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Electrokinetic chromatography with micelles, polymeric and monomeric additives with similar chemical functionality as pseudo-stationary phases

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Abstract

A comparison is made of the retention properties of additives applied as positively charged pseudo-stationary phases for electrokinetic chromatography of neutral analytes. All additives have a quaternary ammonium as functional group. The polymeric additive [poly(*N*,*N*,*N′*,*N′*-tetramethyl-*N*-trimethylenehexamethylenediammonium), Polybrene] has a concentration of 2% (w/w) in the background electrolyte (acetate, pH 5.2). Monomeric octyltrimethylammonium (OTMA) was used at a concentration below or above its critical micelle concentration (CMC) (140 mmol/l). At a concentration (259 mmol/l) above the CMC the system is that normally used for micellar electrokinetic chromatography with cationic micelles. However, even below the CMC, where OTMA is present as monomer, retention of the neutral analytes is observed as well. In all systems coating of the capillary wall with Polybrene establishes an electroosmotic flow directed towards the anode, counter-migrating to the electrophoretic movement of the additive. Based on the measurement of the mobility of the analytes (15 small, monofunctional aromatic compounds with different functional groups), their capacity factors, k_i, were determined in all systems. Low correlation of the k_i values is observed between the particular systems, indicating their different selectivity at least for individual pairs of analytes. Based on the log k_i values, a linear free energy relationship was applied to elucidate the main types of chemical interaction responsible for retention. As a result, cavity formation and n or π electron interactions were found being significant for the micellar OTMA system, which agrees with findings described in the literature for other (cationic and anionic) micellar systems. For the polymeric system and for the monomeric OTMA system, the significant retention parameter is indicating n and π electron interactions.

Keywords: Micellar electrokinetic chromatography; Pseudo-stationary phases; Background electrolyte composition; Linear free energy relationships; Solute descriptors; Surfactants

1. Introduction

Although capillary electrophoresis (CE) is an efficient method for separations of charged analytes, the applicability of electromigration methods especially for neutral solutes was enlarged by the development of techniques like capillary micellar electrokinetic chromatography (MEKC). Since the first introduction of MEKC by Terabe and co-workers [1,2], this method became widely popular and hundreds of studies and applications were reported. The separation mechanism in MEKC is based on differential partitioning between an aqueous bulk solution and a micellar pseudo-stationary phase. Ionic

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[3], non-ionic [4] and, recently, polymeric surfactants or micellar polymers [5–11] can be used as pseudo-stationary phases as well. It is widely accepted that retention in MEKC depends mainly on the hydrophobicity of the solute. Yang et al. [12] related (on a logarithmic scale) the retention or capacity factors, k_i, of the solutes, *i*, in MEKC to the octanol–water partition coefficient, P_{OW}, a widely accepted indicator for hydrophobicity. The large differences in correlation testify the existence of various retention properties in MEKC among various types of pseudo-stationary phases.

There are some disadvantages of MEKC, which have led seeking for alternatives. Capillary electrochromatography (CEC), e.g., combines the foremost features of high-performance liquid chromatography (HPLC) (high selectivity) and CE (high efficiency) and enormous attention has been paid into developments and applications of this method, recently reviewed by Altria [13] and Dermaux and Sandra [14]. In CEC, a capillary is packed with various small-particle-size materials like octadecyl-modified silica gel and others as summarised by Altria et al. [15]. However, packing of capillaries in CEC requires skill from the analyst and can be troublesome, especially in case of preparation the frits at both ends of the packing. One of the major problems in packed CE columns is bubble formation in frits due to Joule heating, leading to the breakdown of the current. The differences in the electroosmotic flow (EOF) velocity between the packed and unpacked regions of the column often causes additional dispersion of peaks, so that the potentially high efficiency is lost.

The technical problem of frit preparation in electrochromatography had been surmounted, e.g., by the use of gels like acrylate based gels attached to the column wall [16,17] or monolithic beds (cf. e.g., Ref. [18]). In another alternative, using open capillaries, a variety of materials was applied as a replaceable pseudo-stationary phase directly added to the background electrolyte (BGE), e.g., microemulsions [19], micelle polymers (see MEKC above), vesicles, resorcarenes, dendrimers and polymer ions [20] (for a recent review cf. e.g., Ref. [21]).

Charged polymers have been successfully used to influence the migration of both, charged and neutral analytes, even if the polymer is not chemically cross-linked or present in the form of polymer micelles [22–28]. The major advantage of polymers added to the BGE as a pseudo-stationary phase compared to conventional chromatographic techniques as well as to CEC is the flexibility and ease of changing the chemical composition. For example, the type and/or composition of the polymer solution can be easily modified or replaced by simply rinsing the capillary with another solution containing a new type of additive.

However, the question arises whether a polymer structure is primarily responsible for separation of (neutral) analytes in an electrokinetic system, or not. Walbroehl and Jorgenson [29] obtained resolution of neutral solutes with non-micellar tetraalkylammonium salts. Later, other quaternary ammonium ions were applied as well [30–32]. In our previous work we investigated the retention of uncharged solutes in electrokinetic systems with polymeric [poly(diallyldimethylammonium), PDADMA] [33] and monomeric additives of similar functionality (tetramethylammonium, tetraethylammonium, dimethylpyrrolidinium) [34]. The extent of the interactions was smaller for the monomers, compared to the polymer, and in fact did not follow the sequence of increasing alkyl substitution of the additive. It is noticeable that the highest retention was observed for PDADMA, and further for dimethylpyrrolidinium ions, both having the quaternary ammonium in the same five-ring structure. It was concluded that the structure of PDADMA is favourable over monomeric ones for the separation of neutral analytes.

In this context the type of interactions between solute and polymeric pseudo-stationary phase was characterised using a linear free energy relationship (LFER) [4,35,36]. By the same method a comparison of PDADMA with both cationic (cetyltrimethylammonium bromide, CTAB) and anionic (sodium dodecyl sulfate, SDS) micelles was made [33]. The most significant difference between polymer solution and micelles was found in cohesive properties. As a reasonable result the cavity formation term represents the major contribution to the retention for micellar systems, whereas for the polymeric additive this term is statistically insignificant.

As charged polymers are used as an alternative to MEKC, a better understanding of the properties of various surfactants would be useful. The LFER methodology can provide valuable information about

the type of underlying solute–micelle and solute–polymer interactions that lead to selectivity differences in both micellar and polymeric systems. It is thus the goal of the present paper to compare the retention behaviour of polymeric and micellar systems of similar functionality, including systems with micelle-forming additives *below* the critical micellar concentration (CMC). All systems consist of cationic pseudo-stationary phases or additives, respectively: a cationic linear polymer (Polybrene), micellar octyltrimethylammonium (OTMA), and monomeric OTMA as additive at concentrations were micelles are not formed. The 15 test solutes were aromatic uncharged compounds with different functional groups.

2. Materials and methods

2.1. Reagents and analytes

Poly(*N,N,N′,N′*-tetramethyl-*N*-trimethylenehexamethylenediammonium)dibromide (Polybrene) of average molecular mass 5000–10 000, and octyltrimethylammonium bromide (OTMA) were from Aldrich (Vienna, Austria). Sodium acetate trihydrate, glacial acetic acid and ethanol (all analytical grade) were purchased from E. Merck (Darmstadt, Germany). Analytes (Merck or Fluka, Buchs, Switzerland) were of analytical grade except 1,3-dinitrobenzene and benzophenone, which were of purum quality. Reagents and standard solutions were prepared in deionized water of 18 MΩ cm resistance (Milli-Q system; Millipore, Bedford, MA, USA). Samples had analyte concentrations of 1 to 5 mmol/l each, depending on the running buffer to get comparable UV signals.

2.2. Instrumentation

The electrokinetic measurements were performed on two different capillary electrophoretic systems. The P/ACE 2100 electrophoretic system (Beckman, Fullerton, CA, USA) was equipped with an on-column UV absorbance detector (214 nm). The ^{3D}CE instrument (Hewlett-Packard, Waldbronn, Germany) was operated with a diode array detector at 214 nm. Uncoated fused-silica capillaries (Composite Metal Services, Hallow, UK) with total and effective lengths of 27.0 cm and 20.0 cm (P/ACE instrument) and 48.5 cm and 40 cm (^{3D}CE system), respectively, were used. All capillaries (50 μm I.D.×375 μm O.D.) were dynamically coated with Polybrene.

Samples were injected by 35 mbar pressure for 1 to 2 s. Applying a constant voltage of −4 kV or −8 kV, the resulting current was between 22 and 51 μA. All measurements were carried out at 25.0°C thermostating temperature.

2.3. Procedures

2.3.1. Capillary treatment and BGE additives

The capillary, treated with a solution of 2% (w/w) Polybrene in water, provided a dynamic, positively charged coating [37,38]. The running buffers were prepared with the additive (Polybrene or OTMA) and 20 mmol/l sodium acetate. Acetic acid was added to adjust pH 5.2. The concentrations of the additives in the buffer solution were 2% (w/w) for Polybrene, 59 mmol/l and 98 mmol/l for OTMA below the CMC, and 259 mmol/l for OTMA above the CMC [39].

2.3.2. Determination of mobilities of analyte–additive associates

Determination of the mobility of associates of OTMA with the analytes (below the CMC) was based on the procedure described in the previous work [33]. The mobility of micellar OTMA was determined as $10.2 \cdot 10^{-9}$ m^2 V^{-1} s^{-1} from the mobility measurements of anthracen (anthracen is assumed being completely incorporated into the micelle). The mobility of Polybrene, $10.7 \cdot 10^{-9}$ m^2 V^{-1} s^{-1}, was determined by the same method as described in Ref. [33]. In all cases the mobility of the anodal EOF occurring after coating was determined from the negative water dip.

The reproducibility of the migration time (expressed by the relative span from measurements made at least in duplicate) of the water dip was less than 1% in runs with Polybrene, and between 6 and 12% with the other additives. The span of the retention time of the solutes was smaller than 1% for Polybrene, and between 5% and 7% for the OTMA containing systems.

3. Results and discussion

3.1. Retention, mobility and capacity factor

Neutral low-molecular-mass solutes are separated when they have different distribution between the pseudo-stationary phase and the ''bulk'' solution. According to the chromatographic model, the distribution of the analyte can be expressed by the capacity factor k_i:

$$k_i = \frac{n_i^{(PS)}}{n_i^{(bulk)}} = K_i q \quad (1)$$

where $n_i^{(PS)}$ and $n_i^{(bulk)}$ are the mole numbers of the ith analyte attached to the pseudo-stationary phase (PS) and present in the bulk solution (bulk). K_i is the distribution constant and q is the phase ratio. The phase ratio q will be expressed in two different ways: as the volume ratio for micellar systems (V_{PS} and V_{bulk} are the volumes of the pseudo-stationary and bulk phases, respectively):

$$q = \frac{V_{PS}}{V_{bulk}} \quad (2)$$

and as the molar ratio for the monomeric and polymeric systems:

$$q = \frac{n_{PS}}{n_{bulk}} \quad (3)$$

Here n_{PS}, n_{bulk} are the total mole numbers of the monomeric or polymeric pseudo-phase and the bulk liquid in the separation column, respectively. It will be assumed that the interaction of the analyte with the polymer can be related to the monomeric entities of the polymer rather than to the entire molecule. Then it is more appropriate to formally take n_{PS} as the mole number of the monomer units.

The migration velocity of the neutral solute, v_i, is the weighted average of its velocity in the bulk solution, given by the velocity of the electroosmotic flow, v_{eof}, and its velocity when associated with the pseudo-stationary phase, $v_{i,PS}$:

$$v_i = \frac{1}{1+k_i} \cdot v_{eof} + \frac{k_i}{1+k_i} \cdot v_{i,PS} \quad (4)$$

All velocities are related to the coordinate system connected with the capillary. As the velocities in Eq. (4) depend on the field strength in the same way, they can be replaced by the respective mobilities, μ_i, μ_{eof}, $\mu_{i,PS}$, and the capacity factor can be expressed by:

$$k_i = \frac{\mu_i - \mu_{eof}}{\mu_{i,PS} - \mu_i} \quad (5)$$

The electrophoretic mobility of an associate, related to the bulk solution, $\mu^0_{i,PS}$, is connected by definition to the mobility of the associate related to the capillary, $\mu_{i,PS}$, as:

$$\mu^0_{i,PS} = \mu_{i,PS} - \mu_{eof} \quad (6)$$

(the relation to the bulk solution is indicated by superscript 0).

The experimentally determined mobilities of the analytes, μ_i, corrected by the mobility of the EOF in the particular systems, $\mu_i - \mu_{eof}$, are given in Fig. 1. It can be seen that they increase roughly in the sequence OTMA (58 mmol/l)<OTMA (95 mmol/l)<micellar OTMA<Polybrene. Note that the CMC of OTMA is 140 mmol/l [39].

It must be pointed out that the mobility $\mu_{i,PS}$ of the associate of analyte, i, with the pseudo-stationary phase is not necessarily the same as that of the pseudostationary phase itself. It can be assumed that the difference between both will be negligible in case of a large pseudo-stationary phase particle and a small analyte, e.g., for micelles and polymeric additives. However, for the present case with monomeric OTMA in submicellar concentration this assumption is certainly not appropriate. For this reason we proposed in our previous paper [33] the estimation of the mobility of such an associate from measurement of the analyte's total mobility in systems with two different concentrations of the additive. This approach has been used also here. These values of the mobility, $\mu_{i,PS}$, were taken then for the calculation of the capacity factors by Eq. (5); they are given in Table 1.

The largest capacity factors are observed in the Polybrene and the micellar system. However, the absolute values of the capacity factors are of less relevance to express separation selectivity than their sequence. From all analytes 1-naphthol and 2-naphthol exhibit the largest k_i values in all systems. Then the sequence in decreasing order of k_i values differs.

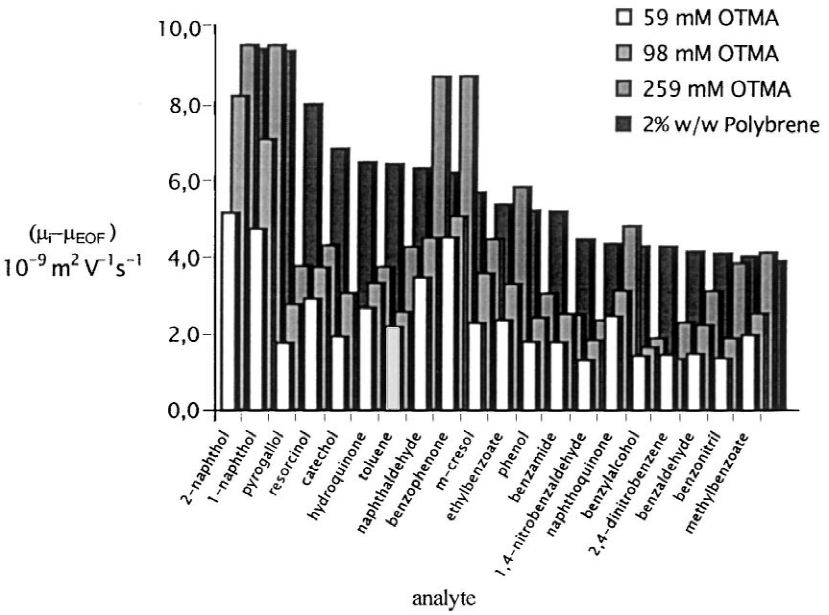

Fig. 1. Mobility of the analytes, μ_i, corrected by that of the EOF, μ_{eof}, determined in the same run in the systems with different additives.

Table 1
Capacity factors, k_i, for submicellar OTMA (59 mmol/l), submicellar OTMA (98 mmol/l), micellar OTMA (259 mmol/l) and 2% (w/w) Polybrene

Analyte	k_i			
	OTMA, 59 mmol/l	OTMA, 98 mmol/l	OTMA, micellar	Polybrene
2-Naphthol	0.482	0.812	14.7	7.37
1-Naphthol	0.345	0.580	14.7	7.07
Pyrogallol	0.112	0.189	0.58	2.95
Resorcinol	0.153	0.257	0.73	1.77
Catechol	0.125	0.211	0.29	1.53
Hydroquinone	0.133	0.223	0.58	1.50
Toluene	0.095	0.161	0.73	1.44
Naphthaldehyde	0.157	0.264	5.92	1.37
Benzophenone	0.195	0.329	6.10	1.01
m-Cresol	0.154	0.259	0.79	1.01
Ethyl benzoate	0.129	0.218	1.37	0.95
Phenol	0.084	0.142	0.43	0.94
Benzamide	0.098	0.165	0.32	0.71
1,4-Nitrobenzaldehyde	0.070	0.118	0.30	0.68
Naphthoquinone	0.124	0.209	0.93	0.66
Benzyl alcohol	0.052	0.088	0.23	0.66
2,4-Dinitrobenzene	0.046	0.078	0.30	0.63
Benzaldehyde	0.084	0.142	0.45	0.62
Benzonitrile	0.066	0.165	0.61	0.60
Methyl benzoate	0.096	0.162	0.68	0.57

The CMC of OTMA is 140 mmol/l.

In the Polybrene system the analytes with the highest capacity factors are all oligophenols: pyrogallol, resorcinol, catechol, hydroquinone. In the micellar OTMA system, on the other hand, the analytes next to the naphthols are naphthaldehyde, benzophenone, and ethyl benzoate. The two OTMA systems below the CMC retard strongest naphthaldehyde and benzophenone as well, followed by resorcinol and *m*-cresol.

Linear correlation between the systems, based on the k_i values, which reflects the differences in selectivities, is low in all cases (linear correlation coefficients are around 0.9). For the OTMA systems below and above the CMC correlation is not higher than for an OTMA and the Polybrene system. If that pair of solutes with the most pronounced effect in all systems (the naphthols) is not taken into account, linear correlation between the systems is almost lost (the linear correlation coefficients are then between 0.67 and 0.07). In fact some doubts about the value of the capacity factors of the two naphthols might arise. This pair of solutes showed a somewhat deviating behaviour in all the electrokinetic systems investigated so far by the authors [33,34,40]. In contrast to other analytes, these two solutes have shown significant adsorption on wall coatings of another linear cationic polymer (PDADMA). Therefore it is questionable whether the strong retardation of these solutes stems solely from their interaction with the additives, or from additional wall contributions.

From the k_i values the distribution constants K_i were calculated using the appropriate phase ratio q (Table 2). In the 2% (w/w) Polybrene system ($q = 0.00102$) values for K_i of several hundreds to several thousands are obtained, where seemingly the phenols exhibit the strongest interaction. OTMA below the CMC, on the other hand, does not follow such a clear figure from the chemical point of view (except for the naphthols, but note the comments given above). There is no straightforward preference to any particular functional group found here. Interestingly, even toluene interacts considerably.

The volume ratio, q, for the micellar system was calculated from the difference between the critical micellar concentration (CMC = 140 mmol/l) and the actual concentration of the surfactant ($C = 259$ mmol/l), because only this amount of additive is

Table 2
Distribution constants, K_i, for OTMA below and above the CMC, and for Polybrene (2%, w/w)

Analyte	K_i		
	Submicellar OTMA	Micellar OTMA	Polybrene
2-Naphthol	449	770	7240
1-Naphthol	321	771	6940
Pyrogallol	104	30	2900
Resorcinol	142	38	1730
Catechol	117	15	1500
Hydroquinone	123	30	1470
Toluene	89	38	1410
Naphthaldehyde	146	311	1350
Benzophenone	182	320	990
m-Cresol	143	41	990
Ethyl benzoate	120	72	930
Phenol	78	23	920
Benzamide	91	17	700
1,4-Nitrobenzaldehyde	65	16	670
Naphthoquinone	115	49	650
Benzyl alcohol	49	12	650
2,4-Dinitrobenzene	43	16	620
Benzaldehyde	78	24	610
Benzonitrile	61	32	590
Methyl benzoate	89	36	560

For details see text.

available for micelle formation. For the calculation of q the ratio of the (pseudo-) phase volumes (Eq. (2)) can be rearranged to:

$$q = V_{PS}/V_{bulk} = V_{PS}^{molar} \cdot (C - CMC) \quad (7)$$

Taking a value of 0.16 l/mol for the molar volume, V_{PS}^{molar}, of the micelles (this value was estimated from literature data for analogous micellar systems and from Ref. [41]), the resulting phase ratio q is 0.01904.

It has to be noticed that the CMC for OTMA is rather high. This means that under the given conditions a high amount of OTMA is present in non-micellar form beside that in the micelles. Therefore the meaning of the calculated values of K_i might be relativized.

3.2. LFER

3.2.1. Solvation parameters

An analogy to the present systems with MEKC implies that a suitable description of their retention properties can be made in the framework of the LFER model [35,42,43] by solvation parameters. We utilise this model, which is based on the following expression for the capacity factor k_i:

$$\log k_i = c + mV_{x,i} + rR_i + s\pi_i + a\alpha_i + b\beta_i \quad (8)$$

The solute descriptors are the McGowan's characteristic volume $V_{x,i}$ (in $cm^3\ mol^{-1}/100$), the excess molar refraction R_i (in $cm^3/10$), the solute polarisability/dipolarity, π_i, the solute's effective hydrogen bond acidity, α_i, and hydrogen bond basicity, β_i. The system constants m, r, s, a, b are defined by their complementary interactions with the solute descriptors. The regression constant c does not reflect any type of interaction. For the present case, constant m is a measure of the relative ease of cavity formation and general dispersion interactions for the solute with the pseudo-stationary phase (Polybrene, OTMA micelle or OTMA monomer, respectively) and the ''bulk'' solution (the mobile phase), respectively. Constant r determines the difference in capacity of the pseudo-phase and the bulk solution to interact with n or π electrons of the solute. Similarly, constant s expresses the difference between both pseudo-phases taking part in dipole–dipole and dipole–induced dipole interactions. Constants a and b are measures for the difference in hydrogen bond basicity and hydrogen bond acidity, respectively.

The descriptors used in the present work are given in Table 3. The system solvation constants were obtained by multiple linear regression analysis of the experimentally obtained k_i values (Table 1) for the various solutes with known descriptors at the level of significance of 0.95. The total correlation coefficients of the regression were 0.92, 0.97 and 0.96 for the OTMA system below CMC, above CMC and Polybrene, respectively.

We will not interpret the obtained results in a too rigid manner, because it is clear to us that the considerably small number of solutes, and probably also some systematic deviations in the determination of the capacity coefficients due to hardly suppressible effects (like wall adsorption, etc.) bias the calculated solvation parameters. This is reflected by the considerably low values of the correlation coefficients. However, the results allow the reasonable conclusion that they reflect at least qualitatively the retention characteristics of the separation system. From the calculated solvation parameters given in Table 4 it can be seen that, not unexpectedly, only in the micellar OTMA system the parameter m, which stands for the relative ease of cavity formation, is positive and contributes most significantly to re-

Table 3
Solute descriptors used as input parameters in the LFER model (data from Refs. [35,42])

Analyte	$V_x/100$	R	π	α	β
1-Naphthol	1.144	1.520	1.050	0.610	0.370
2-Naphthol	1.144	1.520	1.080	0.610	0.400
Benzaldehyde	0.873	0.820	1.000	0.000	0.390
Benzamide	0.973	0.990	1.500	0.490	0.670
Benzonitrile	0.871	0.742	1.110	0.000	0.330
Benzophenone	1.481	1.447	1.500	0.000	0.500
Benzyl alcohol	0.916	0.803	0.870	0.330	0.560
Catechol	0.834	0.970	1.070	0.850	0.520
Ethyl benzoate	1.214	0.689	0.850	0.000	0.460
Hydroquinone	0.834	1.000	1.000	1.160	0.600
m-Cresol	0.916	0.822	0.880	0.570	0.340
Methyl benzoate	1.073	0.733	0.850	0.000	0.460
Phenol	0.775	0.805	0.890	0.600	0.300
Resorcinol	0.834	0.980	1.000	1.100	0.580
Toluene	0.857	0.601	0.520	0.000	0.140

Table 4
Solvation parameters of solutions of OTMA below and above the CMC, respectively, and of Polybrene, obtained by linear multiple regression

System	*c*	*m*	SE	*r*	SE	*s*	SE	*a*	SE	*b*	SE
OTMA, 59 mmol/l (below CMC)	−1.22	*		0.97	0.12	−0.60	0.14	*		*	
OTMA, 259 mmol/l (above CMC)	−1.86	1.39	0.28	1.64	0.20	−1.08	0.22	*		*	
Polybrene	0.09	*		1.56	0.13	−0.91	0.15	*		*	
PDADMA	−0.81	*		0.75	0.06	−0.35	0.07	0.19	0.05	*	
Hexadecyltrimethylammonium bromide	−1.67	3.40	0.10	0.61	0.06	−0.55	0.07	0.58	0.06	−3.08	0.10
Poly(sodium undecenylsulfate)	−2.79	3.86	0.91	*		−0.44	0.66	0.11	0.7	−1.39	0.75
Sodium dodecyl sulfate	−1.82	2.99	0.07	0.46	0.05	−0.44	0.05	−0.30	0.05	−1.88	0.08
Sodium cholate	−1.71	2.45	0.12	0.63	0.08	−0.47	0.09	*		−2.29	0.13
Sodium taurocholate	−2.10	2.43	0.09	0.60	0.07	−0.34	0.07	*		−2.06	0.10

SE is the respective standard deviation in the estimate. Solvation parameters were taken from Ref. [43] for hexadecyltrimethylammonium bromide, SDS, sodium cholate and sodium taurocholate, from Ref. [8] for poly(sodium undecenylsulfate), and from Ref. [33] for PDADMA.
* Parameters that are not significant at the level of significance of 0.95.

tention. It means that the transfer of an analyte between micelle and bulk solution is connected with a high energy difference due to cavity formation, while this process in non-micellar monomer or polymer systems is not significant. This result is in agreement with those obtained for other micellar systems, which are given in Table 4, too, for comparison. An analogy with other systems is also found considering parameter *r*. This means that the systems investigated have a high ability to interact with n and π electrons of the analytes.

As the CMC for OTMA is rather high (140 mmol/l), in the micellar OTMA system (with total concentration of 259 mmol/l) only a fraction (119 mmol/l) of OTMA is in the micellar form. In spite of the fact of ''partial'' micellisation, parameter *m* in the micellar system is significant at a relatively high value, 1.39. This implies the importance of the cohesive properties of the system and the cavity formation term. It could be followed that the appearance of micelles in separation systems seemingly increases the separation ability.

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References

[1] S. Terabe, K. Otsuka, K. Ichikawa, A. Tsuchiya, T. Ando, Anal. Chem. 56 (1984) 111.
[2] S. Terabe, K. Otsuka, T. Ando, Anal. Chem. 57 (1985) 834.
[3] M.G. Khaledi, J. Chromatogr. A 780 (1997) 3.
[4] C.F. Poole, S.K. Poole, J. Chromatogr. A 792 (1997) 89.
[5] C.P. Palmer, N. Tanaka, J. Chromatogr. A 792 (1997) 105.
[6] E. Billiot, R.A. Agbaria, S. Thibodeaux, S. Shamsi, I.M. Warner, Anal. Chem. 71 (1999) 1252.
[7] C. Akbay, I.M. Warner, Electrophoresis 20 (1999) 145.
[8] K.T. Tellman, C.P. Palmer, Electrophoresis 20 (1999) 152.
[9] C. Fujimoto, Y. Fujise, S. Kawaguchi, J. Chromatogr. A 871 (2000) 415.
[10] C.P. Palmer, S. Terabe, Anal. Chem. 69 (1997) 1852.
[11] T. Chen, C.P. Palmer, Electrophoresis 20 (1999) 2412.
[12] S. Yang, J.G. Bumgarner, L.F.R. Kruk, M.G. Khaledi, J. Chromatogr. A 721 (1996) 323.
[13] K.D. Altria, J. Chromatogr. A 856 (1999) 443.
[14] A. Dermaux, P. Sandra, Electrophoresis 20 (1999) 3027.
[15] K.D. Altria, N.W. Smith, C.H. Turnbull, Chromatographia 46 (1997) 664.
[16] J.-L. Liao, N. Chen, C. Ericson, S. Hjerten, Anal. Chem. 68 (1996) 3468.
[17] C. Fujimoto, H. Sawada, K. Jinno, J. High Resolut. Chromatogr. 17 (1994) 107.
[18] J.P. Quirino, S. Terabe, J. Chromatogr. A 856 (1999) 465.
[19] L. Vomastová, I. Miksik, Z. Deyl, J. Chromatogr. B 681 (1996) 107.
[20] B. Maichel, B. Potocek, B. Gaš, E. Kenndler, J. Chromatogr. A 853 (1999) 121.
[21] B. Maichel, E. Kenndler, Electrophoresis 21 (2000) 3160.
[22] S. Terabe, T. Isemura, J. Chromatogr. 515 (1990) 667.
[23] S. Terabe, T. Isemura, Anal. Chem. 62 (1990) 650.
[24] C. Stathakis, R.M. Cassidy, J. Chromatogr. A 699 (1995) 353.
[25] B.F. Erim, J. Chromatogr. A 768 (1997) 161.

[26] M.R. Schure, R.E. Murphy, W.L. Klotz, W. Lau, Anal. Chem. 70 (1998) 4985.
[27] B. Potocek, B. Maichel, B. Gaš, M. Chiari, E. Kenndler, J. Chromatogr. A 798 (1998) 269.
[28] B. Maichel, B. Potocek, B. Gaš, M. Chiari, E. Kenndler, Electrophoresis 19 (1998) 2124.
[29] Y. Walbroehl, J.W. Jorgenson, Anal. Chem. 58 (1986) 479.
[30] T. Takayanagi, E. Wada, S. Motomizu, Analyst 122 (1997) 57.
[31] P.G. Muijselaar, H.B. Verhelst, H.A. Claessens, C.A. Cramers, J. Chromatogr. A 764 (1997) 323.
[32] S. Pedersen-Bjergaard, K.E. Rasmussen, T. Tilander, J. Chromatogr. A 807 (1998) 285.
[33] B. Potocek, E. Chmela, B. Maichel, E. Tesarova, E. Kenndler, B. Gaš, Anal. Chem. 72 (2000) 74.
[34] B. Maichel, K. Gogova, B. Gaš, E. Kenndler, J. Chromatogr. A 894 (2000) 25.
[35] M.H. Abraham, J. Phys. Org. Chem. 6 (1993) 660.
[36] C.F. Poole, S.K. Poole, M.H. Abraham, J. Chromatogr. A 798 (1998) 207.
[37] A.J. Zeemann, J. Chromatogr. A 787 (1997) 243.
[38] E. Córdova, J. Gao, G.M. Whitesides, Anal. Chem. 69 (1997) 1370.
[39] M.J. Rosen, Surfactants and Interfacial Phenomena, Wiley, New York, 1989.
[40] B. Maichel, B. Gaš, E. Kenndler, Electrophoresis 21 (2000) 1505.
[41] H. Matsuki, H. Kamaya, I. Ueda, M. Yamanaka, S. Kaneshina, Langmuir 14 (1998) 4030.
[42] M.H. Abraham, J. Andonian-Haftvan, G.S. Whiting, A. Leo, R.S. Taft, J. Chem. Soc., Perkin Trans. 2 (1994) 1777.
[43] S.K. Poole, C.F. Poole, Analyst 122 (1997) 267.