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Cationic gemini surfactants as pseudostationary phases in micellar electrokinetic chromatography. Part I: Effect of head group

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ABSTRACT

Two cationic gemini surfactants with pyrrolidinium or alkyl ammonium head groups with but-2-yne spacers, but with the same length hydrocarbon chain have been characterized with respect to their aggregation behaviors and separation power as pseudostationary phases (PSPs) for micellar electrokinetic chromatography (MEKC). They were compared with a commonly used PSP, sodium dodecylsulfate (SDS). The results suggest that the head groups of the surfactants have some effect on physicochemical properties such as critical micelle concentration (CMC), C_{20}, γ_{CMC}, partial specific volume, methylene selectivity and mobilities of the surfactants. CMC values of G1, G2 and SDS in pure water were found to be 0.82, 0.71, and 8.08 mM, respectively; they were reduced to 0.21, 0.11, and 3.0 mM when measured in 10 mM phosphate buffer at pH 7.0. G1 ($\alpha_{CH_2} = 2.74$) and G2 ($\alpha_{CH_2} = 2.48$) provided the most and the least hydrophobic environment, respectively. According to their partial specific volumes, geminis were found to have more flexible structures as compared with sodium dodecylsulfate. The effects of the head group structure were also characterized with the linear solvation energy relationship (LSER) model, which was able to evaluate the role of solute size, polarity/polarizability, and hydrogen bonding on retention and selectivity. The cohesiveness, hydrogen bond acidic and basic character of the surfactant systems were found to have the most significant influence on selectivity and MEKC retention of the gemini surfactants. It should be noted that with their large positive coefficient *a* values, G1 and G2 were found to be stronger HB acceptors than anionic and most of the cationic surfactants studied in the literature.

1. Introduction

Micellar electrokinetic chromatography (MEKC) is a hybrid of capillary electrophoresis (CE) and reversed phase high performance liquid chromatography (RP-HPLC), thus, it offers the combination of the unique features of these two techniques: high efficiencies, rapid analysis time, small sample size, low solvent consumption, and excellent selectivity. In MEKC, solutes are separated on the basis of their differential partitioning between the mobile phase and the pseudostationary phase (PSP). The mobile phase is an aqueous buffer and the PSP is usually a charged surfactant added to the mobile phase at concentration above its critical micelle concentration (CMC). MEKC offers the flexibility of changing the chemical composition of the PSP and the aqueous mobile phase, which allows the user to easily control and modify the key parameters that are critical for improved separations and better method development. For example, the addition of a desired surfactant to the aqueous buffer is an effective approach to manipulate the selectivity. Since the introduction of the MEKC, a number of monomeric and polymeric PSPs have been introduced as alternatives to the most commonly used surfactant, sodium dodecylsulfate (SDS) [1,2].

Due to their unique properties, gemini (or dimeric) surfactants have also been introduced as alternative PSPs in MEKC. Gemini surfactants are made up of two hydrophobic chains and two polar head groups covalently linked to each other through a spacer. As compared to their single-chain analogues with the same chain length and head group, geminis generally exhibit superior properties [3,4]. They possess remarkably lower CMC, low Krafft point and C_{20} values, surfactant concentration that reduces the surface tension of the solvent by 20 mN m^{-1}. They have better wetting, solubilizing and foaming properties, closer packing of the hydrophobic groups, and stronger interaction with the oppositely charged surfactants. In addition, the nature of the spacer can be polar or nonpolar, flexible or rigid, short or long. The nature and the length of the spacer can have a significant effect on the physicochemical properties and

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Table 1
Test solutes used in this study and their solvation descriptors[a].

No.	Solutes	*V*	*E*	*S*	*A*	*B*
NHB solutes						
1	Benzene	0.716	0.610	0.52	0.00	0.14
2	Toluene	0.857	0.601	0.52	0.00	0.14
3	Chlorobenzene	0.839	0.718	0.65	0.00	0.07
4	Bromobenzene	0.891	0.882	0.73	0.00	0.09
5	Ethylbenzene	0.998	0.613	0.51	0.00	0.15
6	p-Xylene	0.998	0.613	0.52	0.00	0.16
7	4-Chlorotoluene	0.980	0.705	0.67	0.00	0.07
8	Iodobenzene	0.975	1.188	0.83	0.00	0.12
9	Propylbenzene	1.139	0.604	0.50	0.00	0.15
10	Naphthalene	1.085	1.360	0.92	0.00	0.20
HBA solutes						
11	Benzonitrile	0.871	0.742	1.11	0.00	0.33
12	Acetophenone	1.014	0.818	1.01	0.00	0.48
13	Nitrobenzene	0.891	0.871	1.11	0.00	0.28
14	Methyl benzoate	1.073	0.733	0.85	0.00	0.46
15	Propiophenone	1.155	0.800	0.95	0.00	0.51
16	4-Chloroacetophenone	1.136	0.955	1.09	0.00	0.44
17	4-Nitrotoluene	1.032	0.870	1.11	0.00	0.28
18	Ethyl benzoate	1.214	0.689	0.85	0.00	0.46
19	4-Chloroanisole	1.038	0.838	0.86	0.00	0.24
HBD solutes						
20	Benzyl alcohol	0.916	0.803	0.87	0.33	0.56
21	Phenol	0.775	0.805	0.89	0.60	0.30
22	3-Methylphenol	0.916	0.822	0.88	0.57	0.34
23	4-Chloroaniline	0.939	1.060	1.13	0.30	0.31
24	4-Flourophenol	0.793	0.670	0.97	0.63	0.23
25	4-Ethylphenol	1.057	0.800	0.90	0.55	0.36
26	4-Chlorophenol	0.898	0.915	1.08	0.67	0.20
27	3-Chlorophenol	0.898	0.909	1.06	0.69	0.15
28	4-Bromophenol	0.950	1.080	1.17	0.67	0.20
29	3-Bromophenol	0.950	1.060	1.15	0.70	0.16

[a] Solute descriptors from [39].

morphology of the gemini aggregates. The head group could be anionic, cationic, zwitterionic, and nonionic.

Previously, we synthesized, characterized and applied tartaric acid based anionic geminis and their polymers as PSPs in MEKC [5,6]. They were found to have more hydrophobic character, lower CMC, weaker acidic character than SDS. Anionic geminis have been used in MEKC for separation of naphthalene derivatives and found to be superior to the conventional surfactant [7]. Recently, Van Biesen and Bottaro have studied the effect of the length and the nature (e.g., hydrophobic, hydrophilic and fluorination) of the spacer on selectivity of a number of anionic gemini surfactants using linear solvation energy relationships (LSER) [8–10]. In general, the geminis did not have a drastically different selectivity compared to the common surfactants used in MEKC, however, they could be used at much lower concentration than SDS due to their lower CMC values. No significant differences in selectivity as a factor of the length of the hydrophobic spacer were observed. Nevertheless, the geminis were found to be slightly more cohesive, fairly better hydrogen bond acceptors and poor hydrogen bond donors while there were no differences in dipolarity as compared with SDS [8]. No difference in cohesiveness, polarizability or dipolarity with increasing hydrophilic spacer length was observed, but a clear trend in increasing hydrogen bond accepting and in decreasing hydrogen bond donating ability was found [9]. The selectivity of geminis with fluorinated spacers was found to be similar to those of their non-fluorinated analogues, however, the results indicated that they were somewhat less polarizable.

To the best of our knowledge, only one study on application of cationic gemini surfactants as PSPs in MEKC has been reported in literature [11]. In this report, Chen et al. achieved baseline separation of 17 dihydroergotoxines, aci-alkaloids and oxidation products, which could not be accomplished using single chain conventional surfactants, in MEKC using two geminis with twelve and fourteen carbon chains. Cationic geminis have also been used as coating reagents in capillary electrophoresis in a few reports [12,13], however, no systematic study on understanding the nature of solute-cationic gemini surfactant interaction has been reported.

The LSER has been introduced as a powerful tool for characterization of retention and selectivity of PSPs in MEKC [14–17]. Initially developed by Kamlet et al. [18,19], LSER provides information about the physicochemical properties of separation systems (i.e., PSPs and mobile phase) and the difference in interaction between PSPs and solutes. More recently, Platts et al. [20] modified the model with new symbols:

$$\log k = c + vV + eE + sS + aA + bB \quad (1)$$

where *V*, *E*, *S*, *A*, and *B* are known as Abraham solute descriptors and are correlated to the logarithmic retention factor ($\log k$). *V* and *E* are measures of solute's McGowan's characteristic volume and the excess molar refraction, respectively. The solute dipolarity/polarizability is represented by the *S* term. The *A* and *B* terms represent the hydrogen bond donating ability (acidity) and the hydrogen bond accepting ability (basicity) of the solute, respectively. The system coefficients *c*, *v*, *e*, *s*, *a*, and *b* refer to differences in the aqueous buffer and the PSP. The constant *c* represents the intercept and includes information about the ratio of PSP and aqueous buffer phase. The term *v* is a measure of the relative ease of forming a cavity for the solute in the aqueous buffer and PSP; it is also a measure of hydrophobic interaction. The coefficient *e* is related to the difference in ability of PSP and buffer phase to interact with n- or π-electrons of solute while the *s* coefficient is related to dipolarity/polarizibility difference between the two phases. The coefficients *a* and *b* are the hydrogen bond accepting and hydrogen bond donating strengths of PSP, respectively.

There are a few important requirements that should be fulfilled for successful application of the LSER to characterization of PSPs