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Solute–solvent interactions in micellar electrokinetic chromatography
Selectivity of lithium dodecyl sulfate–lithium perfluorooctanesulfonate mixed-micellar buffers

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Abstract

The solvation parameter model has been applied to the characterization of micellar electrokinetic chromatographic (MEKC) systems with mixtures of lithium dodecyl sulfate and lithium perfluorooctanesulfonate as surfactant. The variation in MEKC surfactant composition results in changes in the coefficients of the correlation equation, which in turns leads to information on solute–solvent and solute–micelle interactions. Lithium perfluorooctanesulfonate is more dipolar and hydrogen bond acidic but less polarizable and hydrogen bond basic than lithium dodecyl sulfate. Therefore mixtures of lithium dodecyl sulfate and lithium perfluorooctanesulfonate cover a very wide range of polarity and hydrogen bond properties, which in turn results in important selectivity changes for analytes with different solute properties.

Keywords: Micellar electrokinetic chromatography; Buffer composition; Micelles, mixed; Solvation parameter model; Solute descriptors; Pseudo-stationary phases; Lithium dodecyl sulfate; Lithium perfluorooctanesulfonate; Surfactants

1. Introduction

Micellar electrokinetic chromatography (MEKC) is nowadays a commonplace laboratory tool because of the high separation efficiencies that can be achieved with this technique and its applicability to complex mixtures of both neutral and ionized solutes [1]. A main advantage of MEKC is the feasibility of changing the chemical composition of the system by simply rinsing the capillary with a solution of a new pseudo-stationary phase. The selectivity of the technique can thus be easily manipulated and controlled by proper selection of the surfactant type or addition of modifiers, such as cyclodextrins or organic solvents [1–3]. The addition of organic solvents produces only small changes in selectivity [4,5], although it significantly alters the phase ratio [5]. Addition of cyclodextrins has been highlighted as one of the major successes of MEKC because it allows separation of isomers and enantiomers [1]. However, it is generally agreed that the choice of surfactant is the most important consideration for

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optimizing selectivity [1,3]. A few years ago, the main limitation of selectivity optimization through variation of the surfactant composition was the limited number and homologous character of the common surfactants employed in MEKC [4]. However, nowadays there are numerous surfactants of variate chemical nature commercially available. Characterization of the separation properties of these surfactants and its influence on the selectivity would be very desirable to achieve proper selection of the surfactant for a particular MEKC separation.

The solvation parameter model has been recommended to characterize selectivity in MEKC [1,3]. The model is based on the linear free energy relationships (LFERs) established with Abraham solute descriptors of excess molar refraction R_2, dipolarity/polarizability π_2^H, and effective hydrogen-bond acidity $\Sigma\alpha_2^H$ and basicity $\Sigma\beta_2^0$, as well as on McGowan's characteristic volume V_X, and it has been successfully applied to a large number of physicochemical and biological processes [6–8]. It is set out below in a form suitable for MEKC:

$$\log k = c + vV_X + rR_2 + s\pi_2^H + a\sum\alpha_2^H + b\sum\beta_2^0 \quad (1)$$

where k is the MEKC retention factor. The coefficients of the equation are calculated by the method of multiple linear regression of the experimental log k values acquired for a group of varied solutes with known descriptors. Since the MEKC retention factor is directly related to the partition of the solute between the micellar and the aqueous phases, the r constant determines the difference in capacity of micelles and aqueous phase to interact with solute π- and n-electrons; the s constant is a measure of the difference in dipolarity/polarizability between micelles and mobile phase; the a and b constants measure the differences in the micellar and aqueous phases hydrogen-bond basicity and acidity, respectively, because an acidic solute will interact with a basic phase, and vice versa. The v constant is a measure of the relative ease of cavity formation and general dispersion interactions for the solute in the micelles and mobile phase [1,3].

Many individual MEKC anionic and cationic surfactants have been characterized through the solvation parameter model [1–4,9–14]: sodium dodecyl sulfate (SDS), sodium *N*-dodecanoyl-*N*-methyltaurine, sodium cholate, sodium deoxycholate, sodium taurocholate, sodium taurodeoxycholate, sodium dodecylsulfonate, sodium dodecylcarboxylate, sodium dodecylcarbonylvaline, sodium dodecylsulfoacetate, potassium deoxycholate, potassium salt of 3β-glucopyranosyl-5β-cholan-12α-hydroxy-24-oic acid, lithium perfluorooctanesulfonate, tris(hydroxymethyl)aminomethane dodecyl sulfate, tetradecylammonium bromide, tetradecyltrimethylammonium bromide, and hexadecyltrimethylammonium bromide. Several mixtures of the neutral polyoxyethylene(23) dodecyl ether (Brij 35) with SDS and sodium *N*-dodecanoyl-*N*-methyltaurine; equimolar mixtures of lithium dodecyl sulfate (LDS) and lithium perfluorooctanesulfonate (LPFOS), SDS and sodium cholate, and SDS and sodium deoxycholate; and a mixture of 2% poly(methylmethacrylate–ethylacrylate–methacrylic acid) (Elvacite 2669) in 3-(cyclohexylamino)-1-propanosulfonic acid at pH 10 have also been characterized [4,10,11,13,14]. The use of mixed micelles is specially interesting because the properties of the pseudo-stationary phase, and therefore the coefficients of Eq. (1) for the MEKC system and the selectivity of the system can be continuously varied by changing the proportion of the two surfactants in the mixture. This fact has been applied to develop MEKC systems that model processes of biological interest such octanol–water partition and tadpole narcosis [10].

In this work we characterize the selectivity of mixtures of LDS and LPFOS. The two individual surfactants have been chosen because they have almost complementary properties and this provides a useful range of selectivity differences in the mixtures [3,9,13,15]. The low aqueous solubility of sodium perfluorooctanesulfonate forced us to prepare the mixtures with LDS instead of the common SDS surfactant.

2. Experimental

2.1. Apparatus and conditions

All separations were performed with a Biofocus 2000, Bio-Rad system with a UV–Vis detector. The fused-silica separation capillaries were 44.5 cm

(effective length 40 cm)×50 μm I.D. for the determination of the system constants and 84.5 cm (effective length 80 cm) for the separation examples given in the figures. The capillaries were activated by the following washing sequence: 5 min of water, 20 min of 1 *M* LiOH, 10 min of water and 20 min of separation buffer. Prior to each separation with the same surfactant the capillaries were flushed with 0.1 *M* LiOH for 2 min followed by the separation buffer for 5 min. When the mixed surfactant was changed the capillary was conditioned for 20 min with 1*M* LiOH, 10 min with water, 10 min with 0.1 *M* LiOH and 10 min with the separation buffer. Retention measurements were made at 25°C and +15 kV for the determination of system constants or +30 kV for the separation examples. Detection was at 214 nm. The separation buffers were prepared by solving the surfactants in water, adding H_3PO_4, and neutralizing with LiOH up to pH 7.0. Water was finally added to obtain separation solutions 40 m*M* in surfactant and 20 m*M* in buffer. Solutes were solved in methanol (used as electroosmotic flow marker) at ca. 2 mg ml^{-1} and contained ca. 2 mg ml^{-1} of dodecanophenone as micellar marker. All sample solutions and buffers were filtered through 45-μm nylon syringe filters (Albet). Samples were introduced into the capillary by applying a high pressure during 1 s.

2.2. Reagents and materials

Phosphoric acid (85% in water), lithium hydroxide (98% in water), methanol (for chromatography) and LDS (>99%) were from Merck. LPFOS was from Fluka (25% in water). Water was Milli-Q plus (Millipore) with a resistivity of 18.2 MΩ cm. The test solutes were reagent grade or better and obtained from several makers.

2.3. Calculation

The retention factor, *k*, was calculated using Eq. (2) with the migration time of methanol used to determine the electroosmotic flow (t_{eo}), and dodecanophenone the migration time of the micelles (t_{mc}). t_R is the solute migration time:

$$k = (t_R - t_{eo})/(1 - t_R/t_{mc})t_{eo} \quad (2)$$

3. Results and discussion

3.1. Characterization of LDS–LPFOS mixtures and solvent properties of the surfactants

Separation systems mixtures of LDS and LPFOS at an overall concentration of 40 m*M* have been characterized for the solvation parameter model through Eq. (1) by analysis of the log *k* data of a series of 40 solutes with known V_X, R_2, π_2^H, $\Sigma\alpha_2^H$, and $\Sigma\beta_2^0$ parameters. The studied solutes and their descriptors are given in Table 1. These solutes have been selected according to the recommendations given in the literature [3], namely they have to embrace a wide range of descriptor values, there should be an absence of significant cross-correlation among the descriptors (Table 2), and the solutes should have a reasonable absorbance between 200 and 250 nm for convenient detection and be neutral at the working pH (pH 7.0). Heptanophenone, 4-aminobenzamide and acetanilide were also studied, but in some systems they showed deviations larger than 2.5 times the overall standard deviation and were excluded in the final correlations. The log *k* values obtained in the different MEKC systems studied are presented in Table 3.

The system constants and the statistics for the fit of the solvation parameter model to the experimental log *k* data are summarized in Table 4. This shows that the solvation parameter model gives good statistical fits and correlation coefficients and constants which are in good agreement with chemical intuition.

For the system with only LDS, we may observe that *v* and *r* coefficients are positive, whereas *s*, *a* and *b* are negative. The largest coefficients in absolute value are *v* and *b*. This means that the hydrogen bond basicity of LDS micelles is slightly lower than the hydrogen bond basicity of water ($a<0$), and that the hydrogen bond acidity of the micelles is much lower than the hydrogen bond acidity of water ($b<<0$). LDS micelles can be polarized more easily than water ($r>0$), but they are less dipolar ($s<0$). It is much easier to create a cavity in the micelle than in the aqueous buffer due to the high cohesive energy of water, therefore the *v* coefficient is very positive. The coefficients obtained for LDS are similar to those reported for SDS [1,11].

Table 1
Solute descriptors used in the solvation parameter model

Solute	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta^0$	V_X
Benzene	0.610	0.52	0.00	0.14	0.7164
Toluene	0.601	0.52	0.00	0.14	0.8573
Ethylbenzene	0.613	0.51	0.00	0.15	0.9982
Propylbenzene	0.604	0.50	0.00	0.15	1.1391
Butylbenzene	0.600	0.51	0.00	0.15	1.2800
Acetophenone	0.818	1.01	0.00	0.48	1.0139
Propiophenone	0.804	0.95	0.00	0.51	1.1548
Butyrophenone	0.797	0.95	0.00	0.51	1.2957
Valerophenone	0.795	0.95	0.00	0.50	1.4366
Pyrrole	0.613	0.73	0.41	0.29	0.5774
m-Cresol	0.822	0.88	0.57	0.34	0.9160
Nitrobenzene	0.871	1.11	0.00	0.28	0.8906
Furan	0.369	0.53	0.00	0.13	0.5363
4-Nitroaniline	1.220	1.91	0.42	0.38	0.9904
2-Nitroaniline	1.180	1.37	0.30	0.36	0.9904
Methyl benzoate	0.733	0.85	0.00	0.46	1.0726
Benzophenone	1.447	1.50	0.00	0.50	1.4808
Resorcinol	0.980	1.00	1.10	0.58	0.8338
Aniline	0.955	0.96	0.26	0.50	0.8162
Bromobenzene	0.882	0.73	0.00	0.09	0.8914
p-Xylene	0.613	0.52	0.00	0.16	0.9982
Phenol	0.805	0.89	0.60	0.30	0.7751
2,3-Benzofuran	0.888	0.83	0.00	0.15	0.9053
Benzaldehyde	0.820	1.00	0.00	0.39	0.8730
4-Chlorophenol	0.915	1.08	0.67	0.20	0.8975
2-Nitroanisole	0.965	1.34	0.00	0.38	1.0902
Pyrimidine	0.606	1.00	0.00	0.65	0.6342
Anisole	0.708	0.75	0.00	0.29	0.9160
3-Nitroaniline	1.200	1.71	0.40	0.35	0.9904
2-Naphthol	1.520	1.08	0.61	0.40	1.1441
Naphthalene	1.340	0.92	0.00	0.20	1.0854
Chlorobenzene	0.718	0.65	0.00	0.07	0.8388
Benzonitrile	0.742	1.11	0.00	0.33	0.8711
Benzamide	0.990	1.50	0.49	0.67	0.9728
2,3-Dimethylphenol	0.850	0.90	0.52	0.36	1.0569
2,4-Dimethylphenol	0.840	0.80	0.53	0.39	1.0569
o-Toluidine	0.970	0.90	0.23	0.59	0.9751
3-Chloroaniline	1.050	1.10	0.30	0.36	0.9390
4-Chloroaniline	1.060	1.10	0.30	0.35	0.9390
4-Chloroacetanilide	0.980	1.50	0.64	0.51	1.2357
Average	0.872	0.97	0.21	0.34	0.9971
SD	0.243	0.33	0.28	0.16	0.1987

Table 2
Correlation matrix between solute descriptors

	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta^0$	V_X
R_2	1				
π_2^H	0.7325	1			
$\Sigma\alpha_2^H$	0.4254	0.4395	1		
$\Sigma\beta^0$	0.3987	0.6633	0.4002	1	
V_X	0.3147	0.2629	−0.1138	0.3116	1

For the LPFOS system the v coefficient is large and positive, the a coefficient is quite negative, the r coefficient slightly negative and s and b coefficients are practically equal to zero. Therefore, we can conclude that cavity formation/solute–solvent dispersion is more favorable in LPFOS than in water ($v>>0$), that LPOS is less polarizable ($r<0$) and much less hydrogen bond basic than water ($a<<0$), and that it has the same polarity ($s=0$) and hydrogen bond acidity ($b=0$) as water. The latter coefficients do not agree completely with the coefficients reported in the literature [1,9] for another LPFOS system studied by Yang and Khaledi [2] and analyzed by Poole and Poole [9], who found a positive s coefficient and a negative b coefficient. The reason of these discrepancies is not clear, although they may come from differences on purity of the tensioactives, obtained from different makers.

The comparison between the coefficients of LDS and LPFOS shows that there are important differences in the properties of the two surfactants.

LPFOS is more dipolar ($s_{LPFOS}>s_{LDS}$), but less polarizable ($r_{LPFOS}<r_{LDS}$) than LDS. This agrees with the chemical nature of the surfactants. Because of the high electronegativity of fluorine atoms, fluoroalkane compounds are less polarizable than similar hydrocarbon compounds [1].

LPFOS is also more hydrogen bond acidic ($b_{LPFOS}>>b_{LDS}$), but less hydrogen bond basic ($a_{LPFOS}<<a_{LDS}$) than LDS. The large acidity of LPFOS in comparison with LDS is surprising because the perfluorooctanesulfonate group has no available protons to act as hydrogen bond acids. Poole and Poole [1] have speculated that the hydrogen bond acidity arises from the inductive effect of fluorine on water molecules in contact with the sulfonate group. Our comparative results between LDS and LPFOS indicate that we can discard the alternative explanation, proposed by the same authors, that the larger hydrogen bond ability of LPFOS in comparison with SDS and other sodium surfactants comes from differences in hydratation of lithium and sodium counter-ions.

The difference in the v coefficients shows that the combination of the cavity formation and solute–solvent dispersion interactions favors solvation of the

Table 3
Retention factor (log k) in the mixed-micelle separation systems

Solute	x_{LPFOS}				
	0.00	0.25	0.50	0.75	1.00
Benzene	−0.519	−0.371	−0.214	−0.109	−0.054
Toluene	−0.189	0.013	0.204	0.323	0.393
Ethylbenzene	0.094	0.344	0.569	0.709	0.791
Propylbenzene	0.417	0.724	0.997	1.173	1.264
Butylbenzene	0.745	1.095	1.422	1.622	1.750
Acetophenone	0.218	0.252	0.278	0.252	0.207
Propiophenone	0.471	0.530	0.583	0.572	0.533
Butyrophenone	0.753	0.833	0.916	0.924	0.887
Valerophenone	1.046	1.143	1.282	1.311	1.285
Pyrrole	−1.253	−1.237	−1.095	−0.950	−0.895
m-Cresol	−0.543	−0.340	−0.177	−0.050	0.058
Nitrobenzene	−0.028	0.027	0.072	0.071	0.231
Furan	−0.779	−0.784	−0.714	−0.672	−0.679
4-Nitroaniline	−0.516	−0.374	−0.214	−0.088	0.024
2-Nitroaniline	−0.166	−0.053	0.087	0.176	0.261
Methyl benzoate	0.391	0.461	0.533	0.531	0.520
Benzophenone	1.046	1.174	1.318	1.362	1.360
Resorcinol	−1.223	−1.157	−0.968	−0.794	−0.695
Aniline	−0.629	−0.548	−0.435	−0.373	−0.310
Bromobenzene	−0.170	0.111	0.372	0.553	0.649
p-Xylene	0.125	0.389	0.607	0.758	0.825
Phenol	−0.894	−0.734	−0.569	−0.443	−0.338
2,3-Benzofuran	−0.150	0.083	0.291	0.429	0.510
Benzaldehyde	−0.060	−0.003	0.038	0.024	0.017
4-Chlorophenol	−0.670	−0.370	−0.089	0.123	0.291
2-Nitroanisole	0.286	0.314	0.335	0.300	0.280
Pyrimidine	−0.703	−0.774	−0.873	−0.965	−1.133
Anisole	−0.135	−0.005	0.097	0.167	0.205
3-Nitroaniline	−0.439	−0.310	−0.183	−0.097	−0.011
2-Naphthol	−0.242	0.144	0.448	0.653	0.810
Naphthalene	0.117	0.486	0.792	0.986	1.112
Chlorobenzene	−0.199	0.042	0.266	0.410	0.507
Benzonitrile	−0.024	0.036	0.071	0.044	0.011
Benzamide	−0.466	−0.368	−0.295	−0.277	−0.289
2,3-Dimethylphenol	−0.315	−0.060	0.139	0.295	0.392
o-Toluidine	−0.382	−0.278	−0.144	−0.074	−0.009
3-Chloroaniline	−0.557	−0.299	−0.061	0.099	0.078
4-Chloroaniline	−0.528	−0.310	−0.041	0.115	0.252
2,4-Dimethylphenol	−0.252	0.032	0.215	0.370	0.465
4-Chloroacetanilide	−0.129	0.066	0.260	0.427	0.569

solute in LDS, rather than in LPFOS ($v_{LPFOS} < v_{LDS}$). Typically, fluorocompounds have lower cohesive energy than corresponding hydrocarbons and therefore the coefficients obtained can be only explained because the solute–solvent dispersion interactions between the hydrocarbon moieties of solutes and hydrocarbon micelles (LDS) are much larger than between the solutes and fluorocarbon micelles (LPFOS) [2]. The ''phobia effect'' [2] between solute hydrocarbons and solvent fluorocarbons has been also observed in reversed-phase liquid chromatography when fluorocarbon bonded stationary phases were compared with hydrocarbon bonded stationary phases [16].

The constant c of correlation Eq. (1) is related to the phase ratio (ϕ) for the separation system because

Table 4
System constants for the mixed-micellar phases at 25°C and pH 7

x_{LPFOS}	System constants						Statistics			
	c	*v*	*r*	*s*	*a*	*b*	*R*	*n*	SD	*F*
0.00	−1.78 (0.08)	2.81 (0.09)	0.36 (0.10)	−0.43 (0.07)	−0.20 (0.06)	−1.54 (0.11)	0.988	40	0.088	344
0.25	−1.79 (0.07)	2.74 (0.07)	0.27 (0.08)	−0.41 (0.06)	−0.37 (0.05)	−1.20 (0.10)	0.991	40	0.081	446
0.50	−1.85 (0.06)	2.64 (0.07)	0.16 (0.08)	−0.31 (0.06)	−0.58 (0.05)	−0.85 (0.09)	0.993	40	0.075	471
0.75	−1.90 (0.07)	2.45 (0.08)	−0.02 (0.09)	−0.16 (0.06)	−0.76 (0.05)	−0.45 (0.10)	0.992	40	0.078	371
1.00	−1.90 (0.08)	2.20 (0.08)	−0.25 (0.09)	0.00 (0.07)	−0.92 (0.06)	0.00 (0.11)	0.990	40	0.091	281

the retention factor (k) is related to the distribution constant in mole fraction (K_X) through this parameter [3]:

$$\log k = \log K_X + \log \phi \quad (3)$$

The phase ratio is related to the molar volume of surfactant, ν, and to the concentration of micellized surfactant through Eq. (4):

$$\phi = \nu(C_{sf} - \mathrm{CMC})/[1 - \nu(C_{sf} - \mathrm{CMC})] \quad (4)$$

where C_{sf} is the overall concentration of surfactant and CMC the critical micelle concentration [2].

Taking into account that the denominator of Eq. (4) is close to unity for low micelle concentrations, the CMC values of LDS and LPFOS are $8.85 \cdot 10^{-3}$ mol l^{-1} [17] and $6.30 \cdot 10^{-3}$ mol l^{-1} [18] respectively, and the overall surfactant concentration is $40 \cdot 10^{-3}$ mol l^{-1} for both surfactants, the difference between the c values of LPFOS and LDS pure systems suggests that the molar volume of LPFOS is about 70% the molar volume of LDS.

Fig. 1 presents the variation of the normalized coefficients and constant of Eq. (1). Variations close to linearity are only observed for the hydrogen bond coefficients a and b, which decrease and increase, respectively, with the proportion of LPFOS in the mixture. The other three coefficients (v, r, and s) show quadratic variations with the mole fraction of LPFOS, which are larger for LPFOS-rich mixtures than for LDS-rich mixtures.

The variation of the constant c of the correlation is more complex. It shows a maximum variation for intermediate LDS–LPFOS mixtures, whereas in LDS-rich and LPFOS-rich mixtures, it remains rather constant. This suggests that when small amounts of one surfactant are added to the other, the volume and structure of the major component remains more or less unaffected. If the two surfactants are in similar amounts, above their critical micellar concentrations, probably separate micelles of LDS and LPFOS are mostly formed. This coexistence of two kinds of micelles has been already reported for mixtures of sodium perfluorooctanoate with sodium laurate and sodium decyl sulfate [19].

3.2. Selectivity of LDS–LPFOS mixtures

Fig. 2 presents the variation of the log k values of some representative solutes with the surfactant composition. The variation is not linear, and in general has positive deviations from ideality. Most of the solutes decrease retention when the content of LPFOS in the mixture increases. However, the log k values of acetophenone and benzonitrile practically do not change with the increase in LPFOS propor-

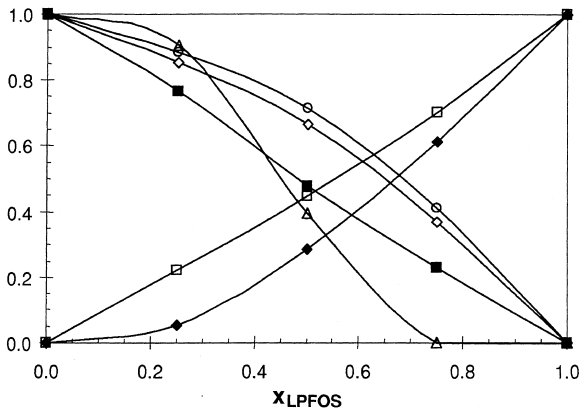

Fig. 1. Plot of the normalized system constants of the solvation parameter model for lithium dodecyl sulfate and lithium perfluorooctanesulfonate mixed-micellar systems. (△) c; (◊) r; (♦) s; (■) a; (□) b; (○) v.

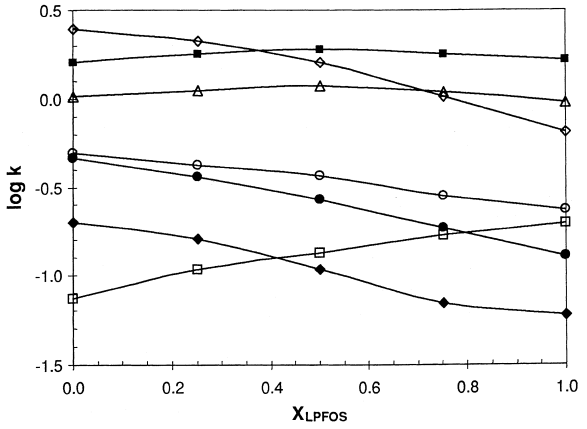

Fig. 2. Variation of the retention of solutes in lithium dodecyl sulfate and lithium perfluorooctanesulfonate mixed-micellar systems. (◊) Toluene; (■) acetophenone; (△) benzonitrile; (○) aniline; (●) phenol; (♦) resorcinol; (□) pyrimidine.

tion, although the maximum retention is obtained for the equimolar mixture of LDS and LPFOS. The log k values of pyrimidine increase with the LPFOS content of the surfactant mixture.

Characterization of the LDS and LPFOS mixtures by the solvation parameter model offers an easy way to explain these facts and determine the selectivity of the micellar systems towards mixtures of analytes.

Table 5 presents the contributions of the different terms of Eq. (1) to the retention (log k) of several typical solutes in LDS and LPFOS pure systems, as well as the differences between the contributions in the two systems. The differences in the contributions of the volume, polarity and polarizability terms are rather constant for all solutes. The differences in the volume (vV_X) and polarizability (rR_2) terms are between 0.4 and 0.6, and in the dipolarity term ($s\pi_2^H$) between -0.2 and -0.4. The overall contributions

Table 5
Contribution of intermolecular interactions to the separation of solutes in MEKC systems

Solute	Micelle	c	vV_X	rR_2	$s\pi_2^H$	$a\Sigma\alpha_2^H$	$b\Sigma\beta^0$	Log k_{calc}
Toluene	LDS	−1.78	2.41	0.22	−0.22	0.00	−0.22	0.42
	LPFOS	−1.90	1.89	−0.15	0.00	0.00	0.00	−0.16
	Difference	0.13	0.52	0.37	−0.22	0.00	−0.22	0.58
Acetophenone	LDS	−1.78	2.85	0.30	−0.43	0.00	−0.74	0.20
	LPFOS	−1.90	2.23	−0.21	0.00	0.00	0.00	0.13
	Difference	0.13	0.62	0.51	−0.44	0.00	−0.74	0.07
Resorcinol	LDS	−1.78	2.35	0.36	−0.43	−0.22	−0.89	−0.62
	LPFOS	−1.90	1.84	−0.25	0.00	−1.01	0.00	−1.32
	Difference	0.13	0.51	0.61	−0.43	0.79	−0.89	0.71
Aniline	LDS	−1.78	2.30	0.35	−0.41	−0.05	−0.77	−0.37
	LPFOS	−1.90	1.80	−0.24	0.00	−0.24	0.00	−0.58
	Difference	0.13	0.50	0.59	−0.42	0.19	−0.77	0.22
Phenol	LDS	−1.78	2.18	0.29	−0.38	−0.12	−0.46	−0.27
	LPFOS	−1.90	1.71	−0.20	0.00	−0.55	0.00	−0.95
	Difference	0.13	0.47	0.50	−0.38	0.43	−0.46	0.68
Pyrimidine	LDS	−1.78	1.78	0.22	−0.43	0.00	−1.00	−1.20
	LPFOS	−1.90	1.40	−0.15	0.00	0.00	0.00	−0.66
	Difference	0.13	0.39	0.37	−0.43	0.00	−1.00	−0.55
Benzonitrile	LDS	−1.78	2.45	0.27	−0.48	0.00	−0.51	−0.04
	LPFOS	−1.90	1.92	−0.19	0.00	0.00	0.00	−0.17
	Difference	0.13	0.53	0.46	−0.48	0.00	−0.51	0.13

of these three differences and the difference in the *c* constant (0.13) determines that all solutes are about 0.8 log *k* units more retained in the LDS system than in the LPFOS system, and therefore these terms do not considerably affect the selectivity of the micellar systems.

However, the large differences in the hydrogen bond properties of LDS and LPFOS systems imply large differences in the selectivity of the systems towards solutes with hydrogen bond properties. Table 4 shows that solute hydrogen bond acidity decreases retention in the LPFOS system ($a=-0.92$) to a larger degree than in LDS ($a=-0.20$). Therefore, the differences in the contribution of solute hydrogen bond acidity ($a\Sigma\alpha_2^H$) are about 0.2, 0.4, and 0.8 log *k* units for aniline ($\Sigma\alpha_2^H=0.26$), phenol ($\Sigma\alpha_2^H=0.60$) and resorcinol ($\Sigma\alpha_2^H=1.10$), respectively. The variation in selectivity of the systems caused by the hydrogen bond acceptor basicity of the solutes are even larger than, and opposite to, variation caused by solute hydrogen bond donor acidity because the hydrogen bond acidities of LDS ($b=-1.54$) and LPFOS ($b=0.00$) differ considerably. Table 5 shows that for solutes with a low hydrogen bond basicity such as toluene ($\Sigma\beta_2^0=0.14$) the difference between the contributions of the $b\Sigma\beta_2^0$ term in LDS and LPFOS is about -0.2, for phenol and benzonitrile with $\Sigma\beta_2^0\approx0.3$, about -0.5, for acetophenone and aniline with $\Sigma\beta_2^0\approx0.5$, the difference is about -0.8, and for resorcinol and pyrimidine, the solutes with the largest hydrogen bond basicity ($\Sigma\beta_2^0\approx0.6$), is about -1.0. Therefore the $b\Sigma\beta_2^0$ term decreases retention in LDS in comparison with retention in LPFOS. For phenol and resorcinol, the differences in both hydrogen bond terms ($a\Sigma\alpha_2^H$ and $b\Sigma\beta_2^0$) are approximately equal and the differences in the contributions of the non-hydrogen bond terms determine that the log *k* value in LDS is about 0.7 units larger than in LPFOS. For toluene, the small, but significant, solute hydrogen bond basicity decreases the difference in the log *k* values to 0.6 units. The large differential contribution in solute hydrogen bond basicity of aniline, not balanced by the small differential contribution of solute hydrogen bond acidity, decreases the log *k* difference to 0.2. For benzonitrile and acetophenone, which have no contribution from the solute hydrogen bond acidity, the negative differential contributions of solute hydrogen bond basicity almost cancel out the positive differential contributions of the non-hydrogen bond terms and they present similar retentions in LDS and LPFOS. Finally, pyrimidine, also with no hydrogen bond acidity, has a very large hydrogen bond basicity and the negative differential contribution of this term surpasses the positive differential contributions of the non-

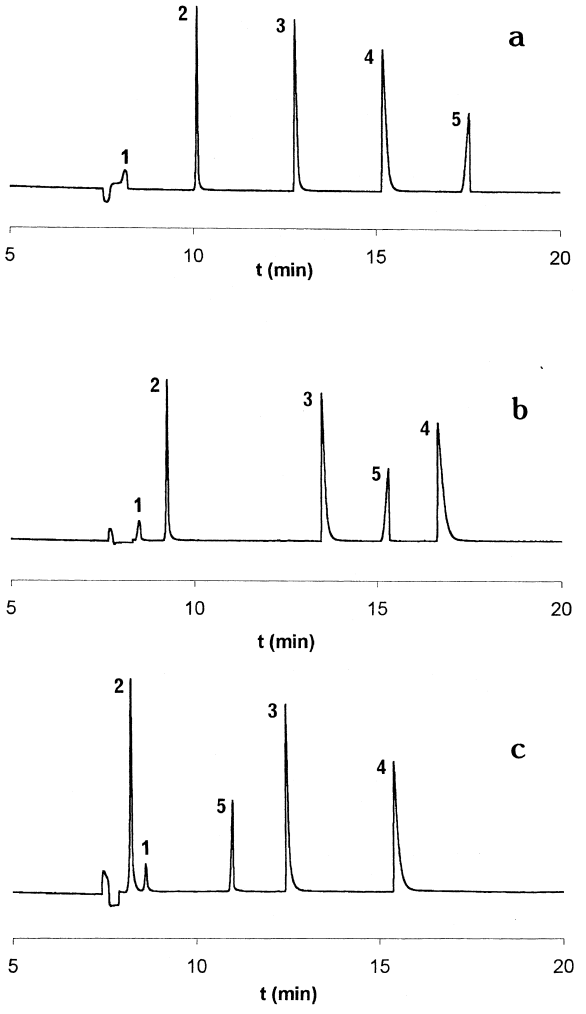

Fig. 3. Separation of a test mixture by MEKC in a lithium phosphate buffer, pH 7.00, 25°C, 30 kV, and 80 cm capillary effective length using (a) $40\cdot10^{-3}$ mol l^{-1} LDS; (b) $20\cdot10^{-3}$ mol l^{-1} LDS + $20\cdot10^{-3}$ mol l^{-1} LPFOS; (c) $40\cdot10^{-3}$ mol l^{-1} LPFOS. Peak identification: 1, pyrimidine; 2, phenol; 3, benzonitrile; 4, acetophenone; and 5, toluene.

hydrogen bond terms and this is the unique studied solute more retained in LPFOS than in LDS.

Some examples of the variation of selectivity of the LDS–LPFOS systems are presented in Fig. 3 for $40 \cdot 10^{-3}$ mol l^{-1} LDS, $20 \cdot 10^{-3}$ mol l^{-1} LDS + $20 \cdot 10^{-3}$ mol l^{-1} LPFOS, and $40 \cdot 10^{-3}$ mol l^{-1} LPFOS systems. The chromatograms show that the retention of benzonitrile and acetophenone slightly increases from the LDS to the LDS + LPFOS systems and then decreases again for the LPFOS pure system to values close to that of the LDS system. In LDS, toluene is more retained than acetophenone, in LDS + LPFOS its retention is between that of benzonitrile and acetophenone, and in LPFOS it is less retained than benzonitrile. The retention of phenol decreases with the increase in the proportion of LPFOS, but the retention of pyrimidine increases. In pure LDS, pyrimidine is much less retained than phenol, but in pure LPFOS it is more retained.

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