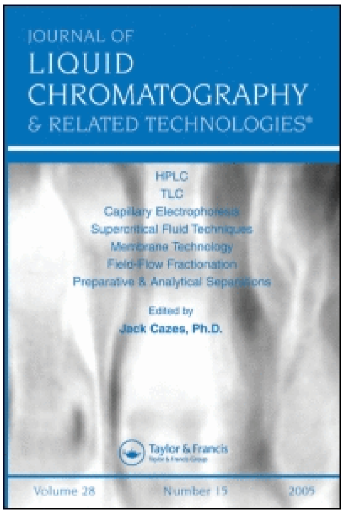

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# EFFECT OF MICELLAR STRUCTURE ON MEKC SEPARATION

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## INTRODUCTION

In order to accomplish the selection of a suitable micelle composition in micellar electrokinetic chromatography (MEKC), and to avoid unnecessary experimental work based on trial and error, an understanding of the structure of micelles and the underlying interaction mechanisms between analyte and this pseudostationary phase is beneficial. MEKC, as a separation mode of CE, is based on interactions between the analyte and a suited type of surfactant which is normally added to the run buffer at concentrations above its critical micelle concentration (CMC), the level at which surfactant monomers tend to form aggregates called micelles.[1]

The following discussion on this topic shall be restricted to aqueous media, the medium for the vast majority of MEKC separations. Surfactants of all categories are employed in MEKC, i.e., anionic, cationic, zwitterionic, and nonionic, with the anionic hydrocarbon sodium-dodecylsulfate (SDS) being the most widely used surfactant. Using cationic surfactants, flow reversal of the electroosmotic flow (EOF) has to be taken into consideration, due to electrostatic interactions with the negatively charged silanol groups of the capillary wall.[2] Nonionic surfactants do not possess an electrophoretic mobility and, thus, elute with the EOF. They are, therefore, usually employed in mixed micelles with SDS and

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function to decrease the electrophoretic mobility of the micelles if the EOF is too slow, or simply, to modify the retention behavior of a micelle.

In aqueous media the hydrophobic tail of the surfactant molecule in a micellar aggregate is orientated towards the center of the micelle, whereas the hydrophilic head group is orientated towards the aqueous phase.[3]

## MICELLAR STRUCTURE

The structure of a micelle is determined by the ratio of the volume occupied by the hydrophobic groups of the surfactant in the micellar core to the length of the hydrophobic group in the core and the cross-sectional area occupied by the hydrophilic head group at the micelle-solute interface. The available cross-sectional area is decreased by increasing concentrations of surfactant.[1] Therefore, in aqueous media (after exceeding the CMC) spherical micelles are initially formed. With increasing concentration of surfactant, the structure is changed to a rather cylindrical shape followed by a lamellar geometry (figure 1).

The micellar size, shape, and the number of surfactant molecules per aggregate, called the micellar aggregation number, are affected by numerous factors. These include structure of the surfactant molecule, temperature, additives, pH, and ionic strength of the liquid phase.

For ionic surfactants which contain a single long alkyl chain, e.g., (SDS), the shape is spherical with aggregation numbers of less than 100 for concentrations up to 0.3 M of surfactant at moderate ionic strength.[1]

## METHODOLOGY

In order to accomplish MEKC or to perform CE at submicellar concentrations, the approximate value of the CMC has to be known. A large number of values for several different surfactants can be found in the literature, e.g.,[1] however, they were often recorded with the aqueous phase being pure water. As are micellar size and shape, the value of the CMC is also greatly influenced by the structure of the surfactant, ionic strength of the aqueous medium, pH, additives, and temperature. For example, the CMC of SDS in pure water is approximately 8.2 µM, whereas in a 100 mM borate-50 mM phosphate buffer at pH 7.0 at 22°C the CMC was found to be 2.8 µM.[4] To obtain the CMC for specific separation conditions, a conductometric titration can be performed. The conductivity increases drastically when the CMC is reached, from the inflection point an approximate value can, therefore, easily be determined.[1]

The following qualitative changes in the CMC for aqueous media can be anticipated from tabulated values and theoretical considerations.[1] The smaller the

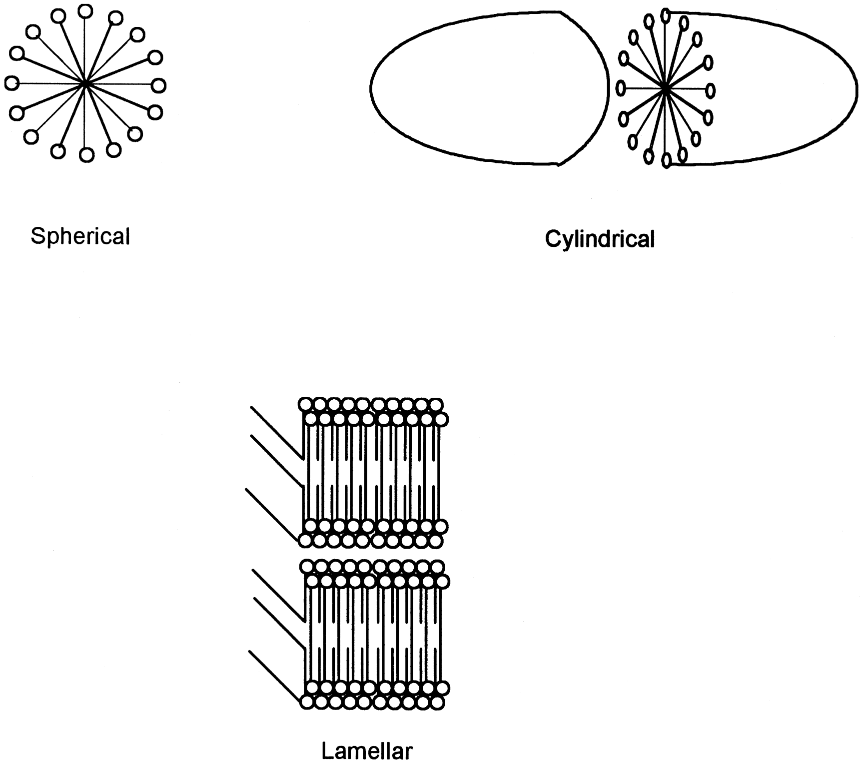

***Figure 1.*** Structure of micelles in aqueous solutions (reprinted with permission from A. A. Fedortchenko, M. Sc. Thesis, Concordia University, Montreal, 1997).

hydrophobic character of the surfactant, the higher the value for the CMC, e.g., a value of 16 μM has been determined for sodium-undecylsulfate compared to 8.2 μM for SDS.[1] To a certain degree, this can be explained by the thermodynamical aspects underlying micellization. If an amphoteric solute molecule is dissolved in an aqueous medium, repulsion of the water molecules from the hydrophobic part of the solute causes the water molecules to form a stronger than normal hydrogen bond network around the surfactant molecules due to the repelling effect. This results in a reduced entropy of the aqueous solution. However, micellization leads to a disappearance of this highly structured hydrogen bond network and the former decrease in entropy is compensated. Therefore, in an approximation, the more hydrophobic the non-polar part of the surfactant molecule the greater its tendency towards micellization. This phenomenon is known as the hydrophobic effect.[4]

Addition of electrolytes to the aqueous phase for ionic surfactants causes, in general, a depression of the CMC due to better compensation of the electrostatic repulsion between surfactant head groups by counterions. Polar organic additives, e.g., amides or alcohols, reduce the CMC because they are probably adsorbed in the outer phase of the micelle. By decreasing the repulsion between surfactant head groups, they decrease the energy required for micellization, thus, facilitating micellization.

The effect of temperature on the CMC is rather complex, for it causes both dehydration of the hydrophilic head group, which favors micellization and disruption of the former mentioned dense hydrogen bond network, which disfavors micellization. The minimum CMC for ionic surfactants was found to be at around 25°C and 50°C for nonionic surfactants.[1]

With the ultimate goal being a rational selection and classification of surfactants in terms of their chemical selectivity, several research efforts have focused on the type of interactions between solute molecules and the surfactant molecules in the pseudostationary phase. In a first approximation, it can be stated that for aqueous systems, nonpolar solutes are typically solubilized in the interior of a micelle, whereas polar solutes interact with the micellar surface with their hydrophobic moieties orientated towards the micellar interior.[3]

It can be seen from thermodynamic considerations, that for several neutral analytes water-micelle partitioning is an entropically driven process. The thermodynamic quantities for micellar solubilization, i.e., standard enthalpy of transfer, $\Delta H^o$, and standard entropy of transfer, $\Delta S^o$, can be obtained from the van't Hoff equation, which states that a linear relation exists between the natural logarithm of the distribution coefficient K and these quantities at different temperatures T:[4]

$$\ln K = - \Delta H^o / RT + \Delta S^o / R \qquad (1)$$

where R is the general gas constant

From here the standard Gibbs free energy of transfer, $\Delta G^o$, can be obtained from the linear free energy relationship:

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (2)$$

The more negative this value the stronger the solute will interact with the pseudostationary phase, thus, exhibiting a longer retention time. The entropy changes become more positive with increasing hydrophobicity of the solute. Again, the hydrophobic effect can be taken into account for describing this phenomenon.[6]

For the characterization of solute-micelle interactions of neutral solutes, linear solvation energy relationship (LSER) modeling can be applied.[5] LSER provides quantitative information about the nature of interactions, which take place between solute and micelles. A multiparameter equation is developed, which relates the logarithm of the capacity factor k' in MEKC to solvatochromic parameters, i.e., the interactions between solute with micellar and aqueous phase:

$$\text{Log } k' = \log k_o + mV/100 + s\pi + b\beta + a\alpha \qquad (3)$$

The solvatochromic parameters of the solute are often tabulated, the solvent dependent coefficients of these parameters can be obtained through multiple linear regression. Solvatochromic properties of the solute are the solute's molar volume V, its dipolarity/polarizability $\pi$, its hydrogen bond acceptor ability $\alpha$, and its hydrogen bond donor ability $\beta$. The solvent dependent coefficients m, s, b, and a of these properties, are the differences in cohesiveness between micellar and aqueous phase, the differences in dipolarity/polarizability, the differences in hydrogen bond donor abilities and hydrogen bond acceptor abilities, respectively. The sign of a coefficient determines whether this type of interaction is favorable or unfavorable for partitioning with the micellar phase. $\log k_o$ is a regression constant, which depends among others, on the phase ratio; it is the only term being affected by the surfactant concentration. For selectivity of a surfactant, the system is represented by other terms; it is not affected by the surfactant concentration. The mV/100 term represents the process of overcoming solvent-solvent interactions in order to form a cavity for the solute. This formation is an important part of nonspecific hydrophobic interactions, whereas the other three terms describe rather specific interactions.

By comparing the order of magnitude of the different types of interactions for several solutes, the types of interaction being predominant for a particular surfactant system in a specified buffer system can be established. If the solute properties are known in advance a suitable surfactant system is predictable.

Investigating different types of anionic hydrocarbon surfactants, it was found that for numerous neutral solutes their molar volumes and their hydrogen bond acceptor abilities are the major types of interaction, whereas their dipolarity/polarizability and their hydrogen bond donor abilities are of minor importance. However, for an anionic fluorocarbon surfactant, the solutes' hydrogen bond donor abilities were found to be of major importance. The hydrogen bond donor abilities of anionic hydrocarbon surfactants are believed to be caused by water molecules residing near the micellar surface.

Another approach to classify surfactant systems and to describe solute-micelle interactions has been made in analogy to the use of retention indices in gas chromatography, which are calculated from the capacity factors of homologous series of neutral solutes with an increasing number of methylene groups. The calculation of retention indices from different surfactant systems can provide information on the different types of interaction with different surfactant systems. Retention indices are also independent of the surfactant concentration.

Future research will further elucidate the contributions of a particular surfactant structure to the different types of interactions and will provide guidelines to a rational selection of a suitable surfactant system for a specific application in MEKC.

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