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Linear solvation energy relationships of anionic dimeric surfactants in micellar electrokinetic chromatography
III. Effect of fluorination

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ABSTRACT

The range of selectivities of pseudostationary phases (PSPs) available for micellar electrokinetic chromatography is limited, and there continues to be interest in the synthesis and evaluation of novel PSPs. With the unique selectivity of lithium perfluorooctanesulfonate (LPFOS) in mind, we synthesized anionic dimeric surfactants with fluorinated spacers of various lengths. Their selectivities, analyzed via linear solvation energy relationships, are similar to those of their non-fluorinated analogues, although the results indicated that they are somewhat less polarizable. While it can be concluded that fluorination has some influence on the behaviour of these dimeric PSPs, the influence on the selectivity is not as dramatic as in LPFOS. This can be explained by the inferred poor hydration of the fluorinated spacer and the positioning of the fluorine substituents, too distant from the surfactant head groups to fully exert the strong inductive effect required to significantly influence the head group chemistry.

1. Introduction

We continue our investigation of the influence of the spacer on the selectivity of anionic dimeric surfactants in micellar electrokinetic chromatography (MEKC) [1,2] by examining the effect of fluorination. The physical properties of organic compounds can be affected dramatically when hydrogen atoms are substituted for fluorine, mainly because of fluorine's high electronegativity and small size (low polarizability). For instance, as a result of weaker intermolecular forces, saturated perfluorinated compounds exhibit boiling points and surface tensions much lower than the analogous hydrocarbons [3]. Likewise, surfactants with fluorocarbon chains exhibit unique properties compared to those of hydrocarbon surfactants. They often have a tendency to produce rod-like micelles instead of spherical micelles, attributed to both the conformation (twisted helical structure [4]) and stiffness of the perfluorocarbon chain [3,5]. Since the perfluorocarbon chain is both hydrophobic and lipophobic, fluorinated amphiphiles also exhibit limited miscibility with hydrocarbon amphiphiles or organic solvents [6]. In general, their critical micelle concentrations (CMCs) are approximately equal to those of the hydrocarbon analogues with 50% longer chains [3].

There are a wide variety of pseudostationary phases (PSPs) available for MEKC, and linear solvation energy relationships (LSERs) are often used to study their selectivities [7]. The application of LSERs and their chemical interpretation has been described in detail elsewhere in some excellent articles [8,9]. Briefly, multiple linear regression is used to fit the log k values of a set of 30–40 or more solutes to the following equation:

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

where E, S, A, B and V are the known solute descriptors (polarizability, dipolarity, hydrogen bond donating ability, hydrogen bond accepting ability, and cohesiveness, respectively), and c, e, s, a, b, and v are the system constants to be determined. Fuguet et al. [7] compiled a list of system constants of 55 single and mixed monomeric and polymeric PSPs. Their analysis indicates that the behaviour of the lone fluorinated PSP in their set, lithium perfluorooctanesulfonate (LPFOS—the lithium salt is used because of its better water solubility than the sodium salt), stands out. The unique properties of this fluorinated PSP are also evident in other reports [8–12]. LPFOS is slightly less polarizable than the aqueous-phase; it is one of only a few PSPs with a small negative e system constant. It is a much better hydrogen bond donor than any other PSP studied to

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date (small negative *b* system constant), only slightly worse than water, and is also a very poor hydrogen bond acceptor (largest negative *a* system constant of all PSPs). LPFOS is also one of the most dipolar PSPs (positive to small negative *s* system constant), while it forms very cohesive micelles (one of the smallest *v* system constants). It should be noted that there is quite some variation in the system constants determined for LPFOS by different authors [7,9,11,12]. This is in contrast to the system constants for other PSPs, which usually fall within a relatively narrow range. The reason for this is not entirely clear, but might be the result of differences in the sets of solutes used to determine the LSERs, although differences in the purity of LPFOS cannot be excluded [12]. Regardless of the variation among sources of the system constants, the above description of the selectivity of LPFOS is believed to be accurate and seems to be generally accepted.

Most attention in the EKC literature with regards to fluorinated PSPs has focused on LPFOS, but other fluorinated PSPs may also be of interest. For instance, ammonium perfluorooctanoate is a PSP with a relatively low boiling point. This can be useful in MEKC–electrospray ionization mass spectrometry (MEKC–ESI-MS) [13,14], where traditional PSPs are notorious for causing signal suppression [15,16]. It is thought that ammonium perfluorooctanoate has a high enough surface activity to promote the formation of small droplets, and is volatile enough not to concentrate in the shrinking droplets [13]. Therefore, there is much less interference with the transfer of cationic analytes from the droplets to the gas phase due to Coulombic attractions, than with non-volatile PSPs. The unique selectivity imparted by fluorination seems to be lost for cationic polymeric PSPs with pendant perfluorinated groups, which have a similar selectivity as their hydrocarbon analogues, although they are slightly more cohesive and better hydrogen bond donors [17].

The monomeric fluorinated PSPs investigated so far have long fluorinated chains, which, according to the interphase model [18], form the hydrophobic core of the micelles in an aqueous solution (the first few carbon atoms of the chain, next to the head group, probably are within the interphase). We were interested in determining the effect of the presence of fluorine in the spacer of anionic dimeric surfactants, since the spacer is situated in the interphase, where extensive interaction with solutes takes place [18]. We synthesized anionic dimeric surfactants with 4, 8, and 12 fluorine atoms in the spacer (Fig. 1, **Ia-c**) and compared their selectivity with a non-fluorinated analogue (Fig. 1, **II**, labelled **IIIa** in Refs. [1,2]), sodium dodecylsulfate (SDS), and LPFOS.

2. Experimental

2.1. Capillary electrophoresis instrument and conditions

All experiments were performed on an Agilent ^{3D}CE system (Agilent Technologies Canada, Canada) with Chemstation software (Rev. A.08.03). Bare fused silica capillaries with an I.D. of 50 μm were purchased from MicroSolv (MicroSolv Technology, Eatontown, NJ, USA) and were cut to lengths of 48–50 cm. New capillaries were used for each PSP, and they were conditioned by flushing with 0.1 M NaOH (5 min), nanopure water (5 min), and background electrolyte (BGE) (10 min), respectively. The BGE consisted of 20 mM Na_2HPO_4 and 20 mM dimeric surfactant, adjusted to pH 7.00 ± 0.03 with dilute H_3PO_4. The PSPs were dissolved by stirring, followed by sonication for 15 min, and were filtered through 0.2 μm nylon filters (National Scientific Company, Rockwood, TN, USA). Analyses were performed at 25 °C, with 25 kV applied (ramped from 0 to 25 kV in 15 s). Samples were injected by applying 10 mbar of pressure for 5 s, followed by BGE at 10 mbar for 5 s, and the detection wavelength was 200 nm. Between runs, the capillary was flushed with BGE for 3 min.

2.2. Solutes

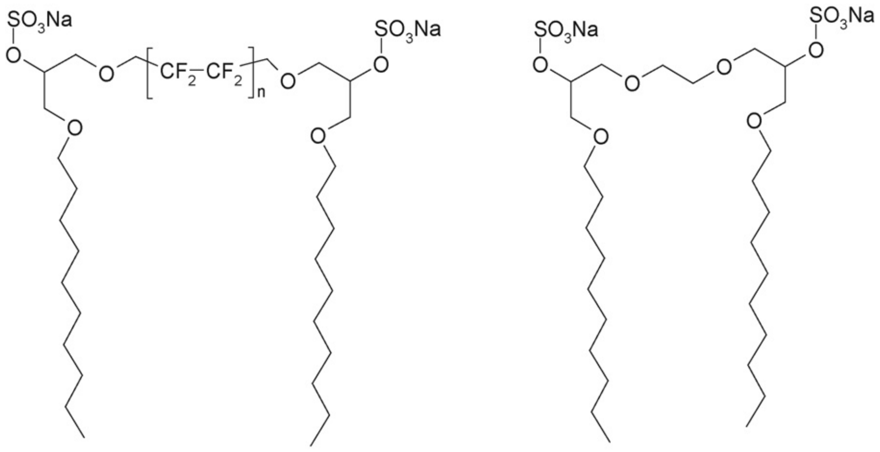
Most of the test solutes [2] were obtained from Sigma–Aldrich (Oakville, Canada) and had a purity ≥98%, except 4-phenylphenol (97%) and 1-methylnaphthalene (97%). The series of *n*-alkyl benzoates (C_1–C_6), used to determine the methylene selectivity, was prepared by reacting the corresponding *n*-alcohols (PolyScience Corporation, Evanston, IL, USA) with benzoylchloride in the presence of triethylamine. The cross-correlation matrix of the 41 solutes shows no correlation between the solute descriptors [2].

Solutions of 4 or 5 solutes (plus dodecanophenone as micelle marker) were prepared in methanol at concentrations between 300 and 600 mg/L, and solutes were identified by comparison of their UV-spectra with entries in a spectral library. All samples were run three to four times, and average retention factors were calculated.

2.3. Calculations

Retention factors were calculated from:

$$k = \frac{t_m - t_0}{t_0(1 - t_m/t_{mc})} \qquad (2)$$



Ia-c

(**a**: n=1; **b**: n=2; **c**: n=3)

II

Fig. 1. Structures of dimeric surfactants with fluorinated spacers (**Ia-c**), and of the non-fluorinated analogue **II** [1,2].