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Phase behavior of semifluorinated catanionic mixtures: Head group dependence and spontaneous formation of vesicles

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ABSTRACT

Hexadecyltrimethylammonium bromide (C_{16}TAB)–sodium perfluorooctanoate (C_8FONa) and hexadecylpyridynium bromide (C_{16}PyB)–C_8FONa catanionic semifluorinated mixtures have been studied by conductivity, dynamic light scattering (DLS), cryo-transmission electron microscopy (cryo-TEM) and polarizing microscopy. The regular solution theory, applicable for a limited fluorinated molar ratio, does not predict long-range electrostatic interactions. The results are consistent with the fact that in the hydrogenated-rich region the interaction is attractive in both catanionic mixtures. The systems containing pyridinium headgroups were of the stronger interaction. A transition from micelles was found in both mixtures as a function of fluorinated molar ratio. Special attention was devoted to the effect of the head group in the system properties. The information related with the mean vesicle radius measured by DLS was compared with the vesicle size distribution as well as the elastic properties of the bilayer measured with cryo-TEM.

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1. Introduction

Since Kaler et al. [1,2] in 1989 observed that vesicles could be formed spontaneously in mixtures of cationic and anionic surfactants (catanionic surfactants) a great deal of work has been devoted to such systems. Aqueous mixtures of single-tailed cationic and anionic surfactants can produce also nanostructures as rodlike micelles, lamellar phases and even precipitate, depending on the strength of intra- and intermolecular interactions, the relative fractions of different groups within the surfactant molecules, and the shape of the surfactant molecules. When cationic surfactant solution and anionic one are simply mixed, the strong reduction in area per headgroup resulting from ion pairing induces formation of molecular bilayers at low concentrations; at the right mixing ratios, vesicles may be established spontaneously. It is possible to consider that the ion pairing induces formation of molecular bilayers and the two single chains of the cationic and anionic surfactants acting as double tailed zwitterionic surfactants (differing from these mainly in that the distance between the two charges is not fixed) [3–5]. The structural resemblance of the vesicles to biological cells makes vesicle phases useful as biological membrane models, drug delivery vehicles or nanocompartments for the formation of biomaterials [6,7].

Several reviews summarize the recent advances in catanionic surfactant mixtures and their ability to form vesicles [6,8]. However, a few investigations have been published on catanionic surfactant resulting from mixtures of hydrogenated and fluorinated surfactants [9,10]. Fluorinated surfactants, where fluorine atoms replace hydrogen atoms, show, with respect to their hydrogenated counterparts, a higher hydrophobicity, a more pronounced lowering of the water surface tension and a lower critical micelle concentration (cmc) [11–15]. Another special property of fluorocarbon surfactants is their tendency to form stiff bilayer aggregates and structures with curvature lower than that of hydrocarbon surfactants [14,15]; i.e., it is easier to pack a fluorocarbon chain closely because the chains are on the average more stretched and less entropy is lost [16]. Fluorinated amphiphiles show high biocompatibility and have been investigated as carriers of oxygen and drugs and contrast agents in magnetic resonance imaging [17,18].

It is well known that mixed systems composed of one fluorinated and one hydrogenated surfactant can, under some circumstances, form two types of micelles, due to the poor miscibility of both kinds of chains [19–21]. The miscibility of these mixtures leads to segregation and phase separation [22]. Moreover, the van der Waals interactions among fluorinated chains are much weaker than those in hydrogenated chains, and this had been involved as a

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possible explanation for fluorocarbon–hydrocarbon mutual phobicity. The possibility of demixing into two different types of micelles in fluorocarbon–hydrocarbon surfactant mixtures was first investigated by Mukerjee and Yang by electrical conductivity and they concluded that in surfactant mixtures with equally charged headgroups, exist a coexistence of hydrocarbon rich and fluorocarbon rich micelles [23]. Thus, the mixing of surfactants with hydrocarbon and fluorocarbon tails largely depends on the interactions between their hydrophobic headgroups [24]. Despite intensive research and controversy about micellar mixing and demixing in this particular mixture, there are several possible descriptions with often conflicting predictions. NMR spectroscopy used for studying ^{19}F and ^{1}H chemical shift data in combination with self-diffusion coefficients for fluorinated and hydrogenated ions was analyzed by Nordstierna et al. [25]. The data were interpreted in the framework of the regular solution theory [26], which is focused on the description of mixed micelles a posteriori, presenting some limitations, mainly associated to the degree of association of ionic surfactant molecules with their counterions in the micelle. The main conclusion drawn for this analysis is that there exists neither complete demixing nor complete mixing on molecular or micellar levels.

Previous studies have shown how strong interactions between headgroups in catanionic mixtures can facilitate micellar growth as well as cause phase separation [27–30]. However, it has been suggested that phase separation and precipitation can be avoided if the mixture is made with asymmetrical chain lengths [31,32]. The influence of the temperature on the phase behavior in aqueous solutions of mixed cetyltrimethylammonium bromide (C_{16}TAB) and sodium octyl sulfate (SOS) has also been examined by Tsuchiya et al. [33]. The experimental findings obtained reveal that pseudo-double-tailed C_{16}TAB/SOS complex undergoes a gel–liquid crystal phase transition. Shen et al. [34] have shown that the salt-free catanionic tetradecyltrimethylammonium laurate vesicular solution with uni- and multilamellar vesicles can be transformed into high-salinity catanionic vesicles by adding salt. The viscoelastic, birefringent and salt-free catanionic solution becomes more and more turbid, then precipitates are formed, and finally yields low viscosity birefringent solution of a much higher salinity.

There are abundant studies on the phase diagrams of hydrogenated surfactant and fluorinated surfactant that strongly support a segregation with separate populations of hydrocarbon-rich and fluorocarbon-rich surfactant micelles [35–37]. Rossi et al. [38] have characterized the structural features of vesicles, micelles, and other aggregates spontaneously formed from a fluorinated surfactant (the ammonium salt of perfluoropolyether) and a hydrogenated surfactant (*n*-dodecylbetaine). Their cryo-TEM micrographs show that the aggregate morphology dramatically changed with surfactant composition. Hoffmann et al. [39] have examined solutions of lithium perfluorooctanoate with small angle neutron scattering and have found spherical micelles in the former and vesicles in the latter. A lamellar phase was found to be the first liquid crystalline phase in many of the perfluorooctanoate with different counterions systems.

The aim of this work is to systematically study the catanionic mixture of sodium perfluorooctanoate with hexadecyltrimethylammonium bromide (C_{16}TAB) or hexadecylpyridynium bromide (C_{16}PyB) to understand the influence of the head group in the self-assembly structures resulting from the mixture. The phase diagram of the two catanionic systems has been performed and the different phases investigated by conductivimetry, cross polarizers microscopy, light scattering, and cryo-TEM. The self-assembly structures have been analyzed and the results discussed as a function of the head group in the cationic surfactant.

2. Experimental

2.1. Materials

Hexadecyltrimethylammonium bromide, C_{16}TAB, (No. C5882) and hexadecylpyridynium bromide, C_{16}PyB, (No. C5881) were from Sigma-Aldrich Co., and used as received. Sodium perfluorooctanoate, C_8FONa, of at least 97% purity was from Lancaster Synthesis Ldt.

2.2. Cryo-transmission electron microscopy

Samples were equilibrated at 25 °C either in the Controlled Environment Vitrification System (CEVS) or in the Vitrobot, in the presence of water and ethanol, to avoid evaporation of volatile components during specimen preparation. Vitrified specimens were prepared on 400 mesh copper grids coated with a perforated Formvar film (Ted Pella). A small drop (5–8 µl) was applied to the grid and blotted with filter paper to form a thin liquid film of solution. The blotted sample was immediately plunged into liquid ethane at its freezing point (-196 °C). The procedure was performed manually in the CEVS, and automatically in the Vitrobot. The vitrified specimens were transferred into liquid nitrogen for storage. Samples were examined in a Philips CM120 transmission electron microscope, operated at 120 kV, using an Oxford 3500 cryoholder maintained below -178 °C. Images were recorded on a Gatan 791 MultiScan cooled charge-coupled device (CCD) camera.

2.3. Dynamic light scattering

The setup for dynamic light scattering is an ALV/DLS/SLS-5000F, CGF-8F-based compact goniometer system from ALV-GmbH (Langen, Germany). The light source is a CW diode-pumped Nd:YAG solid-state Compass-DPSS laser with symmetrizer from Coherent, Inc. (Santa Clara, CA). It operates at 532 nm with a fixed output power of 400 mW. Perfect vertical polarization is achieved using a Glan–Thomson laser polarizer prism with a polarization ratio of better than 105 in front of the cell housing. The scattering cells were immersed in a cylindrical quartz container (a vat) that is filled with a refractive index matching liquid (decalin and toluene, for experiments at 22 and 40 °C, respectively). The vat is positioned in thermostated cell housing. The temperature of the vat can be varied from -12 to $+140$ °C and is controlled to ± 0.01 °C by an F32 Julabo heating circulator. The goniometer has a range of scattering angles (θ) between 12° and 155°. The unpolarized scattered light is collected using a near-monomodal optical fiber and two matched photomultiplers that are put in a pseudo-cross-correlation arrangement. For DLS measurements using photon correlation spectroscopy, two multiple τ digital correlators, ALV-5000/E and ALV-5000/FAST Tau Extension, with a total of 320 exponentially spaced channels are employed to produce the time correlation function of the scattered intensity, $G^{(2)}(t)$ (auto correlation function), with an initial real sampling time of 12.5 ns. For DLS measurements, about 1 mL of the vesicle solution was added directly to the cylindrical light scattering cell.

2.4. Conductivity

The set up for conductivity is a Radiometer Copenhagen. The determination of the conductivity curves were carried out by continuous dilution of concentrated samples. The duration of dynamics processes can vary from 10^{-8} s (which is the time it takes a surfactant to leave or enter a micelle) to 10^{-2} s (the time scale of the fusion of micelles), so equilibrium considerations are guaranteed in just a few seconds after dilution. The specific conductivity (κ) data were analyzed as the difference between the experimental

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