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Polymeric sulfated surfactants with varied hydrocarbon tail: II. Chemical selectivity in micellar electrokinetic chromatography using linear solvation energy relationships study

The effect of hydrocarbon chain length on chemical selectivity in micellar electrokinetic chromatography (MEKC) was investigated using polymeric sulfated surfactants: poly(sodium 7-octenyl sulfate), poly(sodium 8-nonenyl sulfate), poly(sodium 9-decenyl sulfate), and poly(sodium 10-undecenyl sulfate). Linear solvation energy relationships (LSERs) and free energy of transfer studies were conducted to predict the selectivity differences between the four polymeric surfactants. The overall nature of the solute/polymeric micelle interactions was found to be different despite the fact that all polymeric surfactants have the same head group. The polar character and acidic strength of the polymeric surfactant are found to decrease as the hydrocarbon chain length of the surfactant is increased. On the other hand, the polarizability of the polymeric sulfated surfactants increases (upon interacting with solute lone-pair electrons) with increasing hydrocarbon chain length. The LSER results show that the solute size and hydrogen bond accepting ability play the key roles in MEKC retention.

Keywords: Hydrocarbon chain length / Linear solvation energy relationships / Micellar electrokinetic chromatography / Polymeric surfactants / Sodium alkenyl sulfates

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1 Introduction

Micellar electrokinetic chromatography (MEKC) has been extensively used for the separation of both charged and uncharged solutes since its first introduction [1]. A major advantage of MEKC is the feasibility of changing the chemical composition of the separation buffer by simply rinsing the capillary with a solution of a new pseudostationary phase (micellar) solution. Thus, the selectivity of the technique can be easily manipulated and controlled by proper selection of the surfactant type, organic solvents [2, 3] or by addition of different complexing agents such as cyclodextrins, urea, and chiral reagents to the separation buffer. In MEKC, uncharged solutes are sepa-

rated based on their differential partitioning into the micellar phase. Although the hydrophobic interaction between solutes and the pseudostationary phase is a major driving force behind the solute retention in MEKC, some other types of interactions can also influence solute retention and selectivity. Therefore, understanding the nature of the solute-micelle interactions is critical for better understanding retention and selectivity.

In the last several years, linear solvation energy relationship (LSER) has been applied to characterization of retention and selectivity differences between different pseudostationary phases in MEKC [3–19]. The solvation parameter model (see Eq. (1) below) is a revised version of LSER [20–22]. According to this model various molecular interactions contribute to retention in MEKC as follows:

$$\log k' = c + mV_x + rR_2 + s\pi_2^* + a \sum \alpha_2 + b \sum \beta_2 \quad (1)$$

In Eq. (1), $\log k'$ is correlated to known solute descriptors, V_x , R_2 , π_2^* , α_2 , and β_2 . The descriptor V_x represents the McGowan solute characteristic volume ($\text{cm}^3/\text{mol}^{-1}$) [22]. R_2 represents the excess molar refraction of the solute (cm^3) [21]. In order to bring it to the scale with other descriptors, V_x and R_2 are divided by 100 and 10, respectively. Solute polarity and polarizability are repre-

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Abbreviations: HBA, hydrogen-bond acceptor; HBD, hydrogen bond donor; LSER, linear solvation energy relationships; NHB, nonhydrogen bonding; poly-SDeS, poly(sodium 9-decenyl sulfate); poly-SNoS, poly(sodium 8-nonenyl sulfate); poly-SOcS, poly(sodium 7-octenyl sulfate); poly-SUS, poly(sodium 10-undecenyl sulfate); SAIS, sodium alkenyl sulfates

sented by the π_2^* term. The α_2 and β_2 terms represent the solute hydrogen bond donating and solute hydrogen bond accepting abilities, respectively. The subscript 2 denotes that these parameters are solute properties. System coefficients (m , r , s , a , and b) in Eq. (1) reflect relative differences in interaction between the aqueous and the pseudostationary phases for which the solute is transferring. The coefficients of solute descriptors are obtained by multiple linear regression. These coefficients provide information about solute-pseudostationary phase, solute-bulk buffer interactions as well as selectivity of the running buffer in MEKC. The constant c represents the intercept and includes information about separation phase ratio. The m term is a measure of the relative ease of cavity formation in pseudostationary phase by the solute. The r coefficient verifies the difference in ability of the pseudostationary phase and the separation buffer to interact with the n - or π -electrons of the solute. The difference in dipolarity between the pseudostationary phase and 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 pseudostationary phase, respectively.

Although not numerous, some papers have been published using LSER to understand the influence of alkyl chain length of unpolymerized micelles in MEKC [23, 24]. Vitha and Carr [23] investigated retention in micellar solutions of three sodium alkyl sulfate (SAS) surfactants that have C8, C10, and C12 hydrocarbon tails. They found very similar solute/micelle interactions in these three SAS surfactants, implying that the selectivity in all three systems is quite similar. However, two key parameters, solute size and hydrogen bond basicity, were found to play major roles in determining solute retention and selectivity. Sodium *N*-acyl sarcosinates with alkyl chains of 11, 13, and 15 carbon atoms using LSER were examined by Trone and Khaledi [24]. In addition to sarcosinates, they investigated sodium dodecyl sulfate (SDS) and sodium tetradecyl sulfate to determine the chain length effect on selectivity for saturated SAS surfactants. Their study showed that the chain length of the surfactant could have an influence on selectivity in MEKC. However, the chain length effects are reported to be less substantial and dependent on the nature or the type of surfactant head group. For example, the hydrocarbon chain length of sarcosinates, which have a larger organic head group, has a more substantial effect in selectivity than that of alkyl sulfate surfactants with a relatively smaller head group. Despite the fact that the LSER model has been applied to understand the factors determining retention of both hydrogen bonding and nonhydrogen bonding solutes, most of these LSER studies were carried out on

conventional micelles with different head groups [3–19]. Hence, to the best of our knowledge, only three attempts have been made to assess the chain length contribution of polymeric surfactants through the use of LSER model in MEKC [18, 25, 26]. Copolymers of 2-acrylamido-2-methyl-1-propanosulfonic acid (AMPS) and methacrylates with different pendant chain lengths (C8, C12, and C18) were investigated using LSER. The length of the pendant alkyl chains was found to have significant effect on cohesiveness of the polymer and slight effect on other normalized system coefficients. However, the authors showed that chain lengths of these polymers does not contribute to chemical selectivity [18]. Recently, LSER studies were used to characterize the differences in chain length selectivity of siloxane polymers. From these studies, the researchers discovered that alkyl modified siloxane polymers possess very low propensity of interactions with polar and polarizable compounds and are generally less polar and more cohesive. In addition, these polymers were found to be stronger hydrogen bond donors than SDS micelles [25, 26].

In Part I of this series, synthesis, characterization, and retention properties of polymeric sodium alkenyl sulfate (poly-SAIS) were studied [27]. To further characterize the chemical selectivity of the SAIS polymers, LSER was applied in this Part II for a further investigation of hydrocarbon chain length effect on retention and selectivity of the four polymeric surfactants: poly(sodium 7-octenyl sulfate) (poly-SOCS), poly(sodium 8-nonenyl sulfate) (poly-SNoS), poly(sodium 9-decenyl sulfate) (poly-SDeS), and poly(sodium 10-undecenyl sulfate) (poly-SUS).

2 Materials and methods

2.1 Apparatus, materials, solutions and CE procedure

Equipment and materials were the same as described in Part I [27].

2.2 Calculations

The capacity factors, k' , of the test solutes were measured by Eq. (2) [1]:

$$k' = \frac{t_R - t_{eo}}{t_{eo} \left(1 - \frac{t_R}{t_{psp}} \right)} \quad (2)$$

The system coefficients (m , r , s , a , and b) described in Eq. (1) were determined by multiple linear regression using SAS software (SAS Institute, Cary, NC, USA).

3 Results and discussion

3.1 LSER results

The retention behavior of 36 test solutes in each polymeric SAIS surfactant was examined and compared using the solvation parameter LSER model (Eq. 1). Due to detection limitations, benzene derivatives have been chosen. A set of solutes with known descriptors is required to accurately determine the coefficients of Eq. (1). The benzene derivatives, their chemical structures and descriptors are listed in Table 1. Based on their

hydrogen bond abilities, the solutes in Table 1 are characterized as nonhydrogen 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, $\alpha \geq \beta$). Although the NHB solutes that include alkyl- and halo-substituted benzenes and polyaromatic hydrocarbons do not have any hydrogen-bonding functional groups, they act as weak HBA solutes ($\beta \leq 0.2$) due to the aromatic ring(s). Furthermore, the HBA and HBD solutes possess hydrogen bond accepting functional groups and hydrogen bond donating functional groups, respectively.

Table 1. Test solutes and their solvation descriptors^{a)}




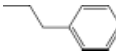




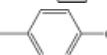
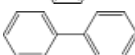







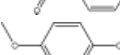
#	Solute	Chemical structure	Solute descriptors				
			V_x	R_2	π_2^H	$\sum \alpha_2^H$	$\sum \beta_2^0$
Nonhydrogen bond donors (NHD)							
1	Benzene		0.716	0.610	0.52	0.00	0.14
2	Toluene		0.857	0.601	0.52	0.00	0.14
3	Ethylbenzene		0.998	0.613	0.51	0.00	0.15
4	Propylbenzene		1.139	0.604	0.50	0.00	0.15
5	<i>p</i> -Xylene		0.998	0.613	0.52	0.00	0.16
6	Chlorobenzene		0.839	0.718	0.65	0.00	0.07
7	Bromobenzene		0.891	0.882	0.73	0.00	0.09
8	Iodobenzene		0.975	1.188	0.83	0.00	0.12
9	4-Chlorotoluene		0.980	0.705	0.67	0.00	0.07
10	Biphenyl		1.324	1.360	0.99	0.00	0.22
11	Naphthalene		1.085	1.360	0.92	0.00	0.20
12	1-Methylnaphthalene		1.226	1.344	0.90	0.00	0.20
Hydrogen bond acceptors (HBA)							
13	Acetophenone		1.014	0.818	1.01	0.00	0.48
14	Benzonitrile		0.871	0.742	1.11	0.00	0.33
15	Nitrobenzene		0.891	0.871	1.11	0.00	0.28
16	Methyl benzoate		1.073	0.733	0.85	0.00	0.46
17	Ethyl benzoate		1.214	0.689	0.85	0.00	0.46
18	4-Chloroanisole		1.038	0.838	0.86	0.00	0.24

Table 1. Continued

#	Solutes	Chemical structure	Solute descriptors				
			V_x	R_2	π_2^H	$\sum \alpha_2^H$	$\sum \beta_2^0$
19	4-Nitrotoluene		1.032	0.870	1.11	0.00	0.28
20	4-Chloroacetophenone		1.136	0.955	1.09	0.00	0.44
21	Methyl 2-methylbenzoate		1.214	0.772	0.87	0.00	0.43
22	Phenyl acetate		1.073	0.661	1.13	0.00	0.54
23	3-Methylbenzyl alcohol		1.057	0.815	0.90	0.33	0.59
24	Phenethyl alcohol		1.057	0.784	0.83	0.30	0.66
Hydrogen bond donors (HBD)							
25	Benzyl alcohol		0.916	0.803	0.87	0.33	0.56
26	Phenol		0.775	0.805	0.89	0.60	0.30
27	4-Methylphenol		0.916	0.820	0.87	0.57	0.31
28	4-Ethylphenol		1.057	0.800	0.90	0.55	0.36
29	4-Fluorophenol		0.793	0.670	0.97	0.63	0.23
30	4-Chlorophenol		0.898	0.915	1.08	0.67	0.20
31	4-Bromophenol		0.950	1.080	1.17	0.67	0.20
32	4-Chloroaniline		0.939	1.060	1.13	0.30	0.31
33	3-Chlorophenol		0.898	0.909	1.06	0.69	0.15
34	3-Methylphenol		0.916	0.822	0.88	0.57	0.34
35	3-Bromophenol		0.950	1.060	1.15	0.70	0.16
36	3,5-Dimethylphenol		1.057	0.820	0.84	0.57	0.36

a) Solute descriptors from [21].

The LSER analysis was performed using 36 benzene derivatives. However, a poor correlation was found between experimental $\log k'$ and calculated $\log k'$ (data not shown). The LSER results showed that phenyl acetate (solute 22) is an outlying solute in all surfactant systems. The outlier solutes were determined using the following approach: (i) Residual values of $\log k'$ (experimental $\log k'$ minus calculated $\log k'$) were calculated. (ii) Normalized residual

values (*i.e.*, residual divided by the standard deviation of the residual) are computed. (iii) The normalized residual values of $\log k'$ were plotted against the solute number (Fig. 1) [28]. The injection of phenyl acetate alone and along with the HBA solutes in all polymeric surfactants provided two peaks, one of which was found to coelute with nitrobenzene (solute 15, in poly-SDeS and poly-SUS) or benzonitrile (solute 14, in poly-SOcS and poly-

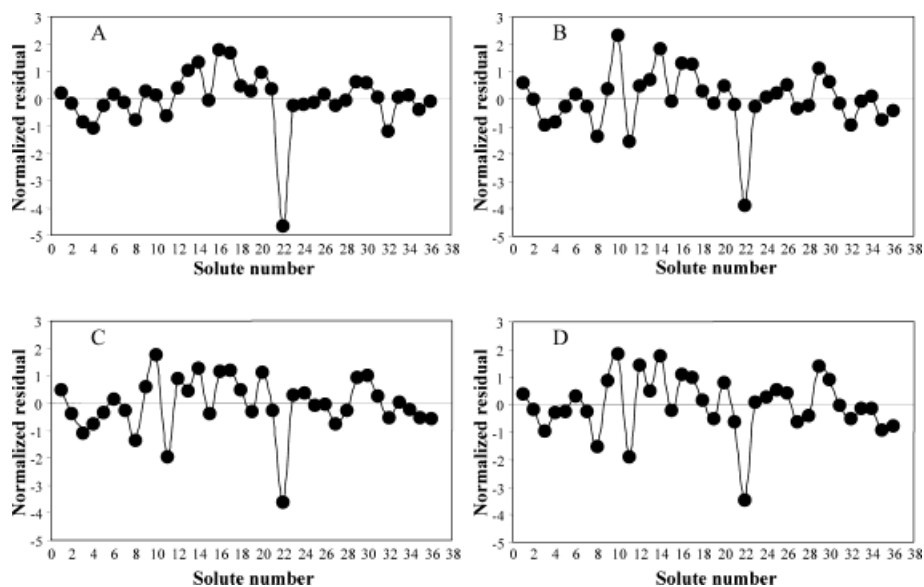


Figure 1. Normalized residuals from (A) poly-SOcS, (B) poly-SNoS, (C) poly-SDeS, and (D) poly-SUS surfactant system.

SNoS). Thus, phenyl acetate was eliminated from the solute list and LSER calculations were carried out using the remaining 35 solutes. The best correlation between experimental $\log k'$ and calculated $\log k'$ values are obtained when the normalized residuals are zero or nearly zero. However, normalized residual range of +2 to –2 is reasonable for statistically sound correlations. As seen in Fig. 1, besides phenyl acetate, the absolute values of normalized residual of a few solutes seem to be slightly higher as well. For example, solute 16 (methyl benzoate) and solute 17 (ethyl benzoate) are the two major solutes that have high normalized residual values in poly-SOcS, whereas, solute 10 (biphenyl) and solute 11 (naphthalene) have slightly higher normalized residuals in the remaining three polymeric surfactants. These data indicate that the type and the number of outlier solutes may vary depending on the type of polymeric surfactant.

The LSER analysis data for different chain length shown in Table 2 were obtained from the experimental $\log k'$ values of the four polymeric SAIS surfactants and solvatochromic parameters listed in Table 1 (excluding phenyl acetate). The constant c is related to the phase ratio, *i.e.*, the ratio of polymeric pseudostationary phase volume to aqueous phase volume ($V_{\text{psp}}/V_{\text{aq}}$) of the separation system. As seen in Table 2, the intercept values, c , of the poly-SAIS surfactants (except poly-SOcS) were very close (*ca.* 2.9–3.0). However, the intercept of poly-SOcS was much higher and less negative (–2.7). A similar trend was also observed for aggregation number (N) of poly-SAIS [27]. Our results are in contrast with those found for the conventional (unpolymerized) micelles of alkyl sarcosinate (C11, C13, and C15) and alkyl sulfate surfactants

(C12 and C14). In both of these surfactant series the c values were generally lower (more negative) at shorter chain lengths [24]. However, our data are in agreement with those of Vitha and Carr [23] who reported higher (less negative) c values for shorter-chain conventional micelles of sulfated surfactants. The calculated $\log k'$ values were obtained by substitution of the system constant (*i.e.*, system coefficient) values (Table 2) in Eq. (1). The plots of experimental $\log k'$ versus calculated $\log k'$ are found to have R^2 values higher than 0.98 (date not shown). This suggests that retention of all benzene derivatives in all polymeric SAIS surfactants is well predicted by the LSER model.

3.1.1 Effect of hydrocarbon chain length on cohesiveness and dispersion interactions

The m values are positive and large for all of the polymeric SAIS surfactants. The positive sign of m indicates that solutes prefer to transfer from more cohesive aqueous phase to less cohesive micellar phase. Different m values for each surfactant system suggest that all polymeric surfactants have different cohesiveness and dispersive interactions with solute molecules. Poly-SOcS and poly-SUS show the smallest and the largest hydrophobic interactions with the solutes, respectively. Furthermore, large positive m values show that the endoergic (disfavorable) cavity formation term has the most important effect on retention. The coefficient m is related to the difference in cohesive energies of the aqueous phase and the polymeric pseudostationary phase. Thus, the larger the m value, the smaller the cohesive energy of the polymeric phase.

Table 2. Hydrocarbon tail effect on migration behavior of benzene derivatives in MEKC ($n = 35$)

Surfactant systems	System constants						Statistics	
	c	m	r	s	a	b	$R^{2a)}$	SE ^{b)}
poly-SOcS	-2.681 (±0.075) ^{c)}	2.253 (±0.085)	0.218 (±0.062)	0.260 (±0.064)	-0.144 (±0.036)	-1.145 (±0.071)	0.983	0.049
poly-SNoS	-3.023 (±0.121)	2.907 (±0.136)	0.482 (±0.099)	0.078 ^{d)} (±0.103)	-0.152 (±0.058)	-1.495 (±0.114)	0.976	0.078
poly-SDeS	-2.929 (±0.104)	2.946 (±0.116)	0.522 (±0.085)	-0.049 ^{d)} (±0.089)	-0.141 (±0.050)	-1.637 (±0.110)	0.983	0.067
poly-SUS	-3.013 (±0.123)	3.182 (±0.138)	0.685 (±0.101)	-0.190 ^{d)} (±0.105)	-0.103 ^{d)} (±0.059)	-1.772 (±0.115)	0.981	0.080

a) Correlation coefficient of linear regression

b) Standard error of the calculated $\log K'$ values

c) Standard deviation for each coefficient

d) Values are not statistically significant at the 95% confidence level.

From the m coefficient values in Table 2, the four surfactant systems are ordered as: $m_{\text{poly-SUS}} > m_{\text{poly-SDeS}} > m_{\text{poly-SNoS}} > m_{\text{poly-SOcS}}$. This indicates that as the alkyl chain length is decreased the cohesiveness increases. Therefore, poly-SOcS provides the most cohesive (most polar) and poly-SUS has the least cohesive (most apolar) media. The data is in a good agreement with the methylene selectivity (*i.e.*, hydrophobicity) and polarity (*i.e.*, I_1/I_3 ratio) of the surfactants presented in Part I of this study [27]. Thus, NHB solutes have strongest affinity toward poly-SUS than the remaining three polymeric SAIS surfactants. The large m values also indicate that, as compared to the micellar systems, water is a very cohesive solvent and is not easy to create a cavity for the solute. Water molecules form a relatively firm hydrogen-bonding network, and hence the creation of any cavity within the aqueous phase takes place at the cost of a significantly large energy. Cavity formation in poly-SUS micelles, however, requires relatively smaller energy. Hence, partitioning of solutes will be more favorable with poly-SUS than with aqueous buffer phase.

3.1.2 Effect of hydrocarbon chain length on hydrogen bonding

The large b coefficient for all surfactant systems shows that the hydrogen bond donating ability of the polymeric SAIS surfactants is also an important factor in MEKC retention and selectivity. The negative sign of coefficient b indicates that all polymeric pseudostationary phases are less acidic (*i.e.*, have poor hydrogen bond donating ability) than the aqueous phase. The negative sign also indicates that the hydrogen bond accepting ability of the

solute resists to its partitioning into the micellar phase [28]. The b coefficients are large and negative for all polymeric surfactant studied. Based on the coefficient b values listed in Table 2, the relative hydrogen bond donating strength of the polymeric SAIS surfactants can be ordered as poly-SOcS > poly-SNoS > poly-SDeS > poly-SUS. Poly-SUS, with a largest negative b coefficient, is the weakest proton-donating phase, while poly-SOcS is the strongest proton-donating phase among all of the surfactant systems. Strength of the interactions between polymeric SAIS and HBA solutes decreases with an increase in chain length of the surfactants. Therefore, poly-SOcS has the strongest interactions with HBA solutes, whereas poly-SUS has the weakest interactions with HBA solutes. It should be mentioned that none of the polymeric sulfated surfactants have a hydrogen bond donating sites in their head group. The water molecules in palisade and Stern layers of the micelles are believed to be responsible for the hydrogen bond donating properties of the micelles. It has been shown that water can penetrate as far as the second or third methylene unit (from the head group) of the surfactant tail in micelles [29–31]. The hydrocarbon tail is also believed to influence the amount of water in the palisade and Stern layer. Surface tension studies on sodium alkyl sulfate surfactants suggest that the water exposure to the interior of the micelle increases with increasing the chain length [32]. Spectroscopic experiments have also showed that the depth of water penetration into the micelle is influenced by chain length of the surfactant [33–35]. All of these studies suggest that as the length of surfactant hydrocarbon tail increases, the amount of water in the palisade and the Stern layer varies due to possible variation in micellar structure. The LSER results of this study seem to support

the literature as well as the suggestion that the water molecules in the palisade and the Stern layer of the micelle influence the hydrogen bonding between micelles and the solutes.

Coefficient a is one of the least important factors in LSER model for polymeric surfactant systems studied. This coefficient represents the difference in hydrogen bond accepting ability (HBA basicity) of the polymeric pseudostationary phases and that of the aqueous phase. Coefficient a is negative for all of the surfactant systems. The negative sign of coefficient a indicates that the aqueous buffer phase is more basic (*i.e.*, has a stronger hydrogen bond accepting ability) than the polymeric SAIS phases. No trend is observed between the hydrocarbon chain length of the SAIS surfactants and the coefficient a value. Statistically, all of the four sulfate surfactants have very similar hydrogen bond accepting abilities, suggesting that the hydrogen bond accepting ability is similar to the bulk aqueous phase, and has an insignificant influence on solute partitioning.

3.1.3 Effect of hydrocarbon chain length on dipolarity and polarizability

The dipolarity (also called dipole-dipole) and polarizability (also called induced dipole-induced dipole) interactions, represented by coefficients s and r , respectively, have relatively small effects on the solute partitioning in MEKC. As seen in Table 2, the sign of coefficient s is positive for poly-SOcS and poly-SNoS (*e.g.*, surfactants with shorter hydrocarbon tails), whereas it is negative for poly-SDeS and poly-SUS (with longer hydrocarbon tails). However, it should be mentioned that the s coefficient is statistically significant at the 95% confidence level only for poly-SOcS surfactant. The coefficient s values indicate that the solutes find a more dipolar microenvironment in poly-SOcS phase than in aqueous phase. Due to their statistically insignificant coefficient s values, poly-SNoS, poly-SDeS, and poly-SUS surfactant systems show essentially the same dipolar microenvironment as the aqueous mobile phase. A fluorescence spectroscopic study supports this observation that the polarity of the surfactant with a short hydrocarbon chain length (*i.e.*, poly-SOcS) is higher than that with longer hydrocarbon chain length [27]. Thus, the LSER data agrees well with fluorescence spectroscopic study.

As discussed previously in the literature [14], the induced dipole-induced dipole interaction (coefficient r) represents the ability of surfactant system to interact with the n - and π -electron pairs of solute. All of the polymeric SAIS surfactants have positive coefficient r (Table 2). The positive values of this coefficient indicate that poly-SAIS sur-

factants can interact with or become polarized by solutes n - and π -electrons. The magnitude of the coefficient r is increased as the hydrocarbon chain length is increased for poly-SAIS, but the effect of this coefficient r is small compared to m and b coefficients. Nevertheless, poly-SUS is more easily polarized upon interacting with the solutes n - and/or π -electrons as compared to the remaining three polymeric surfactants.

Variations of the system coefficients for the polymeric sulfated surfactants as a function of carbon number of the hydrocarbon tail are summarized in Fig. 2. It is clear that an increase in the length of hydrocarbon tail does not have a significant effect on hydrogen-bond basicity of the polymeric surfactants (coefficient a). The cohesiveness (coefficient m) increases much faster than polarizability (coefficient r). However, hydrogen-bond acidity (coefficient b) is decreased significantly with increasing chain length of the surfactants. In addition, it is interesting to note a reverse trend for r and s coefficients (Fig. 2 inset). For example, poly-SOcS has least tendency to interact with n - and/or π -lone pair electrons of the solutes (the smallest coefficient r value), while the same polymeric surfactant has the most tendency to interact with solutes through dipole-dipole interactions (the largest coefficient s value).

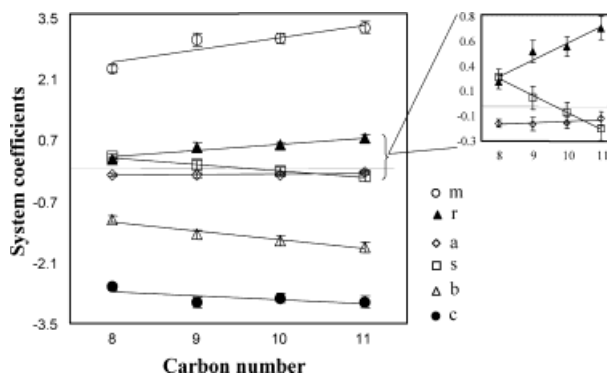


Figure 2. Plot of the system constants derived from the LSER against the carbon number of the hydrocarbon tail of the surfactants. Fit equations and the legends are shown in the plot. The inset represents the expanded plot of coefficients r , s , and a .

3.2 Effect of hydrocarbon chain length on free energy of transfer

Polymeric SAIS surfactants can be further characterized by evaluating the difference in free energy of transfer for different functional groups on benzene ring. The functional group selectivity, τ , can be defined as the ratio of capacity factor of a substituted benzene, $k'_{(Bz-R)}$, to capacity factor of benzene, $k'_{(Bz)}$ [5]:

$$\tau = \frac{k'_{(\text{Bz-R})}}{k'_{(\text{Bz})}} \quad (2)$$

The difference in free energy of transfer, $\Delta\Delta G$, of a functional group from aqueous buffer phase to micellar pseudostationary phase can be determined using the following equation:

$$\Delta\Delta G = -RT \ln \tau \quad (3)$$

where R is the universal gas constant (8.31451 J/mol) and T is the absolute temperature ($0^\circ\text{C} = 273.15 \text{ K}$).

The $\Delta\Delta G$ values for various functional groups are listed in Table 3. A negative $\Delta\Delta G$ value shows that the addition of a functional group to benzene ring leads to an increase in strength of the interaction of solute with polymeric surfactant phase. In contrast, a positive $\Delta\Delta G$ indicates that the addition of a functional group to benzene ring leads to a decrease in the interaction of solute with the surfactant systems. In other words, when $\Delta\Delta G$ value is more positive, solute-polymeric surfactant interaction becomes less favorable.

The first seven solutes in Table 3 have NHB characteristics. As expected, increase in the alkyl chain length of either the polymeric surfactant or the solutes (e.g., methyl benzene, ethyl benzene, and propyl benzene) increases the interaction of alkyl benzene solutes into the surfactant systems ($\Delta\Delta G$ becomes more negative). However, for solutes 1–7 (Table 3), the differences in $\Delta\Delta G$ values using poly-SOcS are significantly lower (more positive) than the remaining three polymeric surfactants. Nevertheless, the overall trend in $\Delta\Delta G$ for NHB solutes (Table 3) is consis-

Table 3. Chain length effect on functional group selectivity

Functional group	$\Delta\Delta G^{\text{a)}} = -RT \ln \tau$			
	poly-SOcS	poly-SNoS	poly-SDeS	poly-SUS
1 -CH ₃	-1.569	-1.933	-2.079	-2.206
2 -CH ₂ CH ₃	-2.954	-3.646	-3.920	-4.259
3 -CH ₂ CH ₂ CH ₃	-4.613	-5.992	-6.340	-7.132
4 -C ₆ H ₅	-8.811	-12.348	-12.578	-13.305
5 -Cl	-2.262	-2.682	-2.975	-3.131
6 -Br	-3.028	-3.646	-3.920	-4.156
7 -I	-4.278	-5.201	-5.470	-5.924
8 -CN	-1.703	-1.641	-1.044	-0.972
9 -NO ₂	-1.922	-1.825	-1.499	-1.442
10 -C(O)CH ₃	-2.504	-2.416	-1.964	-1.928
11 -C(O)OCH ₃	-3.510	-3.719	-3.394	-3.449
12 -C(O)OCH ₂ CH ₃	-5.076	-5.775	-5.450	-5.663
13 -CH ₂ CH ₂ OH	-0.980	-1.045	-0.892	-0.849
14 -CH ₂ OH	0.048	0.269	0.645	0.517
15 -OH	0.048	0.269	0.645	0.517

a) kJ/mol

tent with the coefficient m values (Table 2). Solute 8–13 in Table 3 that have varying degrees of HBA abilities show distinctive retentions in each polymeric surfactant. The HBA solutes are more polar as compared to NHB solutes. Therefore, the observed differences in $\Delta\Delta G$ values (hence, in retention) may be due to a combination of several interactions (e.g., hydrophobic, dipole-dipole, and hydrogen bonding). The retention of the first three HBA solutes (solute 8–10) decreases as the hydrocarbon chain length of polymeric surfactant is increased. Therefore, these three HBA solutes lead to a stronger partitioning into shorter chain surfactants, poly-SOcS, which is a stronger hydrogen bond donor. For the remaining HBA solutes (solute 11–13) no obvious retention trend as a function of varying chain length of surfactant was observed. The HBD solutes (e.g., solute 14, 15 in Table 3) have positive $\Delta\Delta G$ values in all four polymeric surfactants indicating that surfactant systems have stronger interaction with benzene than with benzene derivatives. In addition, these two solutes also possess hydrogen bond accepting characteristics. Therefore, like HBA solutes, these two solutes interact strongest with the shortest chain poly-SOcS surfactant.

3.3 Effect of hydrocarbon chain length on distribution coefficients and chemical selectivity

The logarithms of the distribution coefficients, $\log K$, for the 36 benzene derivatives using the four polymeric surfactants were plotted against each other (Figs. 3A–F). Selectivity differences between the polymeric surfactants can be compared using these plots [36]. If selectivity between all four surfactants were the same, a linear plot with all points falling on the line with a value of R closer to 1.00 would be observed. Alternatively, a scatterplot would indicate selectivity difference between the surfactant systems. Plots of solute retention in poly-SNoS, poly-SDeS, and poly-SUS versus poly-SOcS are shown in Figs. 4A–C. The lower correlation coefficient between poly-SUS versus poly-SOcS ($R^2 = 0.959$) shows that the selectivity difference between these two polymeric surfactants is relatively higher than that between poly-SDeS versus poly-SOcS ($R^2 = 0.963$, Fig. 3B) or between poly-SNoS versus poly-SOcS ($R^2 = 0.983$, Fig. 3A). In addition, correlation coefficients of plots in Figs. 3D–F are relatively higher indicating that poly-SNoS, poly-SDeS, and poly-SUS have very similar chemical selectivity toward the 36 benzene solutes even though there are some deviations from the best-fit line. Further comparison of plots in Fig. 3 shows that most of the HBA solutes fall below the line indicating increased affinity for the shorter chain surfactant (e.g., poly-SOcS in Fig. 3A). This suggests that polymeric SAIS

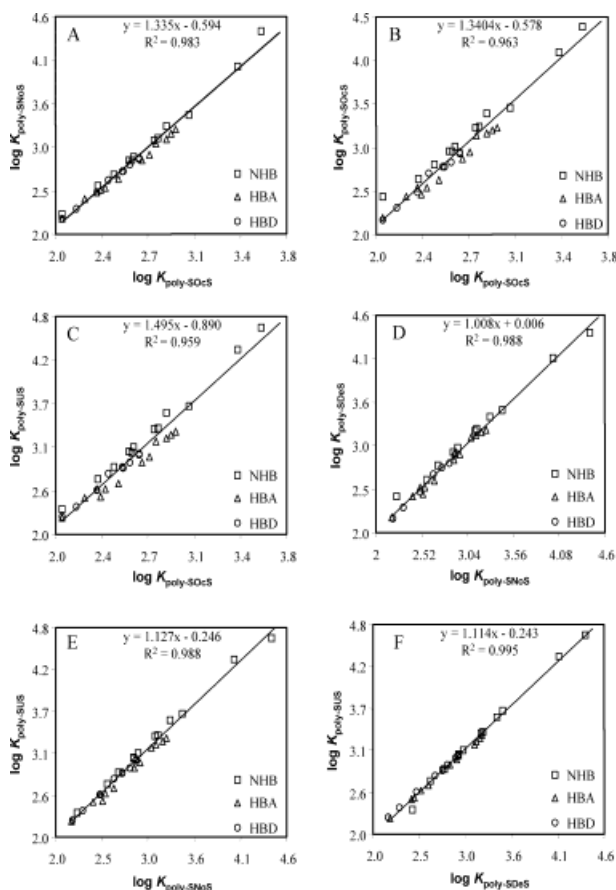


Figure 3. Solute distribution coefficient comparison between (A) poly-SOcS and poly-SNoS, (B) poly-SOcS and poly-SDeS, (C) poly-SOcS and poly-SUS, (D) poly-SNoS and poly-SDeS, (E) poly-SNoS and poly-SUS, and (F) poly-SDeS and poly-SUS. Legends are shown in the plot.

surfactants with shorter carbon tail have relatively more acidic character (stronger hydrogen bond donor). This is in a good agreement with the coefficient b in LSER (Table 2). The NHB solutes, on the other hand, fall above the line showing that the hydrophobic solutes tend to interact strongly with longer chain surfactant systems (e.g., poly-SUS in Fig. 3C). Even though most of the HBD solutes fall on the best-fit line, a few solutes fall slightly below the line indicating that all four polymeric surfactant have similar selectivity toward the HBD solutes. Nevertheless, surfactants with shorter carbon tail have slightly higher affinity for these solutes. This agrees well with coefficient a in LSER, which does not change significantly with the length of the carbon tail of the polymeric surfactants (Table 2). It should be mentioned, however, that the overall selectivity differences between the four poly-SAIS surfactants are minor and limited to specific solutes. This from 0.959 to 0.995) of $\log K$ comparison plots in Fig. 3.

4 Concluding remarks

Four polymeric SAIS surfactants were applied as pseudostationary phases in MEKC. The LSER model was successfully applied to investigate the effect of the hydrocarbon chain length of the surfactant on the retention mechanism and selectivity in MEKC. The phase ratio (c coefficient) remains more or less the same for C9–C11 poly-SAIS but its magnitude decreases (becomes less negative) with C8 hydrocarbon surfactant (i.e., poly-SOcS). The solute size (coefficient m) and hydrogen bond accepting ability (coefficient b) are found to be the most important role in MEKC retention in all four polymeric SAIS surfactant systems. Contrary to previously reported study with conventional alkyl sulfate surfactant [23], our results with polymeric surfactants suggest that hydrocarbon chain length has an influence on retention and selectivity in MEKC. Coefficient m values reveal that cohesiveness increases with decreasing hydrocarbon chain length. As a result, poly-SOcS provides the most cohesive (most polar) and the poly-SUS provides the least cohesive (most apolar) microenvironment for benzene derivatives. Hydrogen bond donating strength of the polymeric SAIS surfactants decrease with an increase in hydrocarbon chain length of the surfactant. Thus, poly-SUS is the weakest proton-donating phase (weakest acidic), whereas poly-SOcS is the strongest proton-donating phase (strongest acidic) among the four polymeric surfactants. Therefore, poly-SOcS has the strongest interactions with HBA benzene derivatives. No significant change was observed in coefficient a as a function of hydrocarbon chain length (Fig. 2). This suggests that poly-SAIS surfactants have similar hydrogen bond acceptor abilities. Poly-SOcS has the highest dipolar character (coefficient s) as compared to the remaining surfactant systems whose dipolar character is more or less the same (the difference is not statistically significant) and equal to the dipolarity of the mobile phase. In contrast, induced dipole-induced dipole interaction, or polarizability character, (coefficient r) between solute and surfactant system is directly proportional to the chain length of the surfactants. Hence, poly-SUS is more easily polarized upon interacting with the solutes n - and/or π -electrons as compared to the remaining three polymeric surfactants. The plots of $\log K$ comparisons of the four polymeric surfactants showed that the overall selectivity differences between the four poly-SAIS surfactants are minor (as evidenced by relatively higher R^2 values ranging from 0.959 to 0.995) and limited to specific solutes (Fig. 3). Free energies of transfer of selected functional groups in each surfactant systems were also calculated and found to be in good agreement with the LSER data. Similarly, comparison of solute distribution coefficients in each polymeric surfactant and LSER data was found to be well-matched.

The evaluation of the coefficients in Table 2 shows that the surfactant systems with large absolute values of a and/or b coefficients (e.g., poly-SUS or poly-SNoS) would be very convenient to separate mixtures of solutes with dissimilar hydrogen-bond acidity. Due to its relatively large coefficient s value, poly-SOcS would be better system of choice to separate compounds by their polarity. Similarly, poly-SUS, which has the largest coefficient r would be a convenient system to separate solutes by their polarizability. All of the surfactant systems show a similar strength to separate compounds according to their size, because all systems have similar coefficient m values, except poly-SOcS, which has relatively small m coefficient.

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