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Chemical selectivity in micellar electrokinetic chromatography II. Rationalization of elution patterns in different surfactant systems

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Abstract

Retention behavior in micellar electrokinetic chromatography (MEKC) is investigated using linear solvation energy relationships (LSERs) for two pseudo-stationary phases, one consisting of cationic micelles of tetradecyltrimethylammonium bromide (C_{14}TAB) and the other of an anionic triblock copolymer, poly(methyl methacrylate–ethyl acrylate–methacrylic acid) (Elvacite 2669). It was found that solutes' migration behaviors in these two MEKC systems are mainly influenced by their size ($V/100$) and hydrogen bonding acceptor (HBA) strength (β). However, solutes' hydrogen bonding donor (HBD) strength (α) has minor effects on their migration in MEKC. The characteristics of these two systems were compared to three other previously reported anionic micellar systems of sodium dodecyl sulfate (SDS) (anionic hydrocarbon), sodium cholate (SC) (anionic bile salt) and lithium perfluorooctane sulfonate (LiPFOS) (anionic fluorocarbon). It was concluded that hydrogen bonding interactions play a major role in providing different chemical selectivity among these five MEKC systems. Both C_{14}TAB micelles and the ionic polymer of Elvacite 2669 provide hydrogen bonding acceptor (HBA) sites for solutes, which is similar to SC micelles. In fact, C_{14}TAB is the strongest HBA, while Elvacite 2669 has HBA strength similar to that of SC micelles. On the other hand, the fluorocarbon micelles of LiPFOS are the strongest hydrogen bond donor (HBD) micelles, followed by the weak HBD SDS micelles. In general, cavity formation has little or no effect on chemical selectivity among hydrocarbon surfactant MEKC systems (i.e., SDS, SC and C_{14}TAB). Information obtained from the LSER analysis is used to rationalize the elution patterns in MEKC with different types of pseudo-stationary phases.

Keywords: Selectivity; Linear solvation energy relationships; Solvatochromic parameters; Micelles; Surfactants

1. Introduction

Micellar electrokinetic chromatography (MEKC) et al. [1] is a powerful capillary electrophoresis (CE) technique for the separation of mixtures of uncharged and/or charged compounds. Sodium dodecyl sulfate (SDS) has been the most widely used surfactant in MEKC since it was first reported by Terabe et al. [1]. This is due to certain merits of SDS such as availability, UV transparency (cutoff wavelength is less than 210 nm), high water solubility, low cost, and low toxicity. It can also be used in a wide pH range [2–4]. However, many reports have demonstrated significant effects of surfactant type on MEKC separations [2–12]. Migration behavior and separation in MEKC can be easily manipulated and controlled through proper selection of the surfactant type [5], mixed micelles [6], or inclusion of buffer additives, e.g., organic solvents [7–9], cyclodextrins [10,11] and urea [12]. In MEKC, it is very easy to

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change the chemical composition of the system by simply rinsing the capillary with a new micellar solution [2–4]. Because solute–micelle interactions are not fully understood, the selection of a suitable micelle composition in MEKC is presently accomplished by trial and error or according to analysts' knowledge and experience.

In our previous papers [13,14], chemical interactions between 60 aromatic compounds and three anionic micelles (i.e., SDS, SC and LiPFOS) were investigated through linear solvation energy relationship (LSER) studies. Based on the LSER methodology [13–21], the logarithm of the capacity factor in MEKC ($\log k'$) can be described as:

$$\log k' = \mathrm{SP}_o + mV/100 + s\pi^* + b\beta + a\alpha \qquad (1)$$

where V is the solute molar volume (size), π^* is a measure of solute ability to engage in dipolar interactions with solvent, β is the solute hydrogen bond accepting (HBA) ability and α is the solutes hydrogen bond donating (HBD) ability. SP_o is the regression constant which includes some MEKC system properties (e.g., phase ratio). Regression coefficients m, s, b and a, on the other hand, represent MEKC system cohesiveness, dipolarity, HBD acidity and HBA basicity, respectively [14]. The term $mV/100$ is the disfavorable cavity formation process of separating the solvent molecules in order to create a properly sized cavity for solutes. The term $s\pi^*$ represents the favorable dipolar interactions between solutes and solvents. In type A hydrogen bonding interaction (i.e., $b\beta$), solutes act as hydrogen bond acceptors (HBAs) (or bases) and solvents are hydrogen bond donors (HBDs) (or acids); on the other hand, in type-B hydrogen bonding interaction (i.e., $a\alpha$), solutes act as HBDs (or acids) and solvents are HBAs (or bases).

In this work, retention behaviors in two MEKC systems are investigated and characterized through LSERs; one consists of cationic micelles of C_{14}TAB and the other involves a triblock copolymer surfactant (Elvacite 2669). The effects of surfactant type and concentration on migration behavior, chemical selectivity and separation is discussed. On the basis of LSER results, elution patterns in different types of surfactants are rationalized in MEKC.

2. Experimental

In the MEKC system using C_{14}TAB surfactant, all experiments were performed on a laboratory-built CE system that was comprised of a 0–30 kV high-voltage power supply (Series EH, Glassman High Voltage, Whitehouse station, NJ, USA). However, in the copolymer (Elvacite 2669) surfactant MEKC system, the experiments were carried out on a Beckman P/ACE system 2100, except where indicated otherwise. A 50 μm I.D., 370 μm O.D. fused-silica capillary tubing (Polymicro Technologies, Phoenix, AZ, USA) was used as the separation column. In the laboratory-made CE system, the total length of the capillary was 62 cm and detection was performed 50 cm downstream. The samples were introduced into the anodic end of the capillary by gravity, at a 10 cm height for 5 s. A negative voltage of 20 kV was applied throughout the experiment with C_{14}TAB surfactant because the electroosmotic flow was reversed under the experimental conditions. A variable-wavelength UV detector (Model 200, Linear Instruments, Reno, NV, USA) was used with a wavelength of 254 nm for C_{14}TAB. The electropherograms were recorded using an integrator (Model SP 4200; Spectra-Physics, San Jose, CA, USA). Temperature was ambient. In the Beckman P/ACE system 2100, the total length of capillary was 57 cm and detection was performed 50 cm downstream. The samples were introduced into the anodic end of the capillary by pressure for 2 s. A positive voltage of 20 kV, detection wavelength of 254 nm and 25°C were kept constant throughout the experiment. The separations shown in Fig. 4a–f were carried out on a homemade CE system with a variable-wavelength UV-Vis detector (Model 500, Scientific Systems (SSI), State College, PA, USA) operating at 254 nm, 62 cm×50 cm capillary, 20 kV and ambient temperature.

2.1. Reagents

The running buffer of tetradecyltrimethylammonium bromide (C_{14}TAB) (Sigma, St. Louis, MO, USA) was made by dissolving the required amount of the surfactant in 50 mM phosphate buffer solution at pH 7.0. The running buffer of poly-

(methyl methacrylate–ethyl acrylate–methacrylic acid) (Elvacite 2669; ICI Acrylics, Wilmington, DE, USA) was made by dissolving the required amount of the surfactant in 100 m*M* 3-[cyclohexylamino]-1-propanesulfonic acid (CAPS) buffer solution at pH 10.0. All the running buffers were filtered through a 0.45-μm nylon-66 membrane filter (Rainin, Woburn, MA, USA). CAPS was purchased from Sigma. All the test solutes were purchased from Aldrich (Milwaukee, WI, USA) [14]. SDS and SC were also purchased from Aldrich. LiPFOS was a gift from 3M Corp. (St. Paul, MN, USA). All test solutes were dissolved in methanol. The migration time of methanol was used as the marker for electroosmotic flow of the systems (i.e., t_{eo}). The marker of micelles (i.e., t_{mc}) was *n*-dodecanophenone.

3. Results and discussion

The results of the LSER analysis of the retention behaviors of 60 aromatic test solutes (see Table I in Ref. [14]) in MEKC using two pseudo-stationary phases, C_{14}TAB micelles and copolymer Elvacite 2669, are listed in Table 1. The results for three anionic micellar systems (i.e., SDS, SC and LiPFOS) that were reported previously [14] are also listed for comparative purposes.

It can be seen that coefficients *m* and *b* are the largest among these four coefficients (i.e., *m*, *s*, *b* and *a*) in C_{14}TAB and Elvacite 2669 MEKC systems. This means that cavity formation (i.e., $mV/100$) and type-A hydrogen bonding interaction (i.e., $b\beta$) are the two most important factors that influence the retention behavior in MEKC systems with these two types of psuedo-stationary phases. However, type-B hydrogen bonding interaction (i.e., $a\alpha$) has a minor effect on retention behavior, since *a* values are much smaller than *m* and *b* values. This is similar to retention behaviors in MEKC with SDS and SC micelles, as well as partitioning in an octanol–water system and retention in reversed-phase LC. However, these are different from retention behavior in fluorocarbon micelles of LiPFOS MEKC systems in which cavity formation and type-B hydrogen bonding interaction are the two dominant factors that influence retention.

The large positive *m* values show that capacity

Table 1
Effect of micelles on chemical interactions in MEKC

SP	SP_o	*m*	*s*	*b*	*a*	$-b/m$	*n*	*r*	S.E.
50 mM phosphate, pH 7.0									
log *k'*									
0.02 *M* SDS	−1.87	4.00	−0.25[a]	−1.79	−0.16[a]	0.45	60	0.9538	0.159
		(0.39)	(0.31)	(0.31)	(0.15)				
0.04 *M* SDS	−1.49	3.95	−0.26[a]	−1.80	−0.18	0.46	60	0.9553	0.156
		(0.39)	(0.31)	(0.31)	(0.15)				
0.01 *M* C_{14}TAB	−1.78	3.96	−0.26[a]	−2.75	0.99	0.69	60	0.9578	0.159
		(0.39)	(0.31)	(0.31)	(0.15)				
0.06 *M* SC	−1.62	3.89	−0.27[a]	−2.88	0.23	0.74	60	0.9684	0.144
		(0.39)	(0.31)	(0.31)	(0.15)				
0.08 *M* SC	−1.38	3.82	−0.32	−2.85	0.18	0.75	60	0.9691	0.142
		(0.39)	(0.31)	(0.31)	(0.15)				
0.04 *M* LiPFOS	−1.51	2.44	−0.25[a]	0.16[a]	−0.98	−0.07	60	0.9511	0.135
		(0.39)	(0.23)	(0.31)	(0.15)				
100 mM CAP, pH 10.0									
log *k'*	−1.55	3.00	0.09[a]	−2.33	0.24	0.78	60	0.9543	0.134
2% Elvacite 2669		(0.31)	(0.23)	(0.31)	(0.15)				
log P_{ow}	0.17	5.62	−0.66	−3.90	0.14[a]	0.69	60	0.9863	0.135
		(0.39)	(0.23)	(0.31)	(0.15)				

n is the number of test solutes, *r* is the correlation coefficient of linear regression; S.E. is the standard error of log *k'* (or log P_{ow}) estimated. The numbers in parentheses represent the 95% confidence intervals for the coefficients.
[a]Values are not significant at the 95% confidence level according to *t*-test results.

factors in MEKC systems increase with solutes' volume (or size) [14]. The coefficient m is linearly related to the difference in the cohesiveness of the aqueous phase and the micellar phase as shown by

$$m = M(\delta^2_{aq} - \delta^2_{mic}) \quad (2)$$

where δ is the Hildebrand solubility parameter and δ^2 is directly related to the cohesive energy of a phase. The subscript aq is for the aqueous phase and the subscript mic represents the micellar phase. M is a proportionality factor. The larger the m value, the smaller δ^2_{mic}, i.e., the micellar phase is less cohesive. An assumption is made that δ^2_{aq} is the same for these systems, even though the bulk aqueous phase in micellar solutions contains monomer surfactants (at a concentration about CMC), as well as buffer salts. According to Table 1, the magnitude of coefficient m can be ranked as:

$$m(\text{LiPFOS}) < m(\text{Elvacite 2669}) < m(\text{SC}) \leq m(\text{C}_{14}\text{TAB}) \approx m(\text{SDS}) < m(\text{1-octanol})$$

thus, the ranking of cohesiveness (δ^2) of micelles is as follows:

$$\delta^2(\text{LiPFOS}) > \delta^2(\text{Elvacite 2669}) > \delta^2(\text{SC}) \geq \delta^2(\text{C}_{14}\text{TAB}) \approx \delta^2(\text{SDS}) > \delta^2(\text{1-octanol})$$

Consequently, C_{14}TAB micelles have a very similar cohesiveness to that of SDS micelles, and both are the least cohesive (or most hydrocarbon-like) among these five micelles. However, the cohesiveness of Elvacite 2669 is between hydrocarbon micelles and fluorocarbon micelles. It is also found that m values are very similar for the hydrocarbon micelles (i.e., C_{14}TAB, SDS and SC). This suggests that cavity formation energy has a minor effect on the difference in chemical selectivity between hydrocarbonaceous surfactants in MEKC. However, differences in selectivity between LiPFOS or Elvacite 2669 and the hydrocarbonaceous surfactants can partly be due to the cavity formation term.

The coefficient b is linearly related to the HBD acidity difference between the micellar phase and the aqueous phase as

$$b = B(\alpha_{mic} - \alpha_{aq}) \quad (3)$$

where α is the solvatochromic parameter for the measurement of solvents' HBD acidity and B is a proportionality constant. The larger b value means higher HBD strength of the micellar phase assuming that α_{aq} is the same for these MEKC systems [14]. Based on Table 1, the relative HBD strength of the micellar systems can be ranked as:

$$\text{LiPFOS} > \text{SDS} > \text{Elvacite 2669} > \text{C}_{14}\text{TAB} > \text{SC} > \text{1-octanol}$$

This suggests that LiPFOS MEKC system is the most HBD acidic system, followed by SDS MEKC system. HBD acidities of Elvacite 2669 and C_{14}TAB are between SDS and SC. The values of coefficient b are very different in these five MEKC systems ranging from -2.88 to $+0.16$, therefore, type-A hydrogen bonding interaction contributes significantly to the chemical selectivity differences among these five systems.

On the other hand, the term ($a\alpha$) corresponds to type-B hydrogen bonding interaction which involves solutes acting as HBD acids and solvents as HBA bases. The coefficient a is linearly proportional to the difference in HBA (basicity) strength between the micellar phase and the aqueous phase as

$$a = A(\beta_{mic} - \beta_{aq}) \quad (4)$$

where β is the solvatochromic parameter for HBD basicity and A is a proportionality factor. The larger value for coefficient a refers to higher HBA strength of the micellar phase assuming that β_{aq} is the same for these MEKC systems. According to Table 1, the HBA strength of the micellar systems can be ranked as:

$$\text{C}_{14}\text{TAB} > \text{Elvacite 2669} > \text{SC} > \text{1-octanol} > \text{SDS} > \text{LiPFOS}$$

This means that the C_{14}TAB MEKC system is the strongest HBA basic system among these five MEKC systems, followed by Elvacite 2669. The values of coefficient a are also very different for these five MEKC systems (-0.98 to 0.99), which suggests that type B hydrogen bonding interaction also contributes significantly to the chemical selectivity among these five MEKC systems.

The term $s\pi^*$ represents the dipolar interactions between solutes and solvents. The coefficient s refers to the difference in dipolarity strength between the micellar phase and the aqueous phase as

$$s = S(\pi^*_{mic} - \pi^*_{aq}) \quad (5)$$

where π^* is the solvatochromic parameter for dipolarity/polarizability and S is the proportionality constant. The larger s values refer to higher dipolar strength of the micellar phase assuming that π^*_{aq} is the same for these MEKC systems. Based on Table 1, the dipolar strengths of the MEKC systems are all extremely similar (within the 95% confidence interval) and are not significant at the 95% confidence interval according to t-test results. Due to the fact that s values are small in magnitude and are similar for the systems studied, it can be concluded that dipolar interactions have little or no effect on retention and selectivity in these MEKC systems.

3.1. Effect of surfactant type on migration behavior in MEKC

The type of surfactant has a significant influence on solute migration behavior in MEKC [2–4,13,14]. As discussed earlier, the chemical compositions of the hydrophobic moieties and ionic head groups of surfactants significantly affect their interactions with solutes. Since SDS is the most commonly used surfactant in MEKC, retention of 60 aromatic solutes in the two micellar systems of C_{14}TAB and Elvacite 2669 were compared to that in an SDS-MEKC system. It is widely believed that retention in MEKC is due to solute hydrophobicity [1–4]. This statement, however, is not accurate and does not reflect the large variations that exist in retention patterns in different surfactant systems.

Previously, Burton et al. [23] and Liu et al. [24] demonstrated different migration behaviors and selectivity patterns between cationic MEKC systems and anionic MEKC systems. This can also seen from Fig. 1 where retention of 60 aromatic test compounds is compared in C_{14}TAB and SDS systems.

The existence of three distinct lines is indicative of different selectivity patterns in SDS and C_{14}TAB micelles. For example, solutes with identical retention in the SDS system have very different

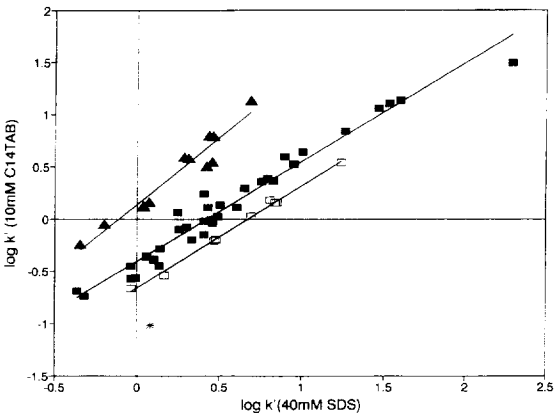

Fig. 1. Plot of log k' (10 mM C_{14}TAB) vs. log k' (40 mM SDS). log k'(10 mM C_{14}TAB)=(0.85±0.16)log k'(40 mM SDS)−0.28 (n=60, r=0.8132, S.E.=0.314). Line 1 (▲) includes phenols (compounds 32–38, 52–55 and 60 in Table I in Ref. [14]). The following regression equation was obtained: log k'(10 mM C_{14}TAB)=(1.28±0.24)log k'(40 mM SDS)+0.14 (n=12, r=0.9662, S.E.=0.109). Line 2 (■) consists of alkylbenzenes, halobenzenes, PAHs, aromatic ethers, nitrobenzenes, alkyl benzyl alcohols, benzonitrile and anilines (compounds 1–5, 11–14, 17–28, 39–45, 47–51, 56 and 57 in Table I in Ref. [14]). It can be described by the following regression equation: log k'(10 mM C_{14}TAB)=(0.95±0.06)log k'(40 mM SDS)−0.41 (n=37, r=0.9815, S.E.=0.107). Line 3 (□) includes alkyl aromatic ketones, aromatic esters (compounds 6–10, 15, 16, 29 and 30 in Table I in Ref. [14]). It can be described by the following equation: log k'(10 mM C_{14}TAB)=(0.88±0.06)log k'(40 mM SDS)−0.66 (n=9, r=0.9973, S.E.=0.030).

capacity factors in the C_{14}TAB-MEKC system. Three lines were observed in these two MEKC systems for different congeneric compounds because of the very different hydrogen bonding interactions in these two MEKC systems (Table 1). Interestingly, the patterns of solutes grouping into three lines can be explained by the LSER models. The first line (top line with filled triangles) includes phenols (HBD compounds) which have the strongest affinity for the HBA–C_{14}TAB micelles. Compounds that can be found in the second line (middle line with filled squares) include alkylbenzenes, halobenzenes, alkyl aromatic ethers, PAHs, nitrobenzenes, anilines, benzonitrile and alkyl benzyl alcohols. They are either non hydrogen bonding (NHB) compounds or weak HBA compounds. The third line (bottom line with open squares) contains alkyl aromatic ketones and aromatic esters that are strong HBA compounds and have a lower affinity for the HBA–C_{14}TAB micelles.

Obviously, they have a higher affinity for HBD–SDS micelles.

Recently, we reported the application of Elvacite 2669 for the separation of highly hydrophobic compounds (e.g., PAHs, *n*-alkylphenones and fullerenes) with high concentrations of organic modifiers [22]. Elvacite 2669 is a triblock copolymer surfactant (Fig. 2). The applications of copolymer surfactants [25,26], synthesized oligomer surfactants [27,28] and dendrimers [29–32], in MEKC have also been investigated by other workers. Differences in retention patterns of these 60 aromatic compounds in Elvacite 2669 and SDS-MEKC systems are illustrated in Fig. 3. Again, three patterns (lines) were observed for different congeneric compounds with different hydrogen bonding and dipolar strengths. The first congeneric group (open squares) includes halobenzenes, phenols, haloanilines, PAHs and halonitrobenzenes which are either HBD or strong dipolar compounds. They have stronger affinity for the HBA Elvacite 2669 than for SDS. On the other hand, HBA or weak dipolar compounds (e.g., alkylphenones, benzonitrile, aromatic esters, alkylanilines and alkyl benzyl alcohols; bottom line with filled squares) have stronger interactions with the HBD SDS than Elvacite 2669. This is also consistent with the LSER results discussed earlier.

Pyridine is an apparent outliner in both Fig. 1 and Fig. 3, which is probably due to the structure and property differences between pyridine and the rest of test compounds.

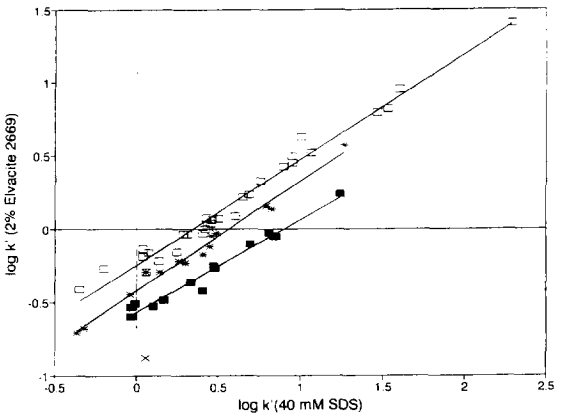

Fig. 3. The plot of log k'(2% Elvacite 2669) vs. log k'(40 m*M* SDS). log k'(2% Elvacite 2669)=(0.78±0.08)log k'(40 m*M* SDS)−0.41 (n=60, r=0.9169, S.E.=0.173). Line 1 (□) includes halobenzenes, phenols, haloanilines, PAHs, 2-chloro-nitrobenzene, 1-bromo-4-nitrobenzene and phenyl acetate (compounds 17–23, 25–27, 31–38, 44–45, 47–55 and 60 in Table I in Ref. [14]). The following regression equation was obtained: log k'(2% Elvacite 2669)=(0.72±0.05)log k'(40 m*M* SDS)−0.25 (n=30, r=0.9894, S.E.=0.062). Line 2 (*) consists of alkylbenzenes, nitrobenzenes, aromatic ethers, halo benzyl alcohols and anilines (compounds 1–5, 12–14, 24, 28, 39, 41, 42, 57 in Table I in Ref. [14]). It can be described by the following regression equation: log k'(2% Elvacite 2669)=(0.75±0.07)log k'(40 m*M* SDS)−0.42 (n=14, r=0.9921, S.E.=0.044). Line 3 (■) includes alkyl aromatic ketones, benzonitrile, aromatic esters, alkylanilines and alkyl benzyl alcohols (compounds 6–11, 15, 16, 29, 30, 40, 43, 56, 58, 59 in Table I in Ref. [14]). It can be described by the following equation.: log k'(2% Elvacite 2669)=(0.63±0.08)log k'(40 m*M* SDS)−0.57 (n=15, r=0.9862, S.E.=0.043).

3.2. Rationalization of elution patterns in MEKC

To demonstrate the usefulness of LSER in interpretation of elution patterns, a test mixture of five aromatic solutes was prepared. The effects of surfactant type and concentration on chemical selectivity and elution pattern in MEKC were investigated. Five substituted benzenes were used as the test solutes and shown in Table 2. These five compounds differ in hydrophobicity (log P_{ow}), size (V/100), dipolarity (π^*) and HBA strength (β). The elution pattern of this simple mixture was examined in these five micellar systems. The chromatograms shown in Fig. 4a and Fig. 4c–f clearly indicate two important points that were discussed previously. First, the overall separation patterns in MEKC strongly depend on the type of surfactant. Second, solutes do not necessarily elute according to their hydrophobicity. This is shown in Fig. 4c where benzene (cpd 1) and

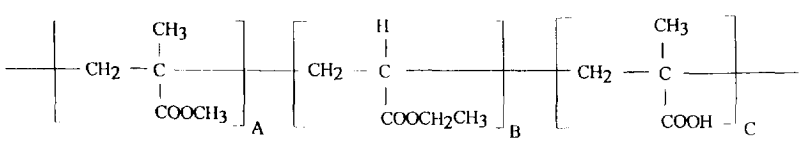

Fig. 2. The structure of poly(methyl methacrylate–ethyl acrylate–methacrylic acid) (Elvacite 2669).

Table 2
Test solutes and their properties

Cpds	$V/100$	π^*	β	α	$\log P_{ow}$
1. Benzene	0.491	0.59	0.10	0	2.13
2. Benzonitrile	0.590	0.90	0.37	0	1.56
3. Nitrobenzene	0.631	1.01	0.30	0	1.85
4. Acetophenone	0.690	0.90	0.49	0.04	1.58
5. Anisole	0.639	0.73	0.32	0	2.11

anisole (cpd 5) that are the most hydrophobic solutes are the least retained in LiPFOS MEKC system. It should be noted that a complete separation of the test mixture was not a concern here. For a given surfactant type, the overall separation in MEKC can also be influenced by adjusting the surfactant concentration so that the capacity factors would fall within the optimum range [1–4]. In our case the selected surfactant concentrations provided similar retention times.

3.2.1. Surfactant concentration

Surfactant concentration can be used in MEKC to improve separations. In MEKC solute's capacity factor (i.e., k') is directly related to its micelle binding constant and surfactant concentration as follows:

$$k' = K_{mw}(C_{sf} - \mathrm{CMC}) \quad (6)$$

where K_{mw} is the solute–micelle binding constant, C_{sf} is the surfactant concentration and CMC is the critical micelle concentration of the surfactant. According to Eq. 6, surfactant concentration has a major effect on solutes' capacity factors, however, it should have no effect on chemical selectivity as follows:

$$\alpha = k'_2/k'_1 = K_{mw,2}/K_{mw,1} \quad (7)$$

where α is the selectivity between solute 2 and solute 1.

Therefore, it has a minor effect on the elution pattern of uncharged solutes. Separations of these five test solutes at different SDS concentrations are illustrated in Fig. 4a (40 mM) and Fig. 4b (60 mM). It is seen that separation patterns are very similar in Fig. 4a and Fig. 4b. It is clearly shown in Table 1 that surfactant concentration has little or no effect on the LSER results. As mentioned earlier, the LSER coefficients represent chemical interactions between solutes and micelles, thus, the chemical selectivity of the MEKC system. Surfactant concentration mainly affects the chromatographic phase ratio as represented by different SP_o values.

3.2.2. Surfactant type

Surfactant type, on the other hand, has a significant impact on the separation of these five compounds as shown in Fig. 4a and Fig. 4c–f. The concentration of each surfactant is chosen in order to keep the last solute having a similar migration time in these five MEKC systems.

Based on LSER results, SDS MEKC systems are less cohesive and more acidic than SC or C_{14}TAB. Separation in SDS MEKC systems is mainly due to solutes' size ($V/100$) and HBA basicity strength (β), as shown in Fig. 4a. For instance, benzene (cpd 1) and benzonitrile (cpd 2) have the smallest sizes, and they are the early-eluting compounds. The size of acetophenone (cpd 4) is larger than that of anisole (cpd 5), which favors more retention. However, the effect of the larger size of acetophenone on retention is somewhat offset by its stronger HBA strength than anisole. As a result, it elutes slightly earlier than anisole. According to the LSER model, retention in SDS-MEKC system decreases as the basicity of solutes increase (i.e., larger β) due to a negative b coefficient.

According to our LSER results, LiPFOS MEKC system is a strong HBD acidic and is the most cohesive system of the MEKC system studied. As a result, HBA compounds have the strongest type A hydrogen bonding interaction with the LiPFOS micelles. In this system, the elution order of these five compounds almost follows their HBA strengths (i.e., β values) instead of hydrophobicity values (i.e., $\log P_{ow}$ values) as shown in Fig. 4c. For example, benzene (cpd 1) that elutes first, has the smallest β values, even though it has the largest $\log P_{ow}$ value.

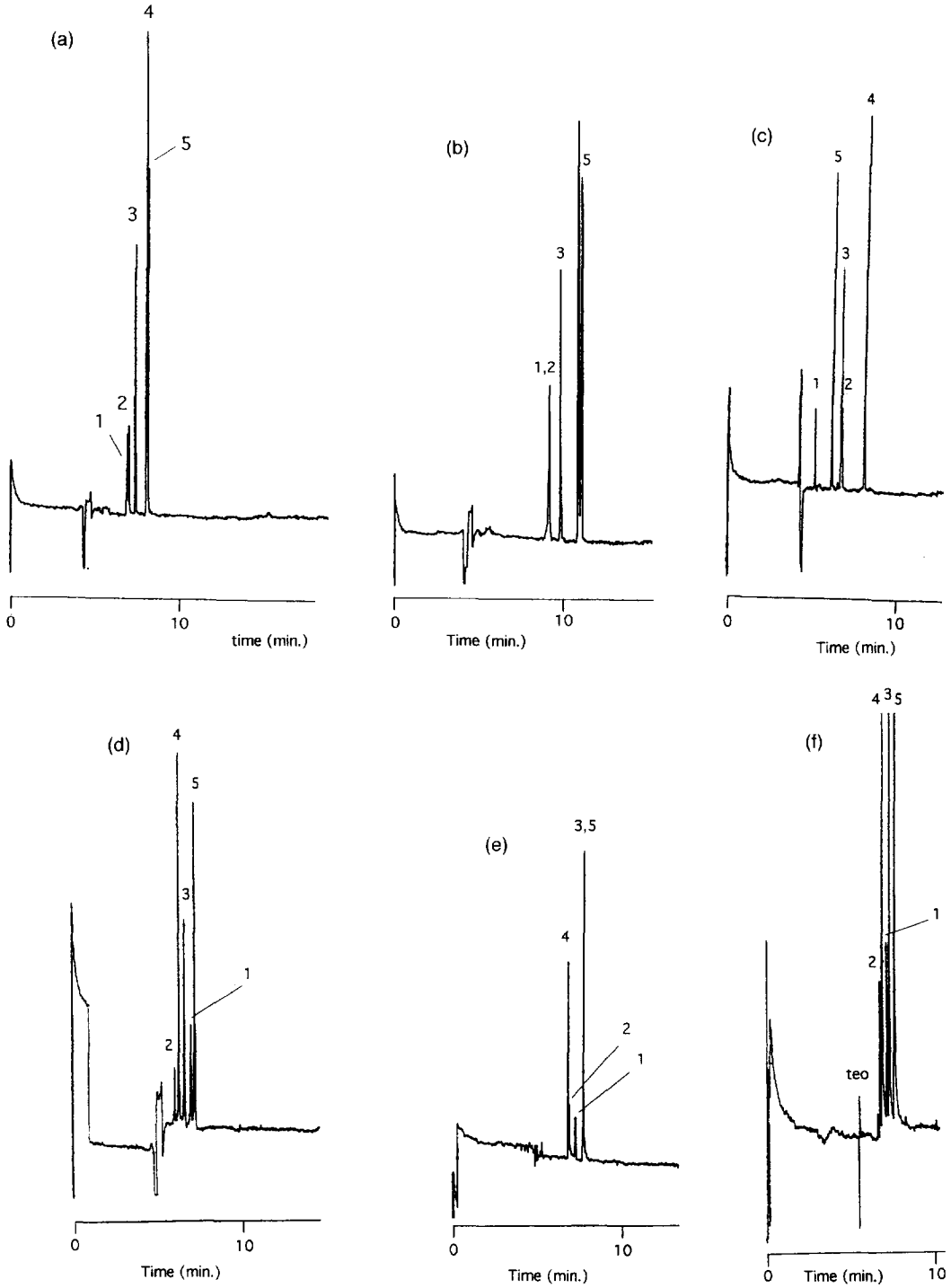

Fig. 4. Separations of test solutes in MEKC. pH 7.0, 50 m*M* phosphate, ambient temperature, 20 kV for panels a–d. (a) 40 m*M* SDS; (b) 60 m*M* SDS; (c) 40 m*M* LiPFOS; (d) 100 m*M* SC. (e) 4% Elvacite 2669, pH 10.0, 100 m*M* CAPS, ambient temperature, 20 kV. (f) 25 m*M* C_{14}TAB, pH 7.0, 50 m*M* phosphate buffer, −20 kV, ambient temperature.

On the other hand, acetophenone (cpd 4) that elutes last, has the largest β value but the second smallest $\log P_{ow}$ value. However, the elution order of nitrobenzene (cpd 3) and anisole (cpd 5) is contradictory to the LSER results. Anisole is slightly more HBA basic, less dipolar and has a larger size than nitrobenzene. It should elute after nitrobenzene according to LSER. This unusual retention behavior may be due to the steric or phobia effect [3] that exist between the $-CH_3$ group on anisole and the $-CF_2$ groups of LiPFOS micelles.

In HBA basic SC-MEKC systems, the elution order of these five compounds is very different from those in both SDS- and LiPFOS-MEKC systems, as shown in Fig. 4d. Retention of solutes in SC MEKC follows their hydrophobicity values (i.e., $\log P_{ow}$) due to the similar hydrogen bonding patterns between SC-MEKC and 1-octanol–water systems [13,14,33]. For instance, benzonitrile (cpd 2) and acetophenone (cpd 4) are the least hydrophobic compounds of the group and elute earlier. Benzene (cpd 1) and anisole (cpd 5) are more hydrophobic and elute later. Anisole elutes later than benzene even though it has slightly smaller $\log P_{ow}$ value, which may be due to its much larger size ($V/100$) than that of benzene.

Interpretation of the elution pattern in Fig. 4e, however, is a bit more complicated. Elvacite 2669 is a unique MEKC system as compared to other MEKC systems. It is a covalently bonded copolymer surfactant [22], and has a molecular mass of about 61 000. It has the characteristics of moderate cohesiveness and moderate hydrogen bonding strengths which are similar to those of SC MEKC system. The elution order of benzonitrile (cpd 2) and acetophenone (cpd 4) is reversed by using Elvacite 2669 in MEKC (Fig. 4e) as compared to SC MEKC system (Fig. 4d). This is due to the smaller β value of benzonitrile.

In the strong HBA basic C_{14}TAB-MEKC system (Fig. 4f), the elution order of these five compounds is slightly different from that in the HBA basic SC-MEKC system (Fig. 4d). The only difference is that the elution order of benzene (cpd 1) and nitrobenzene (cpd 3) is reversed in these two HBA basic MEKC systems. According to the LSER results, C_{14}TAB-MEKC system has slightly larger m value and slightly smaller negative b value than the SC-MEKC system; thus, C_{14}TAB micelles should have more interaction with nitrobenzene than benzene. Interestingly, the elution order of four HBA compounds (i.e., compounds 2–5) is completely reversed in the strong HBA C_{14}TAB-MEKC system as compared to that in the strong HBD-LiPFOS system.

4. Conclusions

The usefulness of LSER methodology for the rationalization of elution patterns in MEKC is examined. Large variations in elution patterns with different surfactants indicate that in MEKC selection of suitable surfactant type is very important, especially for complex mixtures. The characterization of solute–micelle interactions through LSER will play a vital role in understanding chemical selectivity with various surfactants.

Separation of highly hydrophobic and hydrophilic compounds is very difficult in MEKC. This is mainly due to the fact that highly hydrophobic compounds have very strong interactions with micelles and elute near or at t_{mc} and highly hydrophilic compounds have very weak interactions with micelles and elute near or at t_{co}. We have recently demonstrated that Elvacite 2669 MEKC systems with high concentrations of organic solvents can be very useful for the separation of highly hydrophobic compounds (e.g., PAHs, *n*-alkylphenones and fullerenes). This can be attributed to the unimolecular micelle formation of Elvacite 2669 surfactant that can tolerate high concentrations of organic solvents. Commonly used micelle forming surfactants (e.g., SDS, SC, LiPFOS and C_{14}TAB) can not tolerate high concentrations of organic solvents. For the separation of highly hydrophilic HBD acidic compounds, SC- or C_{14}TAB-MEKC systems are wise choices due to their HBA basic characteristics. On the other hand, SDS- or LiPFOS-MEKC systems with HBD acidic properties would be good choices for the separation of highly hydrophilic HBA basic compounds.

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