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Synthesis of a novel type of hybrid fluorocarbon ionic surfactants containing polyoxyethlene chain

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Abstract

A novel type of hybrid ionic surfactants containing oxyethylene chain and fluorocarbon chain in one molecule, n-$C_8F_{17}SO_3^-N^+(C_2H_5)_3(CH_2CH_2O)_nH$ ($n = 4.0$, ~4.1, 8.7, 13.2, 17.8, 22.3), were prepared. The compounds were achieved from the reaction of polyethylene glycol and perfluorooctanesulfonyl fluoride in the presence of Et_3N. The evaluation of their behavior at the air–water interface has been studied from measurements of surface tension versus variation of concentration, and the properties of the hybrid surfactants are not consistent with the empirical rule observed from the fluorinated nonionic surfactant.

Keywords: Hybrid; Ionic surfactant; Fluorinated; Surface tension

1. Introduction

Hybrid surfactants with a fluorocarbon chain and a hydrocarbon chain in one molecule are a new class of surfactants. Such surfactants are very effective in lowering the surface tension and interfacial tension so that they often have unique properties and potential applications [1–7], such as simultaneous emulsify-cation of hydrocarbon oil/fluorocarbon oil/water [1]; formation of small micelles with unusually long lifetime [2]; formation of water/supercritical carbon dioxide type microemulsions [3]; spontaneous vesicle formation [4]; thermoresponsive viscoelasticity of the surfactant solution [5]; flocculation-redispersion ability for dispersed magnetite particles in water [6] and new dental reagents for oral hygiene [7].

Since Guo et al. synthesized the first sulfate hybrid surfactant in 1992 [8], hybrid surfactants have gathered the attention of researchers, for instance, there have been some investigations of sulfonate and phosphate anionic hybrid fluorocarbon surfactants [1–7], hybrid hydrocarbon–fluorocarbon cationic surfactants [9] and hybrid nonionic surfactants bearing oxyethylene hydrophilic chains [10]. Recently, we have synthesized triethylalkylammonium perfluorooctanesulfonate (APFOS) hybrid ionic surfactants [11], but these surfactants tend to exhibit a low solubility in water as the *N*-alkyl chain length increases over 16. Generally, the introduction of oxyethylene units to conventional fluorocarbon surfactants has been attempted to enhance the hydrophilicity of the surfactants. On the other hand, to our knowledge, the study on the surfactants with anionic, cationic and nonionic structure in a molecule is not yet reported. In this paper, we will report a convenient synthesis of a new series of hybrid ionic perfluorinated surfactants containing nonionic oxyethylene hydrophilic chains (Scheme 1). The surface properties, such as the critical micelle concentrations (cmc), the surface excess concentration and the surface areas per head group are determined and discussed.

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$n\text{-}C_8F_{17}SO_3^{-}\ \overset{+}{N}(C_2H_5)_3\ (CH_2CH_2O)_nH$ EAPFOSn

Scheme 1. Abbreviation and general formula of the surfactant.

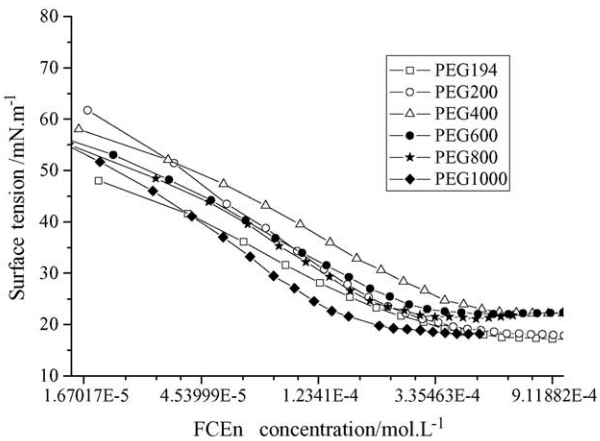

Fig. 1. Water interfacial tension against concentration of EAPFOSn.

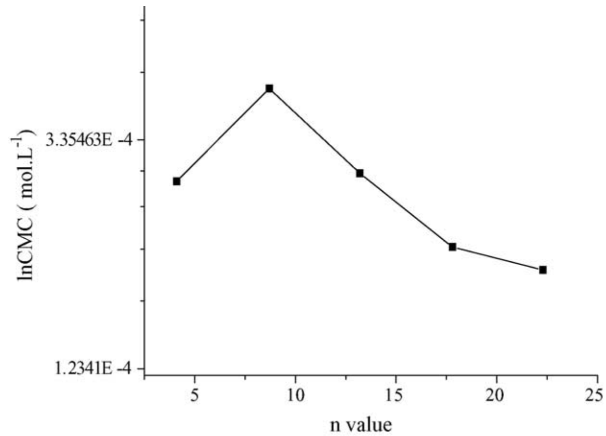

Fig. 2. Relationship between cmc and oxethylene chain length (n) of EAPFOSn.

2. Results and discussion

According to our previous method, the hybrid ionic surfactants (*N*-polyethylene glycol) triethylalkylammonium perfluorooctane sulfonate (EAPFOSn) was synthesized by perfluorooctanesulfonyl fluoride with polyethylene glycol in present of Et_3N in excellent yield, the yields are 84–90%. The surfactants are stable to moisture, thermolysis and hydrolysis.

The surface properties of EAPFOSn were evaluated by measuring the surface tension of its aqueous solution by Wilhelmy plate method at 30.5 °C. The results are shown in Fig. 1. The critical micelle concentration of the investigated surfactants at 30.5 °C were determined by plotting the surface tension (γ) versus $\ln C$ (solute concentration), the cmcs are obtained from the break on the curve, and the γ_{cmc} values are the surface tension values at cmcs (shown in Table 1). Fig. 1 and Table 1 show that the γ_{cmc} values for EAPFOSn are below 25 mN m^{-1}, especially at $n = 22.3$ (19.9 mN m^{-1}). The results demonstrate that surfactants are effective in lowering the surface tension, and have the main properties of fluorinated surfactants.

The surface excesses per ionic surfactant (Γ) have been calculated using the Gibbs equation [12] from the slope the linear portion of the curve obtained by plotting the surface tension against $\ln C$ (Fig. 1). The recorded data apparently indicated that the value n ($n \geq 8.7$) has only a small effect on the Γ values. Moreover, under condition of surface saturation, the Gibbs equation can be used to determine the maximum extent of surfactant adsorption on the surface from which the surface area per EAPFOSn surfactant (A) has been calculated (shown in Table 1). The A values decreased with the lengthening of the oxyethylene groups ($n \geq 8.7$), and it shows that the long OE chains had been probably inserted into the micelles of the surfactants and the packing interface had changed tighter with increasing the number of the oxyethylene groups.

It was also observed the increasing oxyethene chain leads to decrease in the adsorption free energy ΔGad, which is opposite to the empirical rule observed from the fluorinated nonionic surfactant [13,14], and it may be relevant to the hybrid ionic surfactant structure.

Passing on to the cmc results, a series of data in Fig. 2 show that there is a break point ($n = 8.7$) on the curve in Fig. 2, and the logarithm of the cmc decreases incompletely linearly with increasing oxyethene chain length. Interestingly, the surface area (A) and the surface excess (Γ) of EAPFOSn have alike a break point (EAPFOS8.7) in Table 1. It is the reason that ammonium ionic radius of EAPFOS4.0 and EAPFOS4.1 is smaller, as

Table 1
Values of the critical micellar concentration (cmc), surface tension above cmc (γ_{cmc}), surface excess (Γ), surface area (A) and adsorption free energy (ΔGad) for ionic hybrid surface

Surfactant (reagent)	Average ethylene oxide units (n)	10^3 cmc (mol dm^{-3})	γ_{cmc} (mN m^{-1})	ΔGad (KJ mol^{-1})	$10^6\ \Gamma$ (mol m^{-2})	10^2 A (nm^2/mol)
$EAPFOS_{4.0}$ (PEG194)	4.0	0.26	21.4	−25.0	5.12	32
$EAPFOS_{4.1}$ (PEG200)	4.1	0.28	21.7	−27.6	4.97	33
$EAPFOS_{8.7}$ (PEG400)	8.7	0.42	24.2	−29.8	4.42	38
$EAPFOS_{13.2}$ (PEG600)	13.2	0.29	23.7	−30.6	4.49	37
$EAPFOS1_{7.8}$ (PEG800)	17.8	0.21	23.0	−31.0	4.56	36
$EAPFOS_{22.3}$ (PEG1000)	22.3	0.19	19.9	−31.2	4.84	34