS monomers while the later are formed from covalently linked SUS monomers. The covalent bonds formed between monomers in molecular micelles eliminate dynamic equilibrium between free monomers and micelles. Since the chain lengths in monomeric and polymeric (molecular) systems are the same, the difference in cohesiveness (the *v* coefficient) between monomeric and polymeric systems might be related to the degree of hydration in these micellar systems. Research has shown that water can penetrate as far as the second or third methylene unit of the surfactant in a micelle [25–27]. In addition, analyte interaction with the micellar phase occurs via a number of mechanisms; thus, depending upon their physicochemical natures and amount of water that has penetrated into the micelle, analyte may reside in several regions of the micellar phase. For example, hydrophobic analytes with polarizable electrons (e.g., aromatic hydrocarbons) tend to reside near the polar head group, while hydrophobic

Table 3
System constant and regression statistic for the investigated surfactant systems ($n = 29$).

Surfactant systems							
System constants	Poly-SUS	Poly (80:20)	Poly (60:40)	Poly (50:50)	Poly (40:60)	Poly (20:80)	Poly-SUL
c	−2.351(±0.143)	−2.381(±0.136)	−2.405(±0.135)	−2.531(±0.150)	−2.649(±0.165)	−2.442(±0.219)	−2.478(±0.135)
v	2.827(±0.154)	2.748(±0.147)	2.751(±0.145)	2.796(±0.162)	3.197(±0.178)	3.133(±0.236)	2.747(±0.145)
e	0.163(±0.115)	0.160(±0.110)	0.218(±0.109)	0.248(±0.121)	0.444(±0.133)	0.772(±0.177)	0.280(±0.108)
s	0.139(±0.117)[a]	0.104(±0.112)[a]	0.038(±0.110)[a]	0.070(±0.123)[a]	−0.174(±0.135)[a]	−0.674(±0.179)	−0.064(±0.110)[a]
a	−0.152(±0.064)	−0.047(±0.061)[a]	0.027(±0.060)[a]	0.455(±0.067)	0.148(±0.074)[a]	0.127(±0.098)[a]	0.340(±0.060)
b	−1.830(±0.143)	−1.874(±0.137)	−2.010(±0.135)	−2.103(±0.150)	−2.434(±0.165)	−2.699(±0.210)	−2.256(±0.135)
Statistics							
F[b]	111	112	119	96	118	90	127
r^2 [c]	0.960	0.961	0.963	0.954	0.962	0.951	0.965

Standard deviation for each coefficient is given in parenthesis.
[a] Values are not statistically significant at the 95% confidence level.
[b] *F*-test.
[c] Correlation coefficient of linear regression.

alkanes are believed to penetrate into the hydrophobic micellar core. As a result of these diverse mechanisms, the retention of analytes in each pseudostationary phase system is expected to be different. Consequently, the LSER coefficients are also expected to be different.

3.1.3. Influence of molecular mixed-micelle composition on hydrogen bonding

Coefficient *b* has the second (excluding the coefficient *c*) largest magnitude among the system constants indicating the strong influence of hydrogen-bond acidity on MEKC retention and selectivity. The negative sign shows that the aqueous buffer phase is more hydrogen-bond acidic (i.e., have higher hydrogen bond donating ability) than molecular micelles. Based on the coefficient *b* values listed in Table 3, the relative hydrogen bond donating strength of the molecular micelles can be ordered as poly-SUS > poly (80:20) > poly (60:40) > poly (50:50) > poly-SUL > poly (40:60) > poly (20:80). Accordingly, molecular micelle with sulfate head group (i.e., poly-SUS) has the least negative (or largest) coefficient *b* value and thus possess the strongest hydrogen-bond acidic character among the micellar phases studied. In contrast, the surfactant with leucinate head group (i.e., poly-SUL) is the weakest hydrogen-bond donor phase along with poly (40:60) and poly (20:80). Therefore, poly-SUS tends to have stronger interactions with HBA analytes, whereas poly-SUL would interact stronger with HBD analytes. Due to the presence of —NH group in leucinate head group, one would expect that the poly-SUL would be relatively stronger hydrogen bond donor as compared to poly-SUS, which does not have any hydrogen bond donating sites. It is suggested that the water molecules in the palisade and Stern layers of the micelles are responsible for the hydrogen bonding properties of the micelles [28]. Comparison of molecular mixed micelles and monomeric mixed micelles reveals that the former show stronger hydrogen-bond acidic character based on their coefficient *b* values, with an exception of poly (20:80), which is less acidic than its monomeric counterpart [20].

Coefficient *a* is one of the least significant contributor in LSER model for the molecular micelles studied. As seen in Table 3, only three of the surfactants, i.e., poly-SUS, poly (50:50) and poly-SUL, provide statistically significant but relatively very small coefficient *a* values. Thus, due to their statistically insignificant (or practically zero) *a* values, majority of the surfactant systems have very similar hydrogen bond accepting ability as the aqueous phase and has very little influence on solute retention. As verified by their coefficient *a* values, poly-SUS is less basic (i.e., have weaker hydrogen bond accepting ability) while poly-SUL, which has a positive *a* coefficient value, is more basic than the aqueous buffer phase. No trend is observed between the surfactant composition and coefficient *a* values. Based on the coefficient *a* values, it is worth mentioning that poly-SUS and poly-SUL show more basic character than their monomeric forms, i.e., mono SUS and mono SUL [20].

3.1.4. Influence of molecular mixed-micelle composition on dipolarity and polarizability

The coefficient *e* is related to the difference in ability of the pseudostationary phase and the aqueous phase to interact with *n*- or π electrons of the solutes and the coefficient *s* is related to difference in dipolarity/polarizability of the separation system. Both of the coefficients are small in magnitude for all surfactant systems, indicating that they do not have as significant influence on selectivity as the other system coefficient have. The positive sign of the coefficient *e* indicates that the surfactant systems possess higher degree of interaction with *n*- and π-electrons than aqueous phase. It should be noted that the hydrophilic head groups of the molecular micelles possess easily polarizable moieties, i.e., carbon–oxygen or sulfur–oxygen double bonds, which interact with the *n*- or π-electrons of the analytes and thus result in more positive coefficient *e* values. As seen in Table 3, there is a steady increase in coefficient *e* values as a factor of SUL content. The ability of poly-SUL to interact with *n*- or π-electrons of the analytes is greater than that of poly-SUS, which has the smallest coefficient *s* value [along with poly (80:20)]; however, the double bonds (i.e., C=O and S=O) of poly (20:80) are more accessible to the analytes for better interaction, among the surfactant systems studied. It is interesting to note that poly (40:60) and poly (20:80) have greater tendency to interact with *n*- and π-electrons of analytes as compared with their monomeric counterparts, i.e., mono (40:60) and mono (20:80), whereas the reverse is observed for the rest of the surfactants [20]. Due to their statistically insignificant coefficient *s* values, except for poly (20:80), all molecular micelles show essentially the same dipolar microenvironment as the aqueous mobile phase. As evidenced by its negative coefficient *s* value, poly (20:80) provides less dipolar microenvironment than aqueous phase for the test analytes.

Comparison of the system coefficients for the seven molecular micelles as a function of surfactant composition is summarized in Fig. 2. As seen from the plot, some trends among some coefficients are apparent. For example, a similar trend is observed between *v* and *e* coefficients. Inverse trend between *s* (although statistically questionable) and *e* as well as *v* and *b* coefficients is also apparent.

One of practical applications of LSER model is that the LSER coefficients in Table 3 can be used to generate equations that can predict retention of analytes with molecular micelles used in this study.

Using the generated equations, predicted log *k* values for the test solutes were calculated and plotted against the experimental log *k* values. Representative plots for poly-SUS and poly-SUL are provided in Fig. 3. The regression equation and correlation coefficient for poly-SUS and poly-SUL are given in Fig. 3 and those of the rest of the surfactants are as follows: poly (80:20), $y = 0.961x - 0.000$ ($R^2 = 0.961$); poly (60:40), $y = 0.963x - 0.002$ ($R^2 = 0.963$); poly (50:50), $y = 0.954x - 0.001$ ($R^2 = 0.954$); poly (40:60), $y = 0.962x + 0.002$ ($R^2 = 0.962$); and poly (20:80), $y = 0.951x - 0.002$ ($R^2 = 0.951$).

3.2. Influence of molecular mixed-micelle composition on free energy of transfer for different functional groups

The molecular micelles can further be characterized by evaluating the differences in free energy of transfer from aqueous buffer to the pseudostationary phase for different functional groups attached

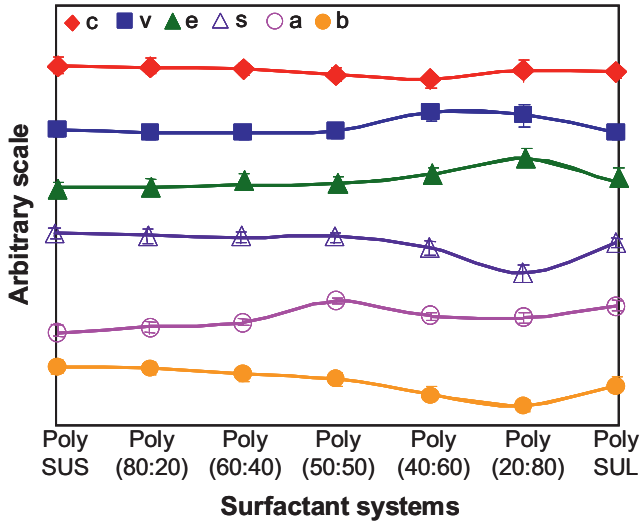

Fig. 2. Comparison of system constants derived from the LSER model as a factor of molecular mixed-micelle composition. Legends are shown in the plot.

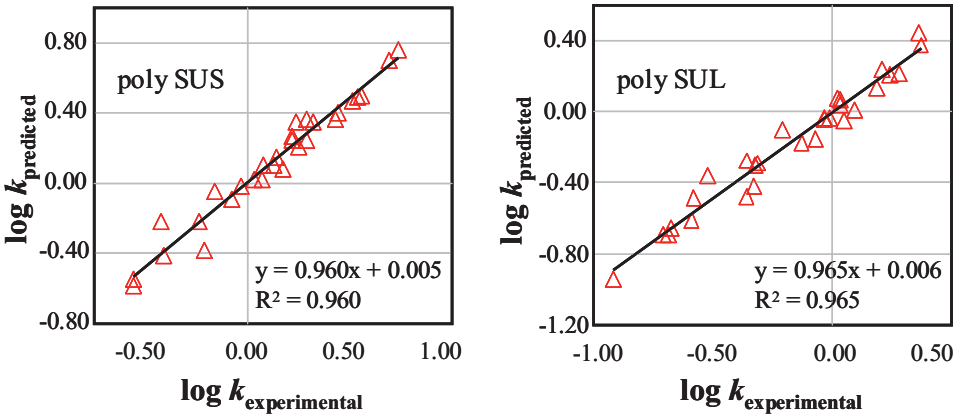

Fig. 3. Representative plots of predicted versus experimental log k values for poly-SUS and poly-SUL using generated equations. Regression equations and correlation coefficients are shown in the plots.

Table 4
Influence of molecular mixed-micelle composition on functional group selectivity.

No	Analytes	Functional group	$\Delta\Delta G = -RT\ln\tau$ (kJ/mol)						
			Poly-SUS	Poly (80:20)	Poly (60:40)	Poly (50:50)	Poly (40:60)	Poly (20:80)	Poly-SUL
3	Chlorobenzene	—Cl	−3.081	−3.081	−3.138	−3.138	−3.480	−3.594	−3.195
5	Bromobenzene	—Br	−3.993	−3.993	−4.050	−3.993	−4.621	−4.849	−4.107
8	Iodobenzene	—I	−5.534	−5.420	−5.534	−5.420	−6.675	−7.302	−5.534
2	Toluene	—CH_3	−2.168	−2.111	−2.111	−2.111	−2.282	−2.282	−2.111
4	Ethylbenzene	—C_2H_5	−3.993	−3.936	−3.879	−3.879	−4.336	−4.507	−3.879
9	Propylbenzene	—C_3H_7	−6.275	−6.047	−6.047	−5.933	−7.644	−8.557	−6.047
13	Acetophenone	—CO—CH_3	−1.883	−1.654	−1.312	−1.141	−0.970	0.057	−0.570
15	Propiophenone	—CO—C_2H_5	−3.594	−3.252	−2.852	−2.681	−2.681	−1.483	−2.168
14	Methyl benzoate	—CO—O—CH_3	−3.309	−3.024	−2.681	−2.510	−2.510	−1.369	−2.054
19	Ethyl benzoate	—CO—O—C_2H_5	−5.248	−4.792	−4.393	−4.222	−4.507	−3.081	−3.765
12	Nitrobenzene	—NO_2	−1.426	−1.255	−1.027	−0.970	−0.856	0.057	−0.628
11	Benzonitrile	—CN	−0.970	−0.799	−0.456	−0.342	−0.171	0.799	0.114
20	Benzyl alcohol	—CH_2—OH	0.856	0.856	1.084	0.342	1.312	2.111	1.312
21	Phenol	—OH	0.856	0.628	0.628	−0.342	0.342	1.027	−0.057

to the benzene ring. The functional group selectivity, τ, can be defined as the ratio of capacity factor of a substituted benzene ($k_{Bz\text{-}R}$) to that of benzene (k_{Bz}) [29]: $\tau = k_{Bz\text{-}R}/k_{Bz}$. The τ value can then be used to determine the difference in free energy of transfer, $\Delta\Delta G$, of a functional group from aqueous buffer phase to the micellar phase using the following equation: $\Delta\Delta G = -RT\ln\tau$, where R is the universal gas constant (8.314 J/mol) and T is the absolute temperature. The change in free energy of transfer for a functional group is related to the changes in free energies due to the cavity formation (coefficient v), hydrogen bonding (coefficients a and b), dipolarity/polarizability (coefficient s) and the n- and π-electron interaction (coefficient e) [30]. The $\Delta\Delta G$ values for various functional groups in different molecular pseudostationary phases are listed in Table 4. A negative $\Delta\Delta G$ value indicates that the addition of a functional group to benzene ring leads to an increase while a positive value leads to a decrease in strength of the interaction between analyte and the pseudostationary phase. In other words, when $\Delta\Delta G$ values are more negative, partitioning of the analyte into the micellar system becomes more favorable. As seen in Table 4, majority of analytes (i.e., NHB and HBA analytes) have negative $\Delta\Delta G$ values and thus have favorable interaction with the pseudostationary phases. Benzyl alcohol has positive $\Delta\Delta G$ values in all surfactant systems and the $\Delta\Delta G$ values for phenol are positive in all pseudostationary phases except in poly (50:50) and poly (80:20) molecular micelles. It should be noted that acetophenone, nitrobenzene and benzonitrile also have positive $\Delta\Delta G$ values in poly (80:20). The free energy changes in Table 4 indicate that almost all functional groups favor transfer from the aqueous buffer to poly-SUS than poly-SUL. In general, no obvious retention trend as a function of surfactant composition was observed.

3.3. *Influence of molecular mixed-micelle composition on retention factor*

Selectivity differences between pseudostationary phases can also be compared by plotting the log k values against each other [6]. A linear plot with all points falling on the line with a correlation coefficient, R^2, value of 1.0 or nearly 1.0 indicates the same selectivity, a scatter-plot with lower R^2 values, on the other hand, indicates selectivity differences between the pseudostationary phases. The log k values for the 29 benzene derivatives in the seven molecular micelles were plotted against each other. Log k plots of poly-SUS versus the remaining six surfactant systems are presented in Fig. 4(A)–(F) and the slope, y-intercept and R^2 values for all surfactant system comparisons are listed in Table 5. The trend line in Fig. 4 represents the correlation line for NHB analytes. Correlation coefficients of plots in Fig. 4(A)–(F) are relatively higher indicating that the surfactant systems have very similar chemical selectivity toward the NHB analytes. Further comparison of plots in Fig. 4 shows that most of the HBA analytes fall below the trend line indicating increased affinity for poly-SUS. This suggests that poly-SUS has relatively more acidic character (stronger hydrogen bond donor). This observation is in good agreement with the coefficient b in LSER (Table 3). Majority of the HBD analytes, on the other hand, fall above the line showing that these analytes tend to interact strongly with SUL-containing molecular micelles, with

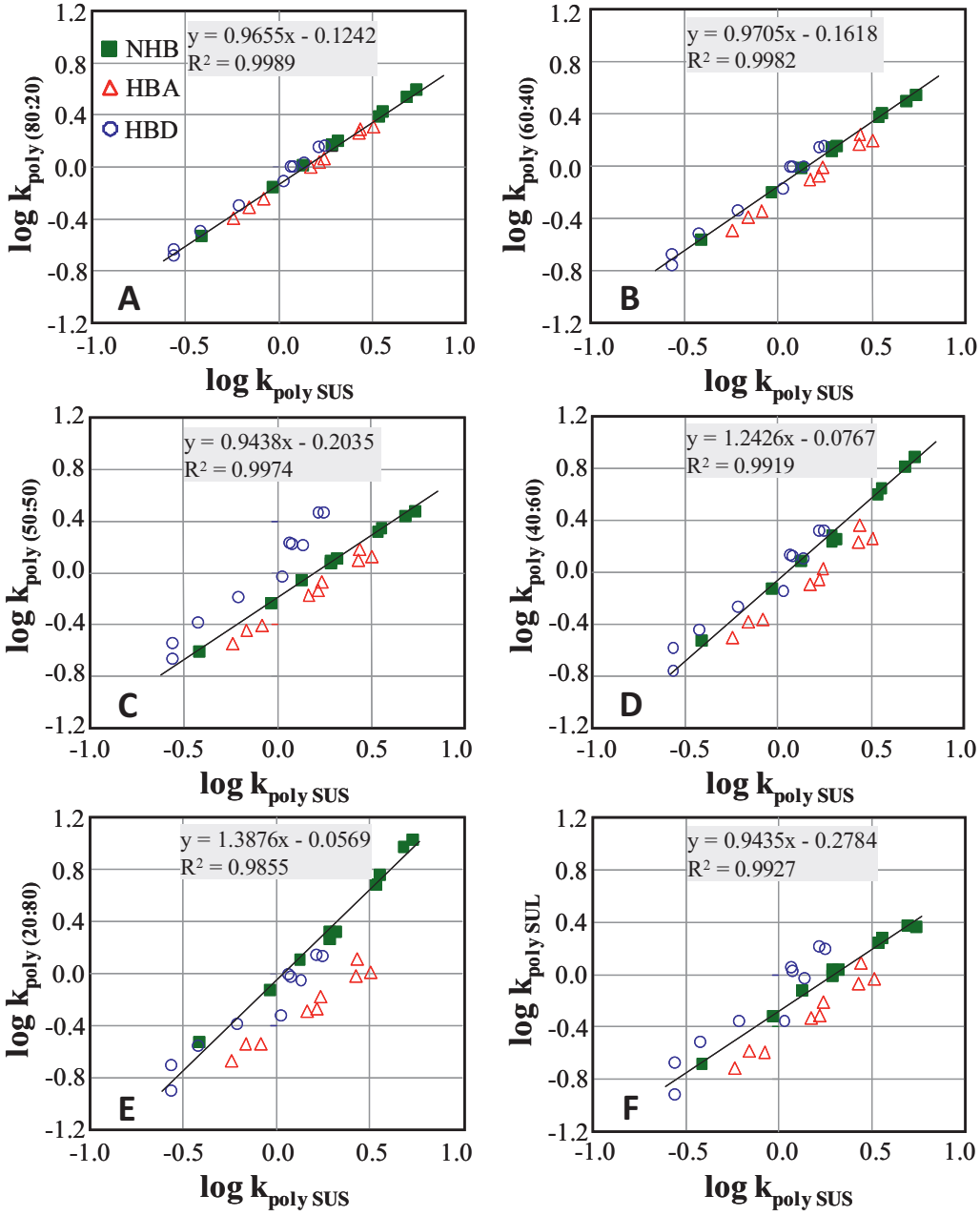

Fig. 4. Representative log *k* comparison between poly-SUS and (A) poly (80:20), (B) poly (60:40), (C) poly (50:50), (D) poly (40:60), (E) poly (20:80), and (F) poly-SUL. Legends are shown in plot A. Solid line represents correlation line for subset NHB analytes and regression equations for NHB analytes are shown in each plot.

the exception of poly (20:80) in which both HBA and HBD analytes fall below the line, indicating its weak acidic and basic character as compared with other surfactant systems (Table 3). As can be seen in Fig. 4 A, the selectivity difference between poly-SUS and poly (80:20) are very minor but the difference increases as the content of SUL is increased in the molecular micelles (Fig. 4(B)–(F)). As seen in Table 5, the lowest R^2 (0.7430 and 0.7534), thus the highest selectivity difference, were observed between poly-SUS – poly (50:50) and poly (50:50) – poly (20:80). The highest R^2 value (the lowest selectivity difference), on the other hand, is seen between poly-SUS and poly (80:20). Low selectivity difference between these two molecular micelles is not surprising because 80 percent mole fraction of poly (80:20) is SUS, thus, it is expected that the benzene derivatives would show very similar affinity for both surfactant systems.

4. Concluding remarks

The solvation parameter model provides a general framework for the interpretation of retention and selectivity differences for neutral compounds in pseudostationary phases. The *c* system constant has unusually high negative values for all the pseudostationary phases studied and decreases, in general, as percent mole fraction of SUL is increased in the molecular mixed micelles. Of all the system constants the *v* system constant has the highest values for the surfactant systems studied. The magnitude of the coefficient *v* shows the greatest influence of cavity formation and dispersion interaction on MEKC retention. Hydrogen-bond acidity (the *b* coefficient) has the second largest magnitude among all system constants, that the hydrogen-bond acidity has strong influence in MEKC retention and selectivity. The negative sign of the

Table 5
Slope, *y*-intercept and correlation coefficient, R^2, values of log *k* comparison plots of all of the analytes (white background) and of NHB analytes (shaded background).

		Poly SUS	Poly(80:20)	Poly(60:40)	Poly(50:50)	Poly(40:60)	Poly(20:80)	Poly SUL
	Slope	1.0000	0.9655	0.9705	0.9438	1.2426	1.3876	0.9435
Poly SUS	Intercept	0.0000	-0.1242	-0.1618	-0.2035	-0.0767	-0.0569	-0.2784
	R^2	1.0000	0.9989	0.9982	0.9974	0.9919	0.9855	0.9927
	Slope	0.9537	1.0000	1.0048	0.9776	1.2835	1.4326	0.9773
Poly(80:20)	Intercept	-0.1245	0.0000	-0.0369	-0.0820	0.0838	0.1224	-0.1570
	R^2	0.9912	1.0000	0.9985	0.9985	0.9875	0.9802	0.9938
	Slope	0.9604	1.0150	1.0000	0.9726	1.2771	1.4248	0.9735
Poly(60:40)	Intercept	-0.1774	-0.0520	0.0000	-0.0461	0.1309	0.1751	-0.1213
	R^2	0.9668	0.9910	1.0000	0.9996	0.9888	0.9804	0.9971
	Slope	0.8463	0.9241	0.9326	1.0000	1.3100	1.4609	1.0011
Poly(50:50)	Intercept	-0.1322	-0.0216	0.0270	0.0000	0.1918	0.2431	-0.0751
	R^2	0.7430	0.8130	0.8607	1.0000	0.9847	0.9756	0.9979
	Slope	1.1345	1.2090	1.2028	1.1324	1.0000	1.1192	0.7513
Poly(40:60)	Intercept	-0.0971	0.0510	0.1136	0.0750	0.0000	0.0279	-0.2177
	R^2	0.9133	0.9517	0.9793	0.8770	1.0000	0.9978	0.9797
	Slope	1.2486	1.3356	1.3408	1.2273	1.1380	1.0000	0.6674
Poly(20:80)	Intercept	-0.2054	-0.0424	0.0274	-0.0165	-0.1003	0.0000	-0.2349
	R^2	0.8088	0.8492	0.8898	0.7534	0.9469	1.0000	0.9704
	Slope	0.9040	0.9819	0.9913	1.0046	0.8269	0.6774	1.0000
Poly SUL	Intercept	-0.2868	-0.1687	-0.1170	-0.1471	-0.2108	-0.1402	0.0000
	R^2	0.8059	0.8724	0.9244	0.9593	0.9502	0.8721	1.0000

b system constant indicates that these pseudostationary phases have very little hydrogen-bond donating ability compared to the aqueous buffer phase. Poly-SUS has the highest hydrogen-bond donating ability, which decreases with an increase in SUL content in the molecular micelles, showing that sulfate head group is more hydrogen-bond acidic than the leucinate head group. The values of hydrogen-bond basicity (coefficient *a*), and the dipolarity/polarizability (coefficients) are relatively small when compared with the other coefficients showing the similarity of these system constants between the pseudostationary phase and the aqueous buffer phase. The free energy changes and log *k* plots agree well with the LSER result.

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