



Thermodynamic parameters and counterion binding to the micelle in binary anionic surfactant systems

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ABSTRACT

Competitive counterion binding of sodium and calcium to micelles, and mixed micellization have been investigated in the systems sodium dodecylsulfate (NaDS)/sodium decylsulfate (NaDeS) and NaDS/sodium 4-octylbenzenesulfonate (NaOBS) in order to accurately model the activity of the relevant species in solution. The critical micelle concentration (CMC) and equilibrium micelle compositions of mixtures of these anionic surfactants, which is necessary for determining fractional counterion binding measurements, is thermodynamically modeled by regular solution theory. The mixed micelle is ideal (the regular solution parameter $\beta_M = 0$) for the NaDS/NaOBS system, while the mixed micelle for NaDS/NaDeS has $\beta_M = -1.05$ indicating a slight synergistic interaction. Counterion binding of sodium to the micelle is influenced by the calcium ion concentration, and vice versa. However, the total degree of counterion binding is essentially constant at approximately 0.65 charge negation at the micelle's surface. The counterion binding coefficients can be quantitatively modeled using a simple equilibrium model relating concentrations of bound and unbound counterions.

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1. Introduction

Precipitation of anionic surfactants is significant in both positive (precipitation of sodium surfactants as a purification technique) and negative (precipitation of divalent cation surfactants in the formation of soap scum) ways. In order to model such precipitation it is necessary to be able to model the compositions of the surfactant species and the counterions in both the solution and micelle phases. Practical applications of surfactants usually involve surfactant mixtures. Surfactants used in commercial applications, for instance sodium alkyl sulfates, are mixtures of homologous anionic surfactants, unreacted raw materials, and by-products. In addition, in many applications surface-active materials are mixed to create synergism due to the presence of the second surfactant. While larger synergies appear in mixtures of ionic and nonionic surfactants [1–4] rather than in mixed ionic surfactant systems with the same charge, a number of researchers have also investigated interactions between surfactants in the micellar phase for these ionic/ionic systems [2,5–8]. Numerous studies have reported the degree of dissociation and/or binding of counterions to the micelle [9–15] which is necessary to determine their concentrations in the solution phase. However, there

are still no definitive results due to differences in values measured by different experimental techniques, and to nonuniform theoretical definition of counterion binding.

In this work, the effect of the counterion on the micelle and the counterion binding to the micelle are investigated by the use of ion-selective electrodes to directly measure the activity of the ionic species present in the bulk solution. These results were then used with the micellization model (which gives the concentration of surfactant species in the micellar phase) to predict the fraction of counterion binding to the micelle for each counterion. An investigation of the mixed micellization behavior of surfactants with an equivalent length of the hydrocarbon chain but having fully aliphatic and partially aromatic tails, as well as a mixture of homologous anionic surfactants to determine nonideality in mixing are also performed in this work, since the ability to predict the CMC is required for the balances needed to estimate the fractional counterion binding. The work presented here can be used to improve the thermodynamic modeling of micellar systems so as to better understand the activities of the monomer surfactant in the solution phase, which requires accurate modeling of the CMC and the composition of the micelle; and the activity of the counterions in the solution phase, which requires accurate knowledge of counterion binding to the micelle. One significant benefit is improved modeling of both solubility and degree of supersaturation in surfactant systems.

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2. Materials and methods

2.1. Materials

Sodium dodecylsulfate (NaDS) was purchased from Carlo Erba with purity greater than 92%. Sodium 4-octylbenzenesulfonate (NaOBS) was purchased from Aldrich with purity greater than 97%. These two anionic surfactants were further purified by twice recrystallizing using deionized water and methanol, respectively. Sodium decylsulfate (NaDeS) was purchased from Fluka with purity greater than 99% and was used as received without further purification. Reagent grade sodium chloride (NaCl), with purity greater than 99.5%, was purchased from Merck and was used as received. Analytical reagent grade calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), with purity greater than 98.0%, was purchased from Sigma–Aldrich and was used as received. Deionized water (18 M Ω cm) was used to prepare all aqueous samples throughout the experiments.

2.2. CMC determination

Measurements of CMCs for surfactant mixtures were carried out by surface tension measurement using a Wilhelmy plate type tensiometer. The surface tensions of the pure NaDS, NaOBS and NaDeS systems are already well characterized in the literature [16–18]. The surface tension measurement was performed by a Krüss (K10ST model) tensiometer equipped with a platinum plate. Equilibration times in the case of surfactant mixtures can be quite long as noted in an earlier study [19]. In the current study, samples were held to equilibrate at 30 °C until the surface tension on the digital reading display stabilized (three matching measurements at consecutive 15 min intervals). The value of the final reading at three hours after the mixing was used if the reading shown on the display was not stabilized by that time. The experimental data can be interpreted to determine the surface excess concentration (Γ_s), the value of the mean molecular area (a_m), and the minimum free energy of the surface [20,21].

The effect of counterions on the CMC of NaDS was investigated by a conductimetric technique. Conductivity was also used to determine the effect the counterion concentration has on the CMC and to measure the CMC of pure NaDS, NaOBS, and NaDeS solutions. Conductivity was measured by an inoLab Cond Level 2 conductivity meter with a 4-cell conductivity epoxy probe, both with and without NaCl at 30 °C. For an investigation of the effect of calcium ions on the CMC, NaDS systems with trace CaCl_2 concentrations were prepared at concentrations below the precipitation phase boundary [22]. The relationship between CMC and unbound sodium ion concentration can be demonstrated on a logarithmic scale at a specific temperature as proposed by Corrin and Harkins [23]:

$$\ln[\text{CMC}] = -K_1 - K_g \ln[\text{Na}^+]_{\text{unb}} \quad (1)$$

where K_1 is a constant determining the CMC in solutions having an unbound sodium ion concentration of 1 M (a reference state) and K_g which determines the effect of the unbound sodium ion on the CMC.

2.3. Activity measurement

Activity measurements were performed using sodium- and calcium-ion-selective electrodes (ISE) at 30 °C. The sodium-selective electrode was the VWR symPHony sodium ion selective glass combination electrode (Na-ISE) where mercury(I) chloride (calomel, Hg_2Cl_2) solution was the internal reference solution. The calcium-selective electrode was a Cole-Parmer calcium ISE double-junction (Ca-ISE), where a potassium chloride solution was the

internal reference solution and was purchased from Cole-Parmer Instrument Company (USA). The electromotive force (EMF) from the electrodes was registered by an Accumet AB15+ pH/mV bench-top meter with an ATC probe purchased from Cole-Parmer (USA). EMF can be used to calculate the activity of ion species of interest through the use of the Nernst equation. The activity of sodium and calcium ions (a_i) was calculated using the following equation [24]:

$$\log a_i = \frac{0.4343F}{RT} (E_i - E_{i,0}) \quad (2)$$

where F is the Faraday constant, R is the universal gas constant and T is the absolute temperature. E_i is the EMF of the solution at any moment and $E_{i,0}$ is a constant depending on the type of reference electrode and the filling solution. The value of $E_{i,0}$ can be determined by projecting the following equation backward to the intercept [25]:

$$\Delta_i = \frac{0.4343F}{RT} E_i - \log[C_i] \quad (3)$$

where C_i is the concentration of the cation of interest, so at the intercept ($C_i = 0$),

$$E_{i,0} = \frac{RT}{0.4343F} \lim_{C_i \rightarrow 0} \Delta_i \quad (4)$$

A plot of the activity of sodium ions in the intermicellar solution as a function of surfactant concentration can be used to calculate the degree of counterion binding to the charged surface of the micelle. The activity of calcium ions in the intermicellar solution at different CaCl_2 concentrations in solution can also be used to calculate the degree of calcium ion binding to micelle. Measurements were performed in mixtures of sodium surfactants and CaCl_2 , and as a result unbound ions acted as an electrolyte minimizing the effect of the charged micelle surface on the measurement of the ion activities.

3. Results and discussion

3.1. Fitting of experimental CMCs with regular solution theory (RST) and prediction of micelle compositions

In a study of counterion binding, the fractional binding of counterions to the surface of the micelle is best estimated by knowledge of the concentration of surfactant in the solution phase, the concentration of counterions in the solution phase, and balances with respect to total concentrations to calculate the concentrations of all species in the micellar phase. Thus, it is critical to perform experiments and modeling of the micellization phenomena in the systems studied.

RST has been employed as in previous studies [2–8] to model the thermodynamic nonidealities of the mixed-surfactant systems. Regular solution theory was first introduced to binary and multi-component amphiphilic systems by Rubingh [26,27], and when the effect of counterion binding to the micelle has a negligible effect on the micelle composition [28] the pseudophase separation model and regular solution theory have been widely used for the analysis of this type of experimental data.

Based on the pseudophase separation theory, a mixture of two different surfactants in the monomeric form at the compositions α_1 and α_2 is assumed to be in equilibrium with micelles that have composition X_1 and X_2 , with mole fractions on a surfactant-only basis. The phase equilibrium can be modeled via the equation:

$$\alpha_i \gamma_{i,m} \text{CMC}_i = X_i \gamma_{i,M} \text{CMC}_M \quad (5)$$

where $\gamma_{i,m}$ and $\gamma_{i,M}$ are activity coefficients of surfactant i in the monomeric and micellar solutions respectively, CMC_i is the CMC of the pure anionic surfactant and CMC_M is the CMC of the binary

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