Mixtures of Hydrogenated and Fluorinated Lactobionamide Surfactants with Cationic Surfactants: Study of Hydrogenated and Fluorinated Chains Miscibility through Potentiometric Techniques

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The work reported herein deals with the aqueous behavior of hydrocarbon and/or fluorocarbon ionic and nonionic surfactants mixtures. These mixtures were studied using potentiometric techniques in NaBr (0.1 mol L^{-1}) aqueous solution as well as in pure water. Mixed micelles were formed from a cationic surfactant (dodecyl or tetradecyltrimethylammonium bromide respectively called DTABr or TTABr) and neutral lactobionamide surfactants bearing a hydrogenated dodecyl chain ($H_{12}Lac$) or a fluorinated chain ($CF_3-(CF_2)_5-(CH_2)_2-$ or $CF_3-(CF_2)_7-(CH_2)_2-$). We showed that concentrations of ionic and nonionic surfactants in the monomeric form as well as the composition of the mixed micelles can be specified thanks to a potentiometric technique. The complete characterization does not request any model of micellization a priori. The activities of the micellar phase constituents, as well as the free enthalpies of mixing, were calculated. The subsequent interpretation only relies on the experimental characterization. Comparison of the behaviors of the various systems with a model derived from the regular solution theory reveals the predominant part of electrostatic interactions in the micellization phenomenon. It also appears that the energy of interaction between hydrogenated and fluorinated chains is unfavorable to mixing and is of much lower magnitude than the electric charges interactions.

Introduction

Fluorinated surfactants are of the highest interest, for both their fundamental and practical importance. From a fundamental viewpoint, they are both hydrophobic as well as oleophobic, and the study of their micellization behavior is of great help in the understanding of the "hydrophobicity" or "solvophobicity" effect. On a practical side, they are used in different industrial fields as part of the formulation of fire-fighting foams, emulsifiers, cosmetics, paper, etc. or in biological and medical fields to favor the membrane proteins studies or the emulsification of perfluorocarbon compounds in blood. In many applications, they are used in mixtures with hydrogenated surfactants to improve the efficiency of the desired properties.[1]

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 the fluorocarbon and hydrocarbon chains.[1−4] These systems were investigated by a variety of techniques, but the experimental evidence of such segregation is often difficult[5] and, depending on the procedures used, can even lead to contrary conclusions. Nordstierna et al.[6] have very recently opened new perspectives about the possibility of segregation of fluorinated and hydrogenated chain as patches in the same micelle.

Theoretical predictions could be of help to design and understand segregating systems in a better way, but most of the theories, like for instance the widely used regular solution theory (RST),[7] focus on the description of mixed micelles a posteriori. Thermodynamics has also been used for this purpose.[8] Molecular thermodynamics was more recently introduced for predictive purposes, in particular for mixed micelles made of ionic and nonionic components.[9−13] It calculates each contribution to the Gibbs energy of micellization, among which electrostatic interactions due to polar heads and the hydrophobic contribution due to the formation of the micellar core. In these models only applied to mixtures of hydrogenated surfactants, the interaction parameter of the RST can be predicted but also a wide number of micellar properties if micelles are remaining spherical.[10,11] One study considers the possibility of mixing hydrogenated surfactants of different chain lengths[13] as a geometrical constraint but the main contribution to synergism is still the reduction of electrostatic repulsions between heads. In the case of fluorinated surfactants, the approach is indeed complicated by the non-spherical shape of the aggregates.[14]

In this context, the experimental Gibbs energy of mixing of surfactants in the micellar pseudophase was reported for some mixtures of fluorinated and hydrogenated surfactants.[12,15,16,17]

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