Introduction

The interaction of organic solubilizates with ionic and nonionic surfactant micelles has been studied widely since the pioneering work of Shinoda [1] and Herzfeld et al. [2]. The presence of solubilizates has a significant impact on micellar properties such as aggregation number, critical micelle concentration values, and the degree of counterion binding) [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. Over the past few years, the interactions of ethoxylated alcohols with ionic surfactants have been gaining attention. This interest has stemmed from the unusual difference in the interactions of alkoxyethanols with anionic and cationic micelles, [8, 10, 11] which parallels the manner in which non-ionic polymers, e.g., poly(ethylene) oxide, interact with sodium dodecylsulfate (SDS) and dodecyltrimethylammonium bromide (DTAB) [14, 15, 16, 17]. In the case of the anionic SDS micelles, Manabe et al. [8] determined that the cmc values of SDS/alkoxyethanol mixed micelles were dependent on the number of ethylene oxide (EO) groups in the alcohol, at a constant alcohol alkyl chain length and at a specific alcohol concentration. Marangoni and Kwak [10] and Rodenhiser et al. [11] determined completely the equilibrium properties (cmc values, aggregation numbers, and distribution coefficients) of SDS/alkoxyethanol and DTAB/alkoxyethanol as a function of alcohol concentration. Their results clearly indicated that the EO groups contributed significantly to the formation of anionic surfactant/alkoxyethanol mixed micelles, but that there was little evidence of any enhancement of the interaction between ethoxylated alcohols and cationic micelles due to the presence of the EO groups. Huang and Verrall [18] determined volumetric and other thermodynamic properties of carboxylate surfactants mixed with ethoxylated alcohols and found that the variation in the properties of the mixed micelles was consistent with the EO groups imparting a contribution to the hydrophobic

Abstract

Estimates of the thermodynamic parameters of micellization ($\Delta_{\text{mic}} G^\circ$, $\Delta_{\text{mic}} H^\circ$, and $\Delta_{\text{mic}} S^\circ$) have been determined for a series of mixed micelles consisting of ionic surfactants (sodium dodecylsulfate and dodecyltrimethylammonium bromide) and medium chain length alkoxyethanols as the co-surfactant. The enthalpies of micellization have been measured directly for the above systems using isoperibol solution calorimetry; the Gibbs energies and entropies of micellization are obtained by application of the mass-action model to the critical micelle concentration values from the calorimetric titration experiments. The thermodynamic properties of mixed micelle formation with alcohol concentration and temperature are in excellent agreement with our previous results. However, there does appear to be some dependence of the thermodynamic properties of mixed micelle formation on the charge of the ionic surfactant. These dependencies are discussed in terms of the manner in which the ethylene oxide group of the alcohol interacts with the ionic head groups and the location of the solubilizes in the micellar interior.
interactions. However, their work did not examine the differences in the interaction of ethoxylated alcohols with anionic and cationic micelles.

There have been few determinations of the enthalpy and entropy of micellization, especially in the presence of water-soluble additives like n-alcohols [5, 6, 7, 19, 20, 21, 22, 23, 24]. In this paper, we present the results from our calorimetric investigation of the formation of ethoxylated alcohol/ionic surfactant mixed micelles as a function of the concentration of the ethoxylated alcohol in the mixed solvent and the temperature. These results indicate that the addition of EO groups to alcohols has a significant impact on the enthalpy and entropy change of micelle formation, with changing alcohol concentration and temperature. All these results are interpreted in terms of the location of the EO groups in the cationic vs. the anionic surfactant/alkoxyethanol mixed micelle.

Experimental

Sodium dodecylsulfate and dodecyltrimethylammonium bromide were obtained from the Aldrich Chemical Co. and were purified by repeated recrystallizations from ethanol and an acetone/ethanol mixture, respectively. Conductivity grade water (1.0 x 10^{-6} S cm^{-1}) was obtained by passing previously deionized water through a Millipore 4000 S purification system.

1-Butanol (C_{4}E_{0}) and ethylene glycol mono- n-butyl ether (C_{4}E_{1}) were reagent grade solvents from the Fisher Chemical Company; diethylene glycol mono-n-butyl ether (C_{4}E_{2}, Spectroscopic Grade) was received from Aldrich. Triethylene glycol mono- n-butyl ether (C_{4}E_{3}) was obtained from Tokyo Kasei. All ethoxylated alcohols were used without further purification.

The alcohol/water mixed solvent systems were prepared on a molarity basis; the surfactant solutions were made up directly in the mixed solvent. The concentration of the surfactant solutions is reported as the moles of surfactant/l of mixed solvent. Densities of the titrant solutions were obtained using an Anton-Parr DMA 45 density meter. Heat capacity data for the titrant solutions and the micellization enthalpies were obtained as described previously [21].

Results and discussion

Micellization enthalpies from calorimetric titrations

For an alcohol/surfactant mixed micelle, the Δ_{mic}H° values refer to the enthalpy change that occurs when \( N_s \) moles of surfactant \( S \) (charge \( a \)), \( N_c \) moles of counterion \( C \) (charge \( b \)), and \( N_a \) moles of additive \( A \) aggregate in aqueous solution to form a mixed micelle, \( M \), of charge \( ±z \):

\[
N_s S^a + N_c C^b + N_a A \leftrightarrow M^{±Z}
\]  

It has been stated that the direct measurement of the \( Δ_{mic}H° \) by calorimetry is the preferred method of obtaining thermodynamic properties of micelle formation [6]. A typical plot of q vs. V for the dilution of a 0.200 M SDS into water is given in Fig. 1; the break in the curve (corresponding to the cmc value) is clearly visible in Fig. 1. The Δ_{mic}H° values are determined from the q vs. volume of added titrant curves (q vs. V plots) from the following equation:

\[
Δ_{mic}H° = \frac{1000}{M} \left( \frac{dq}{dV} \text{(post cmc)} - \frac{dq}{dV} \text{(pre cmc)} \right) \tag{2}
\]

where \( dq/dV \text{(post cmc)} \) and \( dq/dV \text{(pre cmc)} \) are the observed q vs. V slopes from the calorimetric titration curves (Fig. 1), and \( M \) is the molarity of the titrant solution. The Gibbs energy change upon micelle formation, \( Δ_{mic}G° \), is obtained from the simple mass-action model and the calorimetric cmc values as follows:

\[
Δ_{mic}G° = (2 - z)RT \ln X_{cmc} \tag{3}
\]

where \( X_{cmc} = \text{cmc (M)}/55.5 \), and \( z \) is the degree of counterion dissociation (obtained in separate experiments). From the calorimetric \( Δ_{mic}H° \) and the \( Δ_{mic}G° \) values, the \( Δ_{mic}S° \) may be found from the equation:

\[
Δ_{mic}S° = \frac{(Δ_{mic}H° - Δ_{mic}G°)}{T} \tag{4}
\]

Micelle formation enthalpies of surfactant/C_{4}E_{n} mixed micelles

The enthalpy changes upon micelle formation (\( Δ_{mic}H° \) values) are presented in Table 1 for the SDS/C_{4}E_{n} systems and in Table 2 for the DTAB/C_{4}E_{n} mixed micellar systems. The micelle formation enthalpies are plotted in Figs. 2, 3, 4, and 5 for the SDS/alkoxyethanol systems. The corresponding values for the DTAB/alkoxyethanol mixed micelles are plotted in Figs. 6, 7, 8, and 9. The