

The surface tension of aqueous solutions of cetyltrimethylammonium cationic surfactants in presence of bromide and chloride counterions

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Abstract

An improved model of ionic surfactant adsorption was applied for description of CTABr (cetyltrimethylammonium bromide), CTACl and CTAHSO₄ surfactants adsorption from their aqueous solutions containing KCl and KBr at liquid/air interface. The model is based on the assumption that the surfactant ions and their counterions undergo non-equivalent adsorption within the Stern layer. The surface tension isotherms for various concentrations of surfactant ions and Br⁻ and Cl⁻ counterions were calculated and compared with the results of surface tension measurements performed by the pendant drop shape analysis methods. The dependences of surface excess values of all ions on CTA⁺/Br⁻/Cl⁻ bulk concentrations were calculated. Obtained results showed much larger affinity to the interface of Br⁻ anions than Cl⁻ anions. This was explained in terms of a larger repulsion of chloride anions from the interface than bromide anions. It may be caused by the difference in their excess polarizability and the van der Waals interaction with the interface.

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1. Introduction

Surface tension of aqueous solutions of surfactants, either ionic or non-ionic, in the presence of added salt can provide useful information on their adsorption at the air solution interface. Explanation of the mechanism of adsorption is of importance for a variety of practical phenomena such as thin film stability, micellisation, foamability, etc. However, theoretical description of adsorption mechanism of ionic surfactants is very complicated because of multicomponent nature of such systems. They contain surfactant ions, counterions and ions of salt added to control ionic strength of the solution. The successful theoretical model should take into account electrical interactions between all ions and should describe at least semi-quantitatively the electric double layer (EDL) structure in such multicomponent systems. Due to the complexity of the problem there have been only a limited number

of attempts to formulate theoretical models of ionic surfactant adsorption. In general the theoretical models are based on thermodynamics concept of the Gibbs dividing surface, in which the surface excess of any ion is the sum total of its excesses in the actual monolayer and in the electrical double layer [1,2]. The model proposed by Davies and Rideal [3], then extended by Borwankar and Wasan [4] exploited the simple Gouy-Chapman model of the electrical double layer and assumed that surfactant ions adsorb in the Stern layer and the (point-like) counterions remain in the diffuse part of the electric double layer. Due to the latter assumption this model cannot describe any phenomena, which are dependent on the nature of counterion. Similar model was proposed by Fainerman and Lucassen-Reynders [5,6]. They included the correction for activity coefficients of electrolyte solution but the role of the electric interaction of the adsorbing ionic species was not taken explicitly into account. The model proposed by Kalinin and Radke [7] considered the counterion binding to surfactant ions adsorbed in the Stern layer. They adopted Grahame's [8] concept of the triple layer with counterions

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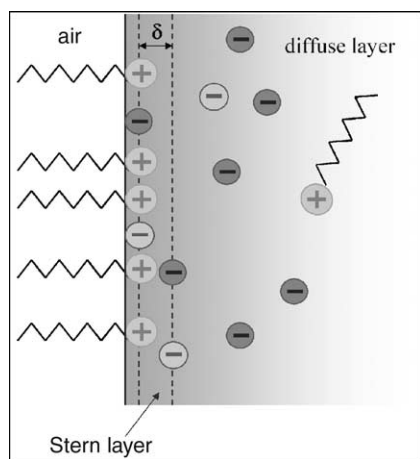


Fig. 1. Schematics of the model of ionic surfactant adsorption.

located at the plane different from that of the adsorbed surfactant head-groups. The adsorption of ionic surfactants was also theoretically considered by Kralchevsky et al. [9]. In our previous papers [10–14] we proposed the alternative model of ionic surfactant adsorption. We assumed that surfactant ions and counterions can adsorb in the Stern layer, which can be regarded as the two dimensional electrolyte without the electroneutrality condition being fulfilled. The adsorption of coions in the Stern layer was neglected. The schematics of our model are shown in Fig. 1. Using this model we described adsorption of anionic [10,12,13] and cationic [11,14] surfactants in the absence and presence of added electrolytes.

The significance of salt addition in ionic surfactant adsorption was demonstrated long ago [15–17] but our understanding of this process still remains incomplete. One can find in the literature only a few systematic works dealing with the effect of the ionic strength and type of electrolyte added, on the interfacial tension of ionic surfactants. There are the results of Matuura et al. [18], who measured adsorption of SDS in solutions of different salts, especially NaCl. These results are valuable since the direct radiotracer method was used (with ^{35}S as a label) for evaluating the quantity of SDS adsorbed. Similar measurements were carried out by Tajima et al. [19] and Tajima [20] who also used the radiochemical methods for studying adsorption of tritium labelled SDS.

The effect of addition of salt with common anion (NaBr) on the CTABr adsorption was studied by Rijnbout [21] and Okuda [22]. Analogous surface tension measurements in electrolytes with the common anion were carried out by Ozeki and Ikeda [23] in the case of dodecyltrimethyl ammonium chloride (DDACl) and by Okuda et al. [24] for dodecyltrimethyl ammonium bromide (DDABr). Góralczyk et al. [25] considered the surface tension of decyl- and dodecylpyridinium chlorides and bromides in presence of NaCl, NaBr and NaI. In these works, the experimental results were interpreted in terms of the Gibbs adsorption equation with no attempt to quantitatively characterise the electrical double layer formed as a result of the surfactant and counterion ad-

sorption. Description of experimental findings in terms of theoretical model of adsorption was initiated by Fainerman [26,27] who measured the effect of NaCl on SDS adsorption and interpreted the results in terms of the Borwankar and Wasan [4] theory. Kalinin and Radke [7] reinterpreted these (and others) results in terms of their model, while Warszynski et al. [10] interpreted their own and Matuura results [18] concerning SDS adsorption in the presence of NaCl using newly proposed theoretical model based on the assumption of counterion adsorption within the Stern layer. In the latter work also the experimental results concerning the dependences of the surface potential on the surfactant ion and counterion concentration were discussed within the frame of the same model.

In this work we examine the influence of two types of halide anions, chloride and bromide on the adsorption of three cetyltrimethylammonium based cationic surfactants CTABr, CTACl and CTAHSO₄. First we discuss briefly the theoretical background of the description of the proposed earlier [13,14] improved model of ionic surfactant adsorption. Then, we apply the model to evaluate the experimental results concerning the surface tension isotherms of the surfactants at the air/solution interface. We discuss the isotherms obtained by setting constant concentration of added electrolyte (KBr or KCl) and varying concentration of surfactant. We elucidate the parameters of the isotherms characteristic for surfactant ions and both counterions and evaluate the composition of the surface layer. Isotherms obtained by keeping the surfactant concentration constant and varying the addition of electrolyte are also considered.

2. Theoretical background

Aqueous solution of any ionic surfactant is a multicomponent system. It contains surfactant ions; its counterions and it may contain ions of an electrolyte added to the solution to regulate its ionic strength or pH. If the ionic surfactant is a weak electrolyte or undergoes hydrolysis, the dissociation equilibrium is established and a non-ionic form of the surfactant is also present in the solution. The example of the latter process is an aqueous solution of sodium dodecyl sulphate (SDS), which is always contaminated by dodecanol, which is a product of SDS hydrolysis [28]. If we neglected the presence of non-ionic contamination the Gibbs adsorption equation for a fully dissociated cationic surfactant can be written in the form:

$$-d\gamma = \Gamma_{\text{S}^+} d\mu_{\text{S}^+} + \Gamma_{\text{C}^-} d\mu_{\text{C}^-} + \Gamma_{\text{B}^+} d\mu_{\text{B}^+} + \Gamma_{\text{C}_1^-} d\mu_{\text{C}_1^-} \quad (1)$$

where γ is the surface tension of the solution, Γ 's are the surface excess concentration for surfactant cations (S^+), surfactant counterions (C^-), cations (B^+) and anions (C_1^-) of the added salt, respectively (they include ions adsorbed in the Stern layer and in the diffuse part of the electric double layer); μ 's are respective chemical potentials, $\mu_i = \mu_{i0} + RT \ln(a_i)$

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