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Historical perspective

Micelle–monomer equilibria in solutions of ionic surfactants and in ionic–nonionic mixtures: A generalized phase separation model

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ABSTRACT

On the basis of a detailed physicochemical model, a complete system of equations is formulated that describes the equilibrium between micelles and monomers in solutions of ionic surfactants and their mixtures with nonionic surfactants. The equations of the system express mass balances, chemical and mechanical equilibria. Each nonionic surfactant is characterized by a single thermodynamic parameter — its micellization constant. Each ionic surfactant is characterized by three parameters, including the Stern constant that quantifies the counterion binding. In the case of mixed micelles, each pair of surfactants is characterized with an interaction parameter, β, in terms of the regular solution theory. The comparison of the model with experimental data for surfactant binary mixtures shows that β is constant — independent of the micelle composition and electrolyte concentration. The solution of the system of equations gives the concentrations of all monomeric species, the micelle composition, ionization degree, surface potential and mean area per head group. Upon additional assumptions for the micelle shape, the mean aggregation number can be also estimated. The model gives quantitative theoretical interpretation of the dependence of the critical micellization concentration (CMC) of ionic surfactants on the ionic strength; of the CMC of mixed surfactant solutions, and of the electrolytic conductivity of micellar solutions. It turns out, that in the absence of added salt the conductivity is completely dominated by the contribution of the small ions: monomers and counterions. The theoretical predictions are in good agreement with experimental data.

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1. Introduction

The existence of surfactant micelles was established in the beginning of the twentieth century by W. B. Hardy, J. W. McBain and coworkers in their studies on electrolytic conductivity of carboxylate solutions [1]. They found that the solutions of sodium laurate and myristate contain both *electrolytic* and *colloidal* constituents (dissociated surfactant monomers and surfactant aggregates) [1]. The term “micelle” became widely accepted about twenty years later [2]. Since then, the micelles and micellar solutions have been a subject of intensive studies stimulated by their great scientific and practical importance.

Firstly, some empirical dependencies have been established. In the case of *ionic* surfactants, Corrin and Harkins [3] found that the critical micellization concentration (CMC) depends linearly on the ionic strength of solution (varied by the addition of salt) when plotted in double log scale. The slope of this plot has been interpreted as degree of binding of counterions to the micelle [4], although this interpretation is uncertain and is considered again in the present article (Section 4.6). In the case of *nonionic* surfactants, it has been found that CMC obeys the empirical Klevens equation [5]:

$$\log(\mathrm{CMC}) = \hat{A} - \hat{B}n \tag{1.1}$$

where n is the number of C atoms in the alkyl chain; $\hat{A}$ and $\hat{B}$ are empirical coefficients tabulated for some homologous series [6]. For linear alkyl ethoxylates, C_nE_m, Eq. (1.1) has been generalized in Refs. [7,8].

Various experimental methods have been applied to study the properties of the micelles: viscosimetry [9,10]; conductometry [11–13]; calorimetry [14,15]; fluorescence quenching [16–19]; stratifying foam films [20–22]; static and dynamic light scattering [10,23,24]; small-angle X-ray scattering (SAXS) [25,26] and neutron scattering (SANS) [27,28]; electron paramagnetic resonance (EPR) [27,29]; nuclear magnetic resonance (NMR) [30–32], and various methods to study the dynamics of micellization [33,34].

In the theoretical aspect, four main approaches to the modeling of micelles and micellar solutions have been developed:

The *mass action model* describes the micellization as a chemical reaction [10,35–38]. This model gives a detailed description of the micelles as polydisperse aggregates and allows modeling of the growth of non-spherical micelles and other self-assembled structures [39–44]. Generalizations to ionic micelles are also available [45–50].

The *phase separation model* is focused on the equilibrium between micelles and monomers with respect to the exchange of each component in a multi-component surfactant mixture [51–56]; reviews can be found in [37,38] and Section 2 of the present article. In this model, the micelle polydispersity is usually neglected; average aggregation numbers and charges per micelle are used, and the micelles are treated as a pseudophase that is equilibrated with the monomers. The regular solution theory has been applied to both binary [53] and multi-component surfactant mixtures [57–59]. In the case of ionic surfactants, various models of the effect of electric double layer and counterion binding on micellization have been proposed [60–67].

Molecular thermodynamic models of the micelles have been developed and extended to surfactant mixtures [68,69]. They consider the detailed surfactant molecular structures and give theoretical description of the micellization process based on various free-energy contributions, including those from the hydrophilic heads and hydrophobic tail configurations [70–76].

The computational methodology based on the *quantitative structure–property relationship* approach (QSPR) has been applied also to micelles. First Huibers et al. [77,78] developed this method to predict the CMC of surfactants using a large database of molecular descriptors. So far, the QSPR method has been applied to predict the CMC values of many of nonionic and ionic surfactants [79–83].

The focus of the present article is on models that describe the micelle–monomer equilibria, with applications for characterizing micelles of ionic surfactants and their mixtures by charge and aggregation number; for a deeper understanding of conductivity of micellar solutions; for interpreting the dependence of CMC on the mole fractions of mixed surfactants and on the electrolyte concentration; for analyzing the precipitation and pH variation in micellar carboxylate solutions; for determining the solubility limits of fatty acids and alcohols in micelles of conventional surfactants, etc. For this goal, the most appropriate is the phase separation model, which is based on chemical equilibrium relationships, supplemented by mechanical and mass balance equations. As demonstrated below, the key issue is how to close the system of equations in order to obtain a physically adequate model.

With the final goal to construct a physically transparent, quantitative and easy for application model of micellar solutions, three main approaches are extended and combined here:

(1) The general thermodynamic approach from Ref. [84] for planar ionic-surfactant adsorption layers is extended to ionic-surfactant micelles. In this approach, the key point is the thermodynamically correct incorporation of the *counterion binding*

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