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A Linear Solvation Energy Relationship Study of the Effects of Surfactant Chain Length on the Chemical Interactions Governing Retention and Selectivity in Micellar Electrokinetic Capillary Chromatography Using Sodium Alkyl Sulfate Elution Buffers

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ABSTRACT

We have used linear solvation energy relationships (LSERs) to study the fundamental chemical interactions responsible for solute retention in micellar electrokinetic capillary chromatography (MEKC). We investigated retention in micellar solutions of sodium dodecyl sulfate (SDS), sodium decyl sulfate (SDecS), and sodium octyl sulfate (SOS). The purpose of the study was to elucidate the effect of surfactant chain length on the solute/micelle interactions that ultimately govern retention and selectivity in MEKC. The nature of the solute/micelle interactions were found to be nearly equivalent in all three systems, implying that the chromatographic selectivity in all three systems will be quite similar. Additionally, the LSERs show that solute size and hydrogen bond basicity play the largest roles in determining solute retention and chromatographic selectivity. Finally, from the LSERs and an analysis of the free energy of transfer of methylene units from water to the micellar phase ($\Delta G^{\circ}_{CH_2}$), we conclude that the solutes reside in the polar, hydrated head group region of the

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micelles, and not in the nonpolar core. Based on the $\Delta G^{\circ}_{CH_2}$ values for five different homologous solute series, the effect of the solutes' functional groups on the location and orientation of the solutes inside the micelles is briefly discussed.

INTRODUCTION

Capillary electrophoresis (CE), introduced by Virtanen in 1974 (1), has rapidly become an important analytical technique for the separation of charged species due largely to the early work of Lukacs and Jorgenson (2–6). Terabe et al. extended its application to neutral molecules by the introduction of micellar electrokinetic capillary chromatography (MEKC) in 1984 (7). Since then, MEKC has been used to analyze a wide range of solutes including environmental contaminants such as polyaromatic hydrocarbons (8), chlorinated phenols (7), and herbicides (9, 10), as well as biologically important agents such as cardiac glycosides (11), β-blockers (12), and amino acid derivatives (13).

While CE offers rapid and efficient separations of ions based on their electrophoretic mobilities, neutral solutes cannot be resolved since they have no electrophoretic migration arising from a fixed charge. When micelles are added to the elution buffer, however, neutral solutes can be separated based on the extent of their interactions with the micelles (7, 14). A neutral solute that does not interact with the micelle will elute at the dead time (t_0). A solute that strongly favors partitioning into the micelles (e.g., large hydrophobic molecules) will elute at the same time as the micelles (t_m), and solutes that spend a significant fraction of time in both the aqueous and micellar phases will elute at some time (t_r) between t_0 and t_m. The actual elution time is determined by the ratio of solute molecules in each phase as measured by the capacity factor, k' (7, 14), where

$$k' = \frac{t_r - t_0}{t_0\left(1 - \frac{t_r}{t_m}\right)} \tag{1}$$

Furthermore, k' is related to the solute's partition coefficient, K, and the standard free energy of transfer (ΔG°) of the solute from the aqueous phase to the micellar phase as shown in the following equation (14):

$$\ln k' = \ln K + \ln \phi = \frac{-\Delta G^{\circ}}{RT} + \ln \phi \tag{2}$$

where ϕ is the ratio of the micellar and aqueous phase volumes. Thus, by measuring k', one is ultimately measuring the partition coefficient and the standard free energy of transfer, provided that the phase ratio is known.

Given the importance of MEKC as a separation technique, it is important to understand the fundamental chemical interactions responsible for retention. This understanding can lead to predictions regarding the probable success or failure of MEKC separations using specific surfactant systems. In this study we used linear solvation energy relationships (LSERs) to dissect ln k' values measured for a variety of solutes in several different micellar elution buffers for the purpose of understanding the chemical interactions that dictate retention in these different systems. The LSER equation we used in these studies is shown in

$$\log k' = \log k'_0 + mV_x + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^H + rR_2 \qquad (3)$$

where V_x, π_2^H, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$, and R_2 are measures of a solute's characteristic volume, dipolarity/polarizability, hydrogen bond acidity, hydrogen bond basicity, and excess molecular polarizability, respectively. Log k'_0 is an intercept term and is determined via a multiparameter linear least squares regression of experimental log k' values versus the solute parameters listed above. The regression also yields the coefficients m, s, a, b, and r, which reflect differences in the properties of the two phases being studied. The interpretation of LSERs and their application to the study of solute/micelle interactions have been discussed in detail by several other authors (15–17) and are therefore not repeated here.

Through the use of LSERs we gain information about the chemical interactions between solutes and micelles, predictive capabilities, and important insights into the selectivity of MEKC separations. Additionally, given that k' is directly proportion to K, by studying the factors that influence k' we are not only learning about retention in MEKC, but fundamentally about the chemical interactions that influence the free energy of partitioning of solutes between the aqueous and micellar phases. In this regard we are using MEKC as a tool for collecting thermodynamic data in the same way we used headspace gas chromatography (HSGC) in previous micellar studies (18).

This article discusses LSERs obtained in three different, but related, surfactant systems: sodium dodecyl sulfate (SDS), sodium decyl sulfate (SDecS), and sodium octyl sulfate (SOS). We studied SDS for two reasons. First, since the LSER for this surfactant had already been determined by HSGC as well as reported in the literature (15–17), we could verify that the MEKC methodology produces results similar to those obtained using other measurement methods. Second, SDS is one of the most commonly used MEKC surfactants. Thus, studying solute retention behavior in an SDS MEKC mobile phase has practical applications.

SDecS and SOS were studied to probe differences in the chemical behavior of the sodium alkyl sulfate surfactants with regards to their interactions with solutes. Based on previous studies which indicate that the solutes are located in the sulfate head group region and not in the nonpolar core of SDS micelles

(16, 18), it is reasonable to suggest that the chemical interactions governing solute partitioning into SDS, SDecS, and SOS micelles should be relatively insensitive to the chain length of the surfactant, provided that the nature of the head group remains constant. Since we have kept the head group constant in the above surfactant systems, the LSERs for the three surfactant systems are predicted to be very similar.

If differences in the LSERs are found, then assuming the validity of the LSER method, these would imply differences in the strength of interactions between solutes and sodium alkyl sulfate (SAS) micelles and would have important implications for the use of these surfactants in a variety of applications. Chromatographically, if these interactions vary in strength depending on the chain length, then there may be advantages to using one surfactant over the others for specific separations. If, however, there are no differences in the interactions, then the surfactants are essentially equivalent in terms of separation capability, at which point other practical operating issues (such as the total surfactant concentration needed, etc.) will dictate which of the surfactants is used in MEKC separations.

Overall, these studies are aimed at investigating the effects of surfactant chain length on the interactions between solutes and micelles, and how these effects may influence the chromatographic selectivity of these systems. To our knowledge, this is the first systematic LSER study of the effects of surfactant chain length on the chemical interactions governing solute/micelle interactions involving more than two homologous surfactants.

EXPERIMENTAL SECTION

Elution Buffer Solution

A phosphate buffer solution of 3.13 mM HPO_4^{2-} and $H_2PO_4^-$ was prepared using $Na_2HPO_4 \cdot 7H_2O$ (J.T. Baker) and $NaH_2PO_4 \cdot H_2O$ (J.T. Baker) as received. The pH was 6.82 and the ionic strength was 12.5 mM. The salt concentration was deliberately kept low to reduce the changes in micellar size and shape that salts can induce (19, 20). Surfactant solutions were prepared using this buffer as the diluent. The following solutions were prepared: 30 mM SDS (Aldrich, 98%), 43.5 mM SDecS (Acros, HPLC grade), 160 mM SOS (Lancaster, 99%). The critical micelle concentrations for SDS, SDecS, and SOS are 8.1 mM (21), 33 mM (21), and 133 mM (22), respectively. The aggregation numbers are 64 (22), 50 (22), and 27 (22), respectively. All surfactants were used as received. Solute solutions were made by dissolving the desired solutes in the surfactant/phosphate buffer solution and adjusting the solute concentration to obtain peak heights generally between 10 and 60 mAUs. The solutes used in each study are listed in Table 1.

TABLE 1
Solutes, Log k' Values, and Solvatochromic Parameters[a] Used to Generate SDS, SDecS, and SOS LSERs

Solute number	Solute	Log k' SDS	Log k' SDecS	Log k' SOS	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	V_x
1	Nitropropane	−0.86	−1.21	−0.69	0.242	0.95	0	0.31	0.706
2	Nitrobutane	−0.44	−0.81	−0.34	0.227	0.95	0	0.29	0.847
3	Nitropentane	0.0053	−0.41	0.15	0.212	0.95	0	0.29	0.988
4	Nitrohexane	0.46	0.052	—[b]	0.203	0.95	0	0.29	1.129
5	Benzene	−0.26	−0.64	−0.086	0.600	0.52	0	0.14	0.716
6	Toluene	0.18	−0.31	0.34	0.601	0.52	0	0.14	0.857
7	Ethylbenzene	0.56	0.11	0.75	0.613	0.51	0	0.15	0.998
8	Propylbenzene	1.02	0.54	—[b]	0.604	0.50	0	0.15	1.139
9	Acetophenone	0.0043	−0.38	0.11	0.818	1.01	0	0.48	1.014
10	Propiophenone	0.33	−0.055	0.41	0.804	0.95	0	0.51	1.155
11	Butyrophenone	0.69	0.25	0.77	0.800	0.95	0	0.51	1.296
12	Valerophenone	1.08	0.60	1.23	0.800	0.95	0	0.51	1.437
13	Anisole	−0.012	−0.42	—[b]	0.708	0.75	0	0.29	0.916
14	2-Nitroanisole	0.084	−0.32	—[b]	0.960	1.30	0	0.35	1.037
15	4-Nitroanisole	0.26	−0.20	0.33	0.960	1.30	0	0.35	1.037
16	Nitrobenzene	−0.11	−0.50	0.014	0.871	1.11	0	0.28	0.891
17	*p*-Ethylnitrobenzene	0.72	0.28	—[b]	0.870	1.11	0	0.28	1.173
18	Benzamide	−0.48	−0.79	—[b]	0.99	1.50	0.49	0.67	0.973
19	Aniline	−0.45	−0.91	—[b]	0.955	0.96	0.26	0.50	0.816
20	4-Ethylaniline	0.75	−0.017	—[b]	0.91	0.95	0.23	0.45	1.239
21	*p*-Nitroaniline	−0.15	−0.49	0.15	1.22	1.91	0.42	0.38	0.991
22	4-Chloroaniline	0.10	−0.35	—[b]	1.06	1.13	0.30	0.35	0.939
23	*N,N*-Diethyl-4-nitroaniline	1.30	0.81	—[b]	0.957	0.84	0	0.41	1.380
24	Phenol	−0.54	−0.86	−0.39	0.805	0.89	0.60	0.30	0.775
25	Benzyl alcohol	−0.50	−0.84	−0.39	0.803	0.87	0.33	0.56	0.916
26	2-Phenylethanol	−0.21	−0.58	−0.090	0.811	0.91	0.30	0.64	1.057
27	3-Phenyl-1-propanol	0.17	−0.31	0.31	0.821	0.90	0.30	0.67	1.198
28	4-Phenyl-1-butanol	0.53	0.11	0.59	0.831	0.90	0.30	0.69	1.339
29	*p*-Cresol	−0.10	−0.50	—[b]	0.820	0.87	0.57	0.31	0.916
30	*p*-Ethylphenol	0.28	−0.081	0.40	0.800	0.90	0.55	0.36	1.057
31	2,4-Dimethylphenol	0.27	−0.14	0.40	0.843	0.80	0.53	0.39	1.057
32	4-Fluorophenol	−0.39	−0.71	—[b]	0.670	0.97	0.63	0.23	0.793
33	4-Chlorophenol	0.14	−0.29	—[b]	0.915	1.08	0.67	0.20	0.898
34	4-Bromophenol	0.30	−0.072	0.47	1.08	1.17	0.67	0.20	0.950
35	4-Cyanophenol	−0.25	−0.51	−0.13	0.94	1.63	0.79	0.29	0.930
36	Catechol	−0.71	−1.00	−0.54	0.97	1.07	0.85	0.52	0.834
37	4-Butylaniline	1.40	1.01	—[b]	0.91	0.95	0.23	0.45	1.571

[a] From Refs. 21–23 or estimated from values therein.
[b] k' values not available.

MEKC Conditions

A Hewlett-Packard HP-3D CE capillary electrophoresis system with Chemstation software was used to collect data. The capillary compartment was maintained at 25.0 ± 0.2°C. The voltages applied to the capillary for each specific surfactant were 25, 20, and 9.5 kV for SDS, SDecS, and SOS, respectively. The currents resulting from these voltages were 12, 27, and 73 μA for SDS, SDecS, and SOS, respectively. A 64.9-cm capillary (56.3 cm from the injection vial to the detection window) was used in the SDS and SDecS studies and a 33.0-cm capillary (25.0 cm from the injection vial to the detection window) was used in the SOS studies. All capillaries (Supelco) were 50 μm i.d. and 363 μm o.d.

The capillary was flushed for a minimum of 2 minutes with 0.1 M NaOH followed by 2 minutes of the surfactant elution buffer prior to each injection. All solute solutions were injected a minimum of three times with standard errors of less than 1.5% except where noted below. Average k' values are shown in Table 1. Methanol and Sudan III were used to measure t_0 and t_m, respectively, as suggested by literature reports (14). Detection was performed with a UV-Vis diode array detector. The wavelengths monitored were 210, 254, and 316 nm. All injections were pressure injections of 50.0 mbar for 3.0 seconds.

RESULTS AND DISCUSSION

SDS LSER

The LSER shown in Table 2 was obtained for retention in the SDS elution buffer using the k' values and solvatochromic parameters (23–25) listed in

TABLE 2
LSERs for Solute Retention in SDS, SDecS, and SOS Elution Buffers[a]

Surfactant	$-\text{Log } k'_0$	r	$-s$	$-a$	$-b$	m	ρ[b]	n[c]	SE[d]
SDS	2.16	0.42	0.34	0.11	1.72	2.90	0.994	36	0.06
	(0.06)	(0.06)	(0.04)	(0.05)	(0.08)	(0.07)			
SDecS	2.43	0.32	0.24	—[e]	1.60	2.69	0.989	36	0.07
	(0.08)	(0.06)	(0.05)		(0.09)	(0.08)			
SOS	1.97	0.45	0.31	0.12	1.87	2.85	0.994	23	0.06
	(0.08)	(0.07)	(0.04)	(0.05)	(0.10)	(0.09)			

[a] Uncertainties in the coefficients are shown in parentheses.
[b] ρ is the correlation coefficient of each regression.
[c] n is the number of solutes in each regression.
[d] SE is the standard error of the regression.
[e] The a coefficient was found to be statistically equal to zero in the SDecS system and was therefore omitted from the LSER.

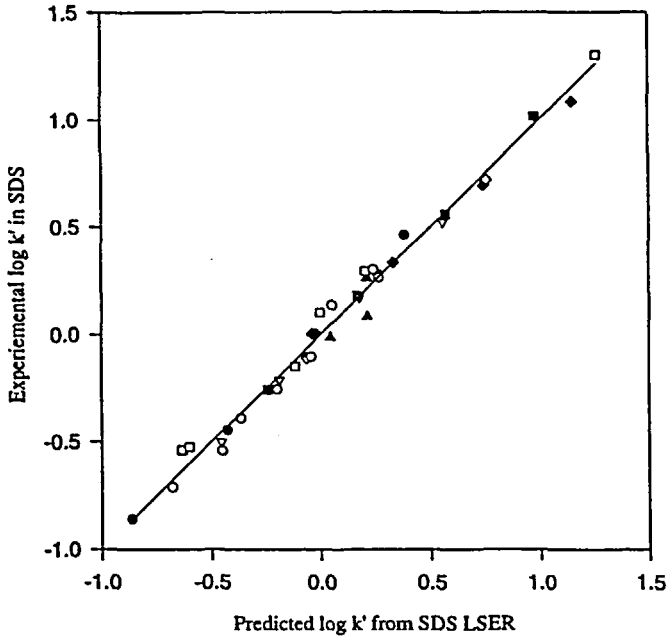

FIG. 1 Experimental versus predicted log k' values in SDS. Symbols are (●) 1-nitroalkanes, (■) *n*-alkylbenzenes, (◆) *n*-alkylphenones, (▲) anisoles, (◇) nitrobenzenes, (□) benzamide and anilines, (▽) phenylalkanols, and (○) phenols. The solid line is a 1:1 line.

Table 1 (excluding 4-butylaniline, which was found to be an outlier). Figure 1 shows a plot of experimental log k' values versus log k' values predicted from the LSER equation for the solutes used in this study. Figure 2 shows the residuals for each solute (experimental minus calculated values) normalized to the overall average standard deviation of the fit. It is seen in Figs. 1 and 2 that the retention of all solutes is well-predicted by the LSER. Furthermore, with the exception of the aniline derivatives, no family of solutes is consistently over- or underpredicted by the LSER, indicating that the behavior of most of the solute classes are generally well described by the LSER. A more extensive discussion of the residuals, including a comparison of the residuals from all of the alkyl sulfate LSERs, is presented below.

Chemical Interpretation of SDS LSER

Table 3 shows that the coefficients of the SDS LSER obtained in this study using MEKC are in good agreement with those of previously reported LSERs

obtained using a variety of methods (15–17, 26). All of the SDS LSERs show that solute volume (V_x) and hydrogen bond basicity ($\Sigma\beta_2^H$) dominate the partition process, with minor contributions from the dipolarity/polarizability (π_2^H), hydrogen bond acidity ($\Sigma\alpha_2^H$), and excess molecular polarizability (R_2) of the solutes. The LSERs lead to the conclusion that water is a better hydrogen bond donor and acceptor than are SDS micelles. They also show that water is more polar, more cohesive, and less dispersive than is an SDS micelle. More detailed analyses of SDS LSERs have been presented elsewhere, and the reader is referred to those reports (15–17, 26).

The fact that the SDS MEKC LSER is in good agreement with those presented in Table 3 lends support to the assertion that MEKC can be used to probe solute partitioning effectively between aqueous and micellar phases. Additionally, the good agreement suggests that the low phosphate concentration used to buffer the system does not significantly alter the partition process by changing the chemical nature of the micellar and aqueous phases. Thus,

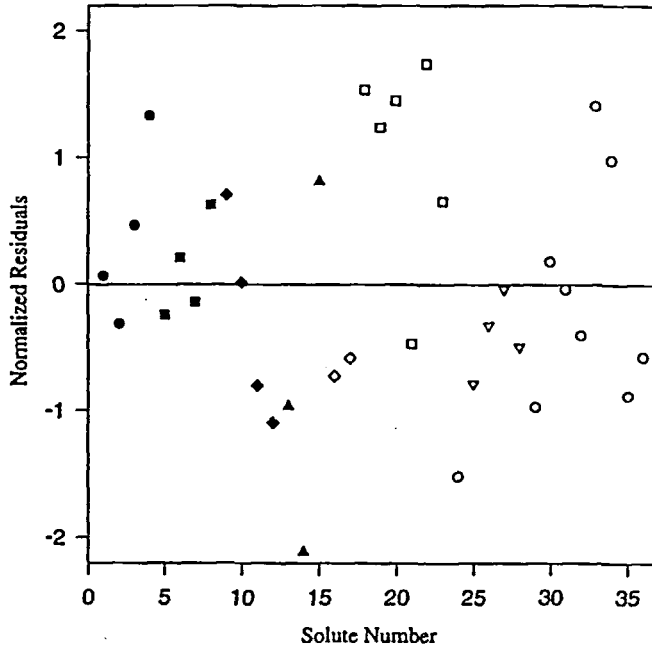

FIG. 2 Normalized residuals from SDS LSER. Solute numbers are the same as in Table 1. Symbols are (●) 1-nitroalkanes, (■) *n*-alkylbenzenes, (◆) *n*-alkylphenones, (▲) anisoles, (◇) nitrobenzenes, (□) benzamide and anilines, (▽) phenylalkanols, and (○) phenols.

TABLE 3
Comparison of the MEKC SDS LSER in This Study to SDS LSERs from the Literature[a]

Source	Log K_0	m	$-s$	$-a$	$-b$	r	n[b]	SE[c]	ρ[d]	Log K_0[e]
This work by MEKC	−2.16[f] (0.07)	2.90 (0.07)	0.34 (0.04)	0.11 (0.05)	1.72 (0.08)	0.42 (0.06)	36	0.061	0.994	0.13
Carr/Vitha[g] by HSGC	0.31 (0.09)	3.02 (0.07)	0.58 (0.09)	0.37 (0.14)	1.65 (0.13)	—[l]	22	0.070	0.998	0.31 (0.09)
Abraham et al.[h] several methods	1.20 (0.06)	2.79 (0.07)	0.40 (0.07)	0.13 (0.06)	1.58 (0.08)	0.54 (0.06)	132	0.171	0.985	0.061 (0.06)
Quina et al.[i] several methods	−0.62[k]	3.25 (0.09)	0.57 (0.08)	0.08 (0.07)	1.84 (0.11)	0.32 (0.07)	66	0.13	0.990	−0.018
Khaledi/ Yang[j] by MEKC	−1.87[k]	4.00 (0.05)	0.25 (0.04)	0.16 (0.02)	1.79 (0.04)	—[l]	60	0.159	0.954	0.049

[a] Uncertainties in the coefficients are shown in parentheses.
[b] n is the number of solutes in each regression.
[c] SE is the standard error of the regression.
[d] ρ is the correlation coefficient of each regression.
[e] Recalculated intercept terms based on a two-phase unit molar standard state partition model.
[f] Log k'_0.
[g] From Ref. 29, unbuffered system.
[h] From Ref. 16, varied methods and conditions.
[i] From Ref. 17.
[j] From Ref. 15, [SDS] = 0.02 M, phosphate buffer, older solute parameters.
[k] No errors were listed for this term.
[l] R_2 was not included in these LSER regression equations.

MEKC is an acceptable alternative to the other methods for studying solute–micelle interactions.

SDecS LSER

The LSER describing retention in SDecS micellar phases shown in Table 2 was obtained using the k' values and solvatochromic parameters in Table 1. Again, 4-butylaniline was an outlier and omitted from the LSER. Additionally, the coefficient of $\Sigma\alpha_2^H$ was found to be statistically insignificant for this surfactant and was therefore omitted from the regression. The omission of $\Sigma\alpha_2^H$ from the LSER does not significantly change the LSER coefficients or the correlation coefficient.

Figure 3 is a plot of experimental log k' values versus log k' values calculated using the LSER equation. Figure 4 shows normalized residuals for each

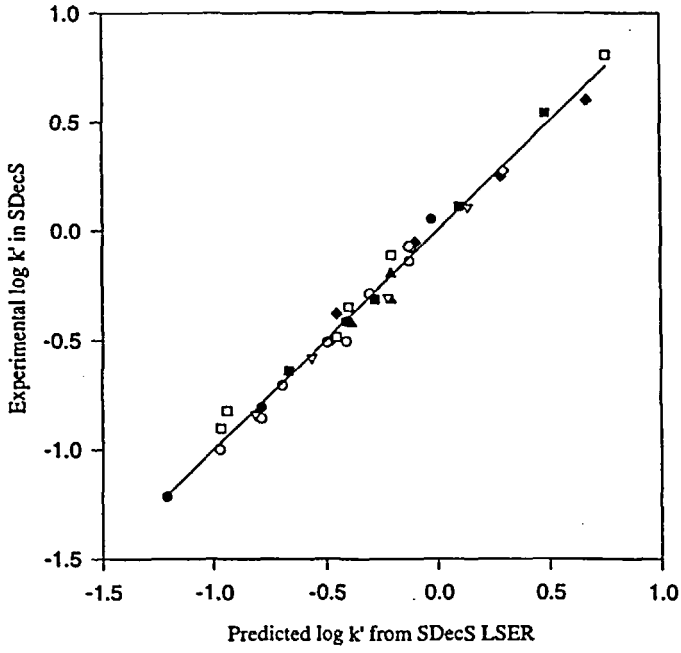

FIG. 3 Experimental versus predicted log k' values in SDecS. Symbols are (●) 1-nitroalkanes, (■) *n*-alkylbenzenes, (◆) *n*-alkylphenones, (▲) anisoles, (◇) nitrobenzenes, (□) benzamide and anilines, (▽) phenylalkanols, and (○) phenols. The solid line is a 1:1 line.

solute. As was the case with SDS, the retention of the solutes is well-predicted by the LSER with little dependence upon solute class.

Interpretation of SDecS LSER

Comparing the LSERs for SDS and SDecS in Table 2, we see that nearly all of the LSER coefficients are equal within one standard deviation, and are definitely so at the 95% confidence interval. Chemically, this means that the interactions governing the retention of solutes in the SDecS system are the same in both type and strength as those in the SDS system. Thus, the interpretation of the SDecS LSER is the same as that given for SDS above.

SOS LSER

Using the solutes shown in Table 1, the LSER in Table 2 was obtained for solute partitioning between water and SOS micelles. Capacity factors for

the full set of 37 compounds were not obtained for this surfactant for two reasons. First, retention times were quite long with this surfactant. More importantly, after obtaining the k' values shown in Table 1, we realized that the SOS LSER based on this truncated data set was already essentially equivalent to those for SDS and SDecS. Thus, we believe the other solutes would have simply served to overdetermine the LSER coefficients. Figure 5 is a plot of experimental log k' values versus log k' values calculated using the LSER equation. Figure 6 shows a plot of normalized residuals. From these graphs it is seen that the retention of all of the solutes are well-predicted by the LSER equation.

Interpretation of SOS LSER

The LSER describing solute transfer from the aqueous phase to the SOS micellar phase is very similar to the LSERs obtained in SDS and SDecS systems. All three show large dependencies on solute volume and hydrogen

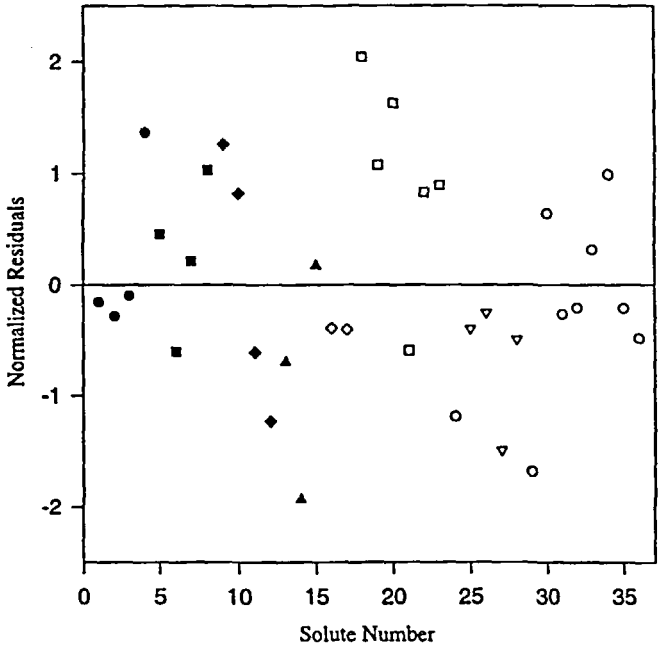

FIG. 4 Normalized residuals from SDecS LSER. Solute numbers are the same as in Table 1. Symbols are (●) 1-nitroalkanes, (■) *n*-alkylbenzenes, (◆) *n*-alkylphenones, (▲) anisoles, (◇) nitrobenzenes, (□) benzamide and anilines, (▽) phenylalkanols, and (○) phenols.

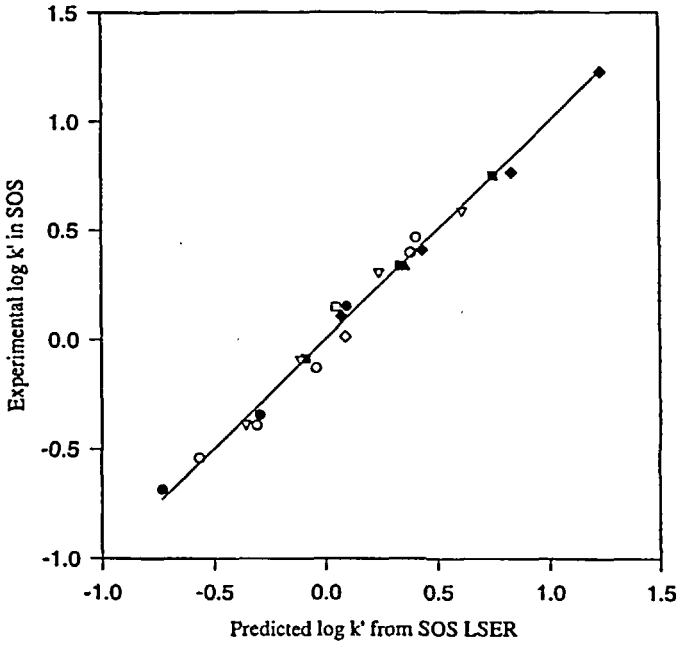

FIG. 5 Experimental versus predicted log k' values in SOS. Symbols are (●) 1-nitroalkanes, (■) *n*-alkylbenzenes, (◆) *n*-alkylphenones, (▲) anisoles, (◇) nitrobenzenes, (□) benzamide and anilines, (▽) phenylalkanols, and (○) phenols. The solid line is a 1:1 line.

bond basicity, with smaller contributions from solute dipolarity/polarizability, hydrogen bond acidity, and excess molar polarizability. The similarities of the LSERs indicate that the contributions to the partition process from the fundamental chemical forces are nearly identical in all the systems. Thus, the chemical interpretation of the SDS LSER presented elsewhere (15–17, 26) also holds for the SDecS and SOS LSERs.

Comparison of LSER Residuals

Figure 7 is a plot comparing the normalized residuals in the three alkyl sulfate micellar systems. It is clear that the pattern is not random since in many cases the same solutes are over- or underpredicted in all three systems. Clearly this cannot be due to experimental errors in the measurement of k'. This suggests that either the LSER model is not accounting for the entire energetics of the system, that is, its form is incorrect, or it lacks an important interaction term. The systematic deviations may also suggest that some of

the solute parameters do not accurately reflect the interaction abilities of the solutes. In this work, both explanations likely contribute to the nonrandom distribution of residuals as will be discussed below by focusing on several particular solutes.

In Figure 7, one trend in residuals that results from the inability of the LSER model to account for the energetics of the system is the systematic decrease in residuals in going from acetophenone (solute number 9) to valerophenone (#12). Since these solutes vary only in size, this suggests that the volume term is not fully accounting for the changes in partitioning arising from changes in the size of the molecules. This result is anticipated for the following reason. As will be discussed below, the free energy of partitioning of a methylene unit in these systems varies with the functionality of the homolog series. This indicates that the increase in the size of a solute by one methylene unit (i.e., the *same* increase in size) leads to different increments in the free energy of partitioning of the solutes depending on the homolog

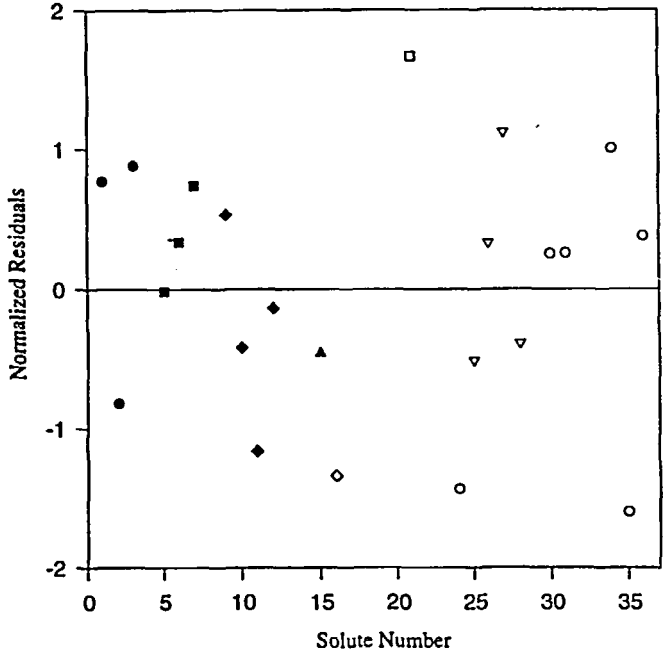

FIG. 6 Normalized residuals from SOS LSER. Solute numbers are the same as in Table 1. Symbols are (●) 1-nitroalkanes, (■) *n*-alkylbenzenes, (◆) *n*-alkylphenones, (▲) anisoles, (◇) nitrobenzenes, (□) benzamide and anilines, (▽) phenylalkanols, and (○) phenols.

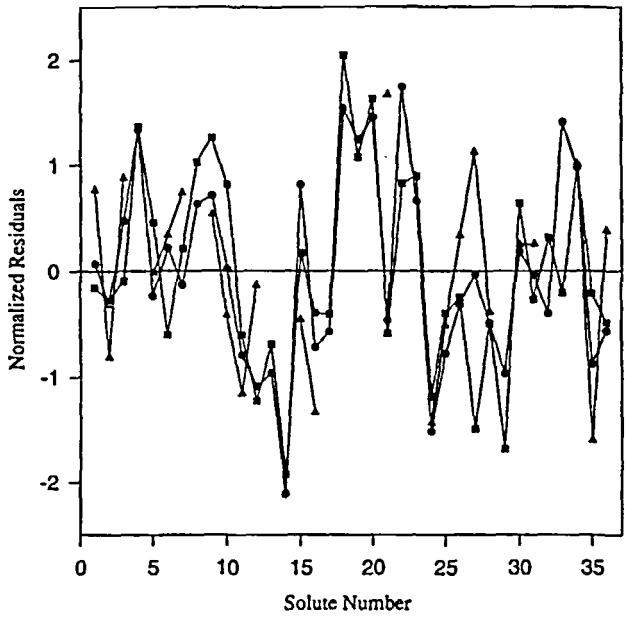

FIG. 7 Comparison of normalized residuals for all solutes in (●) SDS, (■) SDecS, and (▲) SOS.

family. Since the solute volume term is the only term that accounts for changes in the free energy of partitioning due to solute size, this means that the coefficient of V_x cannot be exact for all solutes and must actually allow for systematic errors as a function of solute size.

Given that partitioning in micellar systems is complicated by the fact that the micelles are not distinct phases but rather dynamic entities dissolved in the aqueous phase, and the fact that the LSER model was developed to describe partitioning in simpler bulk two-phase systems, it is not surprising that all of the subtle energetic effects arising from the many possible different solubilization sites (i.e., adsorption to the head groups, partitioning into the polar hydrated head group region, and partitioning into the nonpolar core) are not completely modeled, leading to LSER coefficients that are not exact for all solutes.

It is also noted that 2-nitroanisole (solute number 14), benzamide (#18), aniline (#19) and the aniline derivatives (#20–22), phenol (#24), *p*-cresol (#29), and 4-cyanophenol (#35) are poorly fit by the LSERs. The poor fit of 2-nitroanisole most likely arises from the fact that its solvatochromic param-

eters were assumed to be the same as those for 4-nitroanisole, and that those parameters are estimated rather than measured parameters. Thus, the parameters describing 2-nitroanisole may not properly reflect its interaction abilities. Additionally, it is a significant simplification to assume that the chemical nature of 2-nitroanisole is the same as 4-nitroanisole given that positional isomers can have dramatically different chemical properties that can significantly alter their partition behavior. This difference in behavior is borne out by the fact that in all three systems, 2- and 4-nitroanisole are well-resolved, offering experimental evidence that their retention cannot be modeled using the same interaction parameters.

The fact that benzamide (#18), aniline (#19), and the aniline derivatives (#20–22) all generally have large positive residuals (i.e., their retention is underpredicted by the LSERs) indicates that perhaps the LSER model cannot account for the retention of benzamide and aniline derivatives. It must also be kept in mind that the reproducibility of k' values for some of these solutes was typically worse than 3% and reached as high as 13% (compared to less than 1.5% for all other solutes). Furthermore, the behavior of anilines in aqueous systems is not easily described. In fact, a different set of β-parameters (denoted $\Sigma\beta_2^0$) developed by Abraham is used for aniline derivatives when considering systems containing water versus nonaqueous systems (23). This suggests that the behavior of the aniline derivatives in aqueous systems is complicated and therefore not easily modeled. This can lead to improper modeling of the behavior of these solutes and to large residuals relative to solutes with well-characterized behavior. Given all of these factors, it is not possible to elucidate the exact origin of the systematic nature of the residuals of benzamide and the aniline derivatives. In fact, a combination of all of these complications likely contributes to the residuals.

From the large residuals of phenol (#24), *p*-cresol (#29), and 4-cyanophenol (#35), one may conclude that the LSER is not properly modeling the retention of phenol derivatives and solutes with strong hydrogen bond donating ability. This conclusion, however, ignores the fact that the behavior of 10 other phenols and hydrogen bond donors are well-modeled by the LSER. Thus, it seems that if there are any inaccuracies of the LSER model regarding phenols and hydrogen bond donors, these inaccuracies are slight and do not seriously affect the ability of the LSERs to describe solute retention.

Comparison of Sodium Alkyl Sulfate LSERs to Other Important LSERs

It is very instructive to compare the water-to-sodium alkyl sulfate (SAS) micellar LSERs (Table 2) with LSERs describing the transfer of solutes from water to bulk organic liquids. These comparisons help elucidate the effect of

water within the micelles on the partition coefficients. In that regard, two important bulk phase partitioning systems are water/octanol and water/hexadecane systems. The water/octanol system is important because it is used to predict biological activity and interactions of solutes with membranes (27). The water/hexadecane system is important because it represents two extremes in solvents and has also been used as a model of the stationary phase in liquid chromatography (28–30). We give below the LSERs reported by Abraham et al. for solute transfer from water to hexadecane ($K_{hd,w}$, Eq. 4) (25), and water to 1-octanol ($K_{o,w}$, Eq. 5) (25).

$$\log K_{hd,w} = 0.09 + 4.43V_x - 1.62\pi_2^H - 359\Sigma\alpha_2^H - 4.87\Sigma\beta_2^H + 0.67R_2$$
$$n = 370, \quad \overline{SD} = 0.12, \quad \rho = 0.998 \qquad (4)$$

$$\log K_{o,w} = 0.09 + 3.81V_x - 1.05\pi_2^H + 0.03\Sigma\alpha_2^H - 3.46\Sigma\beta_2^H + 0.56R_2$$
$$n = 613, \quad \overline{SD} = 0.12, \quad \rho = 0.997 \qquad (5)$$

SAS Micelles Compared to Hexadecane

A comparison of the coefficients of the water/SAS LSERs with those in the water/hexadecane LSER readily shows how the presence of water in the micelles affects partitioning. If SAS micelles were exactly like water, we would expect all the coefficients to be zero. In other words, for a hypothetical transfer of solutes from water to water, all of the coefficients and the intercept must be zero. When real transfer processes are studied, deviations from zero indicate that the phase being studied is chemically different from water, and the magnitude of the deviations reflects the degree of difference. Comparing the water/SAS LSERs to the water/hexadecane LSER, we see that all the coefficients in the water/SAS LSERs are closer to zero than those in the water/hexadecane LSER. This means that the properties of SAS micelles are closer to those of water than are the properties of hexadecane.

It is at this point that we can begin to comment on the nature of the solutes' environment in the micelle and on the nature of the micelle itself. If the locus of solubilization were the micellar core, which is said to be alkane-like (20, 31, 32), we would expect the coefficients of the water/SAS LSERs to be very similar to those of the water/hexadecane LSER. Instead, we see marked and systematic differences between the LSERs. For instance, the *a* and *b* coefficients, which represent the difference in the solvents' abilities to participate in hydrogen bonding with the solutes, are very much smaller in the SAS LSERs than in the hexadecane LSER. This means that SAS micelles are much more like water in their ability to participate in hydrogen bonding than is hexadecane. This difference between micelles and hexadecane must be due to the hydrogen bond accepting ability of the anionic sulfate head groups

and/or the presence of water within micelles. This means that the solutes are solubilized in a region containing water and/or the head groups, otherwise the presence of water and the head groups would have no effect on the SAS LSERs relative to the hexadecane LSER.

We believe that water inside the micelles, and not just the sulfate head groups, must be playing some role in governing partitioning because of the greatly diminished *b* coefficient in the SAS LSERs relative to that observed in the water/hexadecane LSER. Since SAS monomers are not themselves hydrogen bond donors, the acidity of SAS micelles must result from the only other hydrogen bond donor present in the micelles, namely water. The fact that water is present near the head groups and penetrates to at least two carbons beyond the sulfate head groups is well accepted (33–35). The smaller *b* coefficient for SAS micelles relative to hexadecane is therefore consistent with current knowledge about micellar structures and reveals the extent to which the water affects partitioning of hydrogen bond bases. Overall, from the comparisons of the SAS and hexadecane LSERs, we conclude that the solutes are solubilized in the polar, hydrated head group region of the micelles.

We can also learn something from the mV_x terms in the LSERs about the relative cohesivity/polarizability of SAS micelles. We see that the *m* coefficient is not as large for partitioning from water into SAS micelles as it is for partitioning into hexadecane. If the two coefficients were equal, we would conclude that net size-dependent interactions (cavity formation/dispersion) in SAS micelles are the same as in hexadecane. The *m* coefficient for SAS micelles, however, is considerably smaller than for bulk hexadecane. Thus, the net size-dependent interactions in the water/SAS transfers are somewhat less influential in determining the extent of partitioning than they are in the water/hexadecane transfer. The *m* coefficient, therefore, reveals that there are differences in the structure and interactions of SAS micelles when compared to hexadecane. Given these differences and those mentioned above, we conclude that hexadecane is not a good model of micelles and that solutes do not partition into the micellar core but rather into the polar, hydrated head group region. In fact, the most significant inference here is that because the micellar environment is so chemically different from that of hexadecane, polar solutes can interact with and partition into the micelles. If the *s*, *a*, and *b* coefficients were as negative for micelles as they are for hexadecane, micelles would be very poor solubilizing agents for polar solutes, very much limiting their utility as solubilizing agents. Thus, the greater polarity and hydrogen bond ability of the micelles relative to hexadecane greatly enhances their utility as solubilizers in a wide variety of applications.

Regarding the discussion of the *m* coefficient above, we note that the methylene unit free energy of transfer from gas to bulk alkanes is independent of the density of the bulk alkane (36). Since the characteristic volume of a

molecule is a linear function of the number of methylene units (37), this means that the transfer free energy per unit volume is also independent of the density of the bulk alkane. In other words, the *m* coefficient from a regression of the transfer free energy versus solute volume is independent of the alkane density. Thus, differences in the density of the alkane chains in the SAS micelles and in bulk hexadecane cannot explain the difference in the *m* coefficients for the two LSERs discussed above.

SAS Micelles Compared to 1-Octanol

Partition coefficients in micellar systems have often been correlated with octanol/water partition coefficients (16, 38, 39). In Eq. (5) we show the LSER for transfer of solutes from water to octanol. The coefficients in this LSER are closer to those found in the SAS LSER than are the coefficients in the alkane LSER. Additionally, the volume and hydrogen bond basicity terms are dominant in each LSER. Thus, octanol appears to be a better model of SAS micelles than is bulk hexadecane. This supports the conclusion that solutes do not partition into the nonpolar core of the micelles, but rather are located in a polar environment which is capable of hydrogen bonding. We note, however, that the SAS and 1-octanol LSERs still exhibit rather large differences, especially with regards to the magnitude of the *b* and *m* coefficients. The ratio of *b* to *m* is -0.91 for water–1-octanol systems and averages to -0.62 for the water–SAS micelles, indicating an increased dependence on solute hydrogen bond basicity relative to cavity formation/dispersion for water-to-octanol partitioning relative to water-to-SAS partitioning. Thus, 1-octanol, although being a better model of the micellar environment than hexadecane, is still chemically different from SAS micelles. The difference in LSERs means that correlations between $K_{o,w}$ and $K_{w,m}$ values, although useful, are limited.

Additionally, the differences between 1-octanol and SAS micelles are quite important since both systems have been advocated as models of biological systems (29, 40–42). Octanol/water partitioning has been used extensively to correlate biological phenomena such as toxicity and solubility of chemicals in lipid membranes (27, 41), while micelles have been used to model the location and behavior of proteins and peptides in lipid bilayers (40, 42). The differences in the LSERs of octanol and SAS micelles indicate that one or the other system will better model biological phenomena. In other words, since the two systems are chemically dissimilar, it is likely that the chemical interactions in biological systems will be more closely reproduced by either octanol or SAS micelles, depending on the biological system being studied. We have done some preliminary comparisons of biological LSERs which support this conclusion.

Overall, from the comparison of the LSERs we conclude that solutes partition into a rather polar, hydrated region of SAS micelles and not into the alkane-like core. Thus, 1-octanol, while still chemically quite different than SAS micelles, is a better micellar model than is hexadecane. These conclusions are the same as those we reached in a previous paper (18) by comparing partition coefficients for several solutes and their methylene units in several different solvent systems.

Application of Results to Selectivity in MEKC

While these studies were undertaken primarily to provide insights into the fundamental chemical forces governing solute partitioning, they also provide very practical information about retention in MEKC using sodium alkyl sulfate surfactants. For example, one conclusion that can be drawn from the LSERs regarding the practice of MEKC is that the selectivity of the separation is not altered by changing the chain length of the sodium alkyl sulfate surfactant. This can be shown by considering the definition of the selectivity (α) of a separation of solutes A and B, where B elutes after A,

$$\alpha = k'_B/k'_A \tag{6}$$

which can be rewritten as

$$\log \alpha = \log k'_B - \log k'_A \tag{7}$$

The solutes A and B will have the solvatochromic parameters π^H_{2i}, $\Sigma\alpha^H_{2i}$, $\Sigma\beta^H_{2i}$, V^x_{2i}, and R_{2i}, where i is either A or B depending on which solute is being discussed. Substituting the proper solute parameters into the LSER for a given surfactant system (e.g., SDS) yields Eqs. (8) and (9):

$$\log k'_{A\text{-SDS}} = \log k'_{o,SDS,A} + r_{SDS}R_{2A} + s_{SDS}\pi^H_{2A} + a_{SDS}\Sigma\alpha^H_{2A} + b_{SDS}\Sigma\beta^H_{2A} + m_{SDS}V^x_{2A} \tag{8}$$

$$\log k'_{B\text{-SDS}} = \log k'_{o,SDS,B} + r_{SDS}R_{2B} + s_{SDS}\pi^H_{2B} + a_{SDS}\Sigma\alpha^H_{2B} + b_{SDS}\Sigma\beta^H_{2B} + m_{SDS}V^x_{2B} \tag{9}$$

Substituting Eqs. (8) and (9) into (7) yields Eq. (10):

$$\log \alpha_{SDS} = r_{SDS}(R_{2B} - R_{2A}) + s_{SDS}(\pi^H_{2B} - \pi^H_{2A}) + a_{SDS}(\Sigma\alpha^H_{2B} - \Sigma\alpha^H_{2A}) + b_{SDS}(\Sigma\beta^H_{2B} - \Sigma\beta^H_{2A}) + m_{SDS}(V^x_{2B} - V^x_{2A}) \tag{10}$$

which can be rewritten as Eq. (11):

$$\log \alpha_{SDS} = r_{SDS}(\Delta R_2) + s_{SDS}(\Delta \pi_2^H) + a_{SDS}(\Delta \Sigma \alpha_2^H) + b_{SDS}(\Delta \Sigma \beta_2^H) + m_{SDS}(\Delta V_2^x) \quad (11)$$

Writing the same equations for a different surfactant system (e.g., SOS) yields Eq. (12):

$$\log \alpha_{SOS} = r_{SOS}(\Delta R_2) + s_{SOS}(\Delta \pi_2^H) + a_{SOS}(\Delta \Sigma \alpha_2^H) + b_{SOS}(\Delta \Sigma \beta_2^H) + m_{SOS}(\Delta V_2^x) \quad (12)$$

The values of ΔR_2, $\Delta \pi_2^H$, $\Delta \Sigma \alpha_2^H$, $\Delta \Sigma \beta_2^H$, and ΔV_2^x are independent of the micellar systems since they depend only on the solutes being studied. Thus, these values are the same in both Eqs. (11) and (12). Finally, if $r_{SDS} = r_{SOS}$, $s_{SDS} = s_{SOS}$, $a_{SDS} = a_{SOS}$, $b_{SDS} = b_{SOS}$, and $m_{SDS} = m_{SOS}$, then $\log \alpha_{SDS} = \log \alpha_{SOS}$. Thus, different micellar systems with identical LSER coefficients do not provide different selectivities. We note that this result is general for all chromatographic systems. Regarding this specific study, this means that SDS, SDecS, and SOS will provide very similar selectivities since their LSER coefficients are quite similar. SDS, however, is the most commonly used of these surfactants because it has the lowest CMC, keeping operating currents low.

We note that it is possible that real chemical effects such as electrostatic, steric effects, and solute localization, which could distinguish the solute/micelle interactions in these different systems, may exist but are not explicitly modeled in the LSER equation. Thus, the behavior of these systems may exhibit subtle differences regarding their respective selectivities. However, the LSERs do reveal that, based on several important general solute/micelle interaction modes, these surfactants do behave quite similarly.

Using a similar approach to the one described above, one can look at the selectivity of a separation in a single surfactant system arising from each *specific* chemical interaction. For example, if one is interested in the selectivity of the separation of solutes that differ only in their hydrogen bond basicities (i.e., $\Delta \Sigma \beta_2^H \neq 0$ while ΔR_2, $\Delta \pi_2^H$, $\Delta \Sigma \alpha_2^H$, and ΔV_2^x are zero, or a system in which b is the only significant coefficient), then

$$\log \alpha = b(\Delta \Sigma \beta_2^H) \quad (13)$$

From this equation it is seen that surfactant systems with larger magnitudes of b will lead to larger selectivities. Conversely, if the coefficient of interest is small, such as the a coefficient for SDS, SDecS, and SOS, then the selectivity of those systems with regards to separations based on the solutes' hydrogen bond acidities will be small. Thus, looking at the LSERs, we can say that SDS, SDecS, and SOS will provide little selectivity based on solute hydrogen bond acidity, dipolarity/polarizability, and excess molecular polarizability,

TABLE 4
Comparison of Free Energies of Transfer of Methylene Groups for Five Homolog Series in SDS, SDecS, and SOS Micellar Systems[a]

	SDS	ρ[b]	n[c]	SDecS	ρ	n	SOS	ρ	n
4-Alkylanilines	−657 ± 56	0.996	3	−652 ± 64	0.995	3	—[d]	—[d]	—[d]
Nitroaliphatics	−603 ± 10	0.999	4	−571 ± 16	0.999	4	−567 ± 59	0.995	3
Alkylbenzenes	−572 ± 13	0.999	4	−542 ± 24	0.998	4	−559 ± 6	0.999	3
Alkylphenones	−491 ± 13	0.999	4	−443 ± 9	0.999	4	−483 ± 27	0.997	4
Phenylalkanols	−473 ± 17	0.999	4	−425 ± 36	0.993	4	−449 ± 21	0.998	4

[a] Data taken at 25°C.
[b] ρ is the correlation coefficient of the regression of log k' versus the number of methylene units in each compound used to calculate ΔG_{CH_2}.
[c] n is the number of compounds in each regression.
[d] Data not available.

while providing greater selectivity based on solute size and hydrogen bond basicity. These results are similar to those generally found in LSER studies of retention in reversed-phase liquid chromatography (RPLC) (43, 44).

Free Energy of Partitioning of Methylene Units

The free energies of partitioning of methylene units ($\Delta G^\circ_{CH_2}$) for different homolog series in SDS, SDecS, and SOS are shown in Table 4 and Fig. 8. Clearly, there are differences in the methylene unit partitioning depending on the functionality of the homolog series. These differences will be discussed below. Before beginning that discussion, however, we note that there is very good agreement between the $\Delta G^\circ_{CH_2}$ values we determined using HSGC (18) and those determined by MEKC. For alkylbenzenes, the $\Delta G^\circ_{CH_2}$ values from HSGC and MEKC are −534 ± 6 and −573 ± 13 cal/mol, respectively. Additionally, for the 1-nitroaliphatics the $\Delta G^\circ_{CH_2}$ value is −608 ± 11 cal/mol from HSGC and −603 ± 10 cal/mol from MEKC. Thus, two entirely different measurement methods produce very similar results. This lends confidence that the $\Delta G^\circ_{CH_2}$ values determined by MEKC are reliable and reflect the chemistry of the system being studied.

Generally, from the $\Delta G^\circ_{CH_2}$ values the conclusion can be drawn that none of the solutes are located in an alkane-like environment when inside the micelle. If they were, one would expect a methylene unit increment similar to that for the transfer of solutes from water to a bulk alkane ($\Delta G^\circ_{CH_2} \approx -860$ cal/mol) as discussed elsewhere (18). Instead, the $\Delta G^\circ_{CH_2}$ values for all the homolog series are considerably smaller in magnitude, being better represented by the methylene unit transfer from water to short, polar solvents

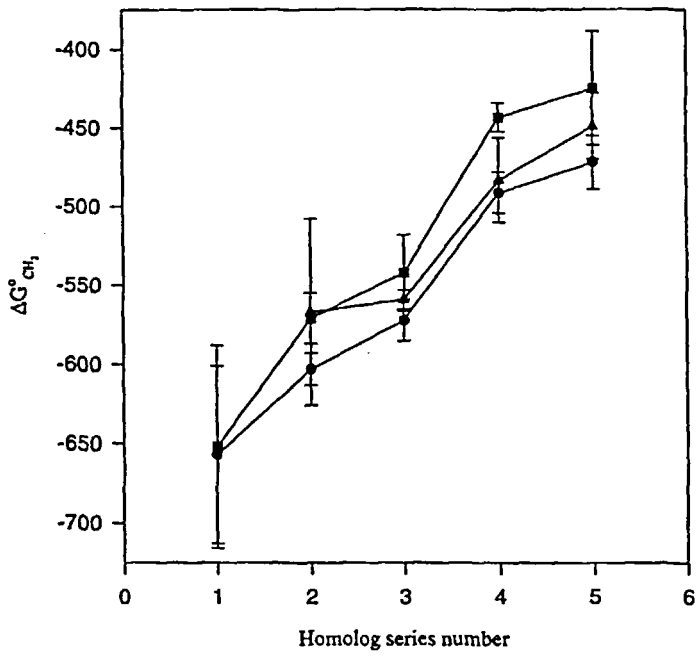

FIG. 8 $\Delta G^{\circ}_{CH_2}$ values for five homolog series in (●) SDS, (■) SDecs, and (▲) SOS. The homolog series numbers are: (1) 4-alkylanilines, (2) nitroaliphatics, (3) alkylbenzenes, (4) alkylphenones, and (5) phenylalkanols.

such as acetonitrile ($\Delta G^{\circ}_{CH_2(CH_3CN)} = -660$ cal/mol) and nitromethane ($\Delta G^{\circ}_{CH_2(CH_3NO_2)} = -620$ cal/mol) (18).

As stated above, there are considerable differences in the $\Delta G^{\circ}_{CH_2}$ values of partitioning depending on the functionality of the homolog series. Additionally, these dependencies are the same in each surfactant system. In all these systems the order of increasing magnitude of $\Delta G^{\circ}_{CH_2}$ values is: phenylalkanols $<$ alkylphenones $\ll$ alkylbenzenes $<$ nitroaliphatics $<$ 4-alkylanilines. The fact that this sequence is the same in all three surfactants suggests that the differences are real and chemically meaningful. We believe that they reflect different loci of solubilization of the solutes inside the micelles. For example, the 4-alkylanilines and the nitroaliphatics have the most negative $\Delta G^{\circ}_{CH_2}$ values. We infer that these solutes may be located further inside the micelles than the other homologs. In other words, they may be located deeper into the alkane-like core of the micelle and further away from the polar, hydrated head group region than are the other solute homolog series. This may arise

from the alkyl chains of these homologs "pulling" the solutes deeper into the core where their interactions with the surfactant alkyl chains is increased.

The fact that the 4-alkylaniline and 1-nitroaliphatic homolog series have greater negative $\Delta G^{\circ}_{CH_2}$ values than the alkylbenzenes is surprising and difficult to interpret. Chemical intuition suggests that the alkylbenzenes, being the most nonpolar series studied, would be the most likely compounds to partition into a nonpolar environment leading to the most negative $\Delta G^{\circ}_{CH_2}$, especially if the alkyl chains of the solutes can "pull" solutes further into the core as postulated above. The fact that this behavior is not observed supports literature reports suggesting that benzene is actually sorbed onto the surface of the micelle (45), or at least remains localized in the relatively polar head group region (46, 47).

The phenylalkanols and alkylphenones have the least negative $\Delta G^{\circ}_{CH_2}$ values. This indicates that the methylene units are in a more polar environment than are the methylene units of the 4-alkylaniline and nitroaliphatic solutes. This can arise if the solutes reside in the head group region with the alkyl chains oriented perpendicularly (tangentially) to the surfactant chains. It may also arise from the functional group "pulling" the solutes out into the hydrated head group region to increase specific interactions. For example, the hydroxyl functionality of phenylalkanols may limit the depth to which they can partition because they have strong favorable hydrogen bond interactions with water. These orientation effects have been suggested in the literature (32, 34, 48, 49). Due to the increased contact between methylene units and water arising from these orientations, the $\Delta G^{\circ}_{CH_2}$ value would decrease in magnitude relative to solubilization further into the nonpolar core where interactions with water are less likely and where the attractive interactions with hydrocarbon chains are more likely.

Finally, we note that generally for each homolog series, the magnitude of the $\Delta G^{\circ}_{CH_2}$ values is largest in SDS and smallest in SDecS. The magnitude of the errors in the $\Delta G^{\circ}_{CH_2}$ values, however, cause considerable overlap, and thus no trend in $\Delta G^{\circ}_{CH_2}$ values as a function of the surfactant chain length can be definitively assigned.

Homoenergetic and Homeoenergetic Retention

In 1980 Horvath et al. introduced a method of classifying chromatographic systems based on the relative energetics of retention (50). In their method the logarithm of the capacity factor of a series of solutes measured on one phase are regressed against the logarithms of capacity factors of the same solutes on a different phase. Pairs of phases yielding a slope of unity are said to be homoenergetic, meaning that the intrinsic thermodynamic behavior of the phases is *identical*. Pairs of phases with a strong linear relationship ($r >$

0.95) having a nonunity slope are said to be homeoenergetic, suggesting that the physicochemical basis of retention is *similar* for the two phases. If no strong correlation is found ($r < 0.95$), the retention is said to be heteroenergetic, implying little similarity in the solvation of the solutes in the two systems.

We have applied the same analysis to retention in MEKC and find that it strongly supports the conclusion that the retention in all three of the surfactant systems studied is quite similar if not identical. The following regressions were obtained (standard errors for the intercept and slope are shown in parentheses):

$$\log k'_{SDS} = 0.42\ (\pm\ 0.01) + 1.08\ (\pm\ 0.02) \log k'_{SDecS} \qquad (14)$$
$$r = 0.996, \quad n = 35, \quad SE = 0.04$$

$$\log k'_{SDS} = -\ 0.14\ (\pm\ 0.01) + 1.02\ (\pm\ 0.02) \log k'_{SOS} \qquad (15)$$
$$r = 0.994, \quad n = 23, \quad SE = 0.05$$

$$\log k'_{SDecS} = -0.51\ (\pm\ 0.01) + 0.92\ (\pm\ 0.03) \log k'_{SOS} \qquad (16)$$
$$r = 0.990, \quad n = 23, \quad SE = 0.06$$

It is seen that in all cases the slope is between 0.92 and 1.08 (i.e., very close to unity) and all three regressions have strong correlations. This analysis shows that the interactions of solutes with micelles that give rise to retention are quite similar but possibly not identical in these systems. This means that the nature of the underlying fundamental thermodynamic forces controlling solute/micelle interactions is insensitive to the length of the surfactant alkyl chain length, at least in the limited chain length range studied here.

CONCLUSIONS

Overall, we conclude that changing the surfactant chain length of sodium alkyl sulfate surfactants from C_8 to C_{12} does not significantly affect the fundamental nature of the interactions between solutes and micelles. Practically, this means that the chromatographic selectivities of the three micellar phases studied are equivalent. Additionally, these studies show that of the different interactions explored, selectivity is greatest when based upon solute size and/or hydrogen bond basicity. Also, the $\Delta G^{\circ}_{CH_2}$ values for five homolog series suggest different orientations or regions of solubilization of solutes depending on the functionality of the solutes. Most importantly, the constancy of the LSER as a function of the surfactant chain length matches the prediction of similar LSERs for SDS, SDecS, and SOS that was made based upon the view that solutes reside in the head group region and not in the nonpolar core.

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