Physicochemical properties of $\alpha$-sulfonated fatty acid esters

Abstract The physicochemical properties and surface activities of $\alpha$-sulfonated fatty acid esters (SFE) were reviewed mainly based on the recent investigation of the authors. The relationship between the behavior in solution and molecular structures were examined. Four solid phases with different hydration were detected in the phase diagram of C$_{16}$SF methyl ester/water system. The favorable characteristics of SFE, such as hard water tolerance and low Krafft point, were discussed with regard to their crystal structures.

Key words $\alpha$-Sulfo fatty acid esters – surface activity – water hardness tolerance – Krafft point – phase diagram – crystal structure

Introduction

The application of $\alpha$-sulfonated fatty acid esters, especially the methyl ester, has attracted considerable attention, mainly due to the recent demand for renewable sources for the hydrophobic part of surfactants in addition to their characteristic behavior in hard water. General formula of $\alpha$ sulfonated fatty acid esters, also called $\alpha$-ester sulfonates, abbreviated SFE, is R-CH(SO$_3$M)-COO-R' (where R = long alkyl, M = alkali counter ion, R' = alkyl, polyoxyalkylene or polyol). It is noteworthy that SFEs obtained by the ordinary sulfonation reaction with SO$_3$ are regarded as racemic mixtures since their structures have chirality on the $\alpha$-carbon atom.

Fatty acid esters used for producing $\alpha$-sulfonated fatty acid esters are readily obtained by transesterification of the corresponding triglycerides with alcohols. Although investigations of the sulfonation reaction of fatty acids and their esters have been intensively carried out since the 1930s, the large scale production and application of $\alpha$-sulfonated fatty acid esters began very recently, as technological advances concerning the reduction of unfavorable byproducts, e.g., disalts of the $\alpha$-sulfonated fatty acids, which show poor surface activities.

An extensive review covering a wide range of $\alpha$-sulfonated fatty acid esters, such as their synthesis, physicochemical properties, and applications, was recently made by Schwuger and Lewandowski [1]. In this article, characteristic properties and fundamental surface activities of $\alpha$-sulfonated fatty acid methyl and longer alkyl esters and some other esters in aqueous solutions and solid forms will be reviewed mainly on the basis of our recent investigations from the viewpoint of their molecular aggregation states including crystal structures.

Chemical structures of the sulfonation products of fatty acid methyl esters

The sulfonation of sufficiently hydrogenated fatty acid methyl esters with sulfur trioxide proceeds through several intermediate reactions [2–4]. The neutralized products of the sulfonation reaction are racemic mixtures since they have chirality on their $\alpha$-carbon as shown in Fig. 1. In this article, each SFE is abbreviated as shown in Fig. 1, so that
C_{m-2}H_{2(m-2)} + \text{CH}_C\text{HOOCH}_{2n+1} \rightarrow \text{SO}_3\text{Na}

**Fig. 1** Molecular structures of $\alpha$-sulfonated fatty acid esters (SFE) abbreviated as $C_m$-$C_n$ SF

$C_m$ and $C_n$ mean a fatty acid residue and alkyl residue of the ester substituent, respectively. The $\alpha$-sulfonated fatty acid ester salt abbreviated as $C_{m-14}$-$C_{n-1}$ SF Na, for instance, means an SFE sodium salt derived from the myristic acid methyl ester.

**Solubilities, c.m.c, and Krafft points**

Effects of hydrophobic chain length and structures of ester substituents in SFE Na salts

The temperature dependence of solubilities for a series of $C_m$-SFE sodium salts is similar to that of other conventional anionic surfactants, such as alkyl sulfates. Solubility curves of SFE with various carbon chain lengths both in the fatty acid residue and in the alkyl ester residue are shown in Fig. 2 [5]. The longer the acyl chain length, $m$, of the SFE-methyl ester, the solubility curves move to a higher temperature region. On the contrary, equilibrium solubilities of SFE with $m = 14$ (derived from myristic acid) show a maximum in $C_n = 3$ (there is no plot for $C_m = 14$ $C_n = 3$ in Fig. 2 since they are readily soluble in water even in the vicinity of $0 \, ^\circ C$). When $C_m$ exceeds 3, however, the solubility curves move again to a higher temperature region. Krafft points and the c.m.c of $C_m$-$C_n$ SF are listed in Table 1. The existence of an optimum solubility may be due to the difference in molecular alignments in the hydrated solid states of SFE. The n-propyl group as the ester substituent of SFE seems to most significantly contribute to the excellent solubility by its sterically restraining effect.

The logarithmic plots of the c.m.c. of sodium salts of $C_m$-$C_{n-1}$ SF and $C_{14}$-$C_n$ SF decrease linearly with the increase in $C_m$ as shown in Fig. 3. The cohesive energy change to transfer a methylene group of a surfactant molecule from a hydrophobic environment to an aqueous medium, $\omega$, is calculated from the slope of the plots of ln c.m.c. $\sim C_m$ and the degree of counter ion dissociation from micelles. For alkyl sulfates, $\omega$ is reported to be $1.1kT$ [6]. As shown in Fig. 3, the cohesive energy change for $C_{m-1}$ SF is substantially equal to $\omega$ for alkyl sulfates. However, $\omega$ for $C_{14}$-$C_n$ SF is half the value of $C_{m-1}$ SF.

It is well known that the increase in the unit number of the polyoxyethylene group inserted between the alkyl and hydrophilic groups in alkylpolyoxyethylene ether sulfate would cause a decrease in the c.m.c., while it increases the surface tension and the dissociation degree of the micelle [7]. SFE with polyoxyethylene esters, however, increase the c.m.c. regardless of their hydrophobic chain length, while keeping the Krafft points below $0 \, ^\circ C$ [8]. A typical relationship between the c.m.c. and the oxyethylene unit number of $C_{14}$-$\text{(C}_2\text{H}_4\text{O)}_n$ SF is shown in Fig. 4. The role of the polyoxyethylene group in SFE-polyoxyethylene ethers is different from that in alkylpolyoxyethylene ether sulfates.

Surface activities and properties of micelles

Some results of the surface activity measurements are listed in Table 2. $C_{16}$-$C_1$ SF shows a favorable depression