Micelle Formation in Sodium Dodecyl Sulfate and Dodecyltrimethylammonium Bromide at Different Temperatures

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pH changes as a function of concentration for sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium bromide (DTAB) were observed by the addition of 1 N HCl and 1 N KOH. pH values increased up to the critical micellar concentration (CMC) for the SDS/HCl system and decreased for the DTAB/KOH system. In the SDS/HCl and DTAB/KOH systems, the micellar phase had a fixed composition and was homogeneous and monodisperse above the CMC. However, in the SDS/KOH and DTAB/HCl systems, pH values increased in a continuous and gradual manner below and above the CMC, and the properties of the micellar phase changed with temperature as a function of concentration, giving rise to inhomogeneity and polydispersity

Key Words: Critical micellar concentration, dodecyltrimethylammonium bromide, sodium dodecyl sulfate, hydrochloric acid, potassium hydroxide, pH, phase separation.

Introduction

In an aqueous medium, both pure and mixed surfactants form micelles after reaching a concentration called the critical micellar concentration (CMC), whose determination has considerable practical importance normally to understand the self-organizing behaviors of surfactants in exact and detailed ways. Many studies have been devoted to the elucidation of micellar structures under different conditions[1−5].

Some early investigators observed fairly abrupt changes in a number of physicochemical properties at or near the CMC and concluded that micelle formation had at least some of the properties of a phase change. A phase-separation or two-phase model was often used to describe the thermodynamics of micelle formation[6−8]. The two-phase model predicts a homogeneous monodisperse micellar phase and a constant monomer concentration above the CMC[9]. Careful experimental measurements using highly purified systems revealed that somewhat gradual and continuous changes in physicochemical properties occurred near the CMC[10−13], that micelles appeared to be polydisperse[14], and that monomer activities changed above the CMC[10,15].

For example, gradual and continuous decreases in the equivalent conductance of sodium dodecyl sulfate (SDS) in water[12,16] and changes in the heat of micelle formation for alkyl carboxylates[13,17] in water

have been observed. In addition, a significant decrease in surface tension was observed for SDS in water above the CMC, indicative of a change in monomer activity[10].

The purpose of this study is to propose an explanation for micelle formation and phase separation of SDS/HCl, SDS/KOH, DTAB (dodecyltrimethylammoniumbromide)HCl and DTAB/KOH systems by measuring pH as a function of concentration.

Experimental Procedures

SDS [$CH_3(CH_2)_{11}OSO_3Na$], DTAB[$CH_3(CH_2)_{11}N^+(CH_3)_3$]-$Br^-$, HCl, and KOH were obtained from Merck (Darmstadt, Germany) and were all of analytical grade.

The effect of pH on surfactant concentration was determined at different temperatures with a digital pH meter, Model 3040 (Jenway Ltd., Felsted, Dunmow, Essex, United Kingdom), pH range –2 to 16,000, resolution 0.001, and accuracy ±0.005.

First, 55 mM SDS and DTAB solutions were prepared, separately, and then each stock solution was diluted with water from 55 to 10 mM in increments of 5 mM. For the SDS/HCl systems, a solution of 29.91 mL of 55 mM SDS and 0.09 mL of 1 N HCl (30 mL total) was subjected to pH measurement at different temperatures, and then diluted with water to 50 mM. The same amount of acid (0.09 mL of 1 N HCl) was added to this diluted solution and pH was measured at temperatures ranging from 25 to 45 °C. Again, the solution was diluted to 45 mM and the same procedure was repeated until 10 mM by diluting the solutions.

For the SDS/KOH systems, first, pH was measured in a solution consisting of 29.55 mL of 55 mM SDS and 0.45 mL of 1 N KOH (30 mL total), and then it was diluted to 50 mM. The same amount of alkali (0.45 mL of 1 N KOH) was added to this diluted solution, and the solutions were diluted as above to 10 mM by adding the same amount of alkali (0.45 mL of 1 N KOH); pH values were then measured at different temperatures.

However, for the DTAB/HCl and DTAB/KOH systems, procedures similar to those above were followed. Here, DTAB was taken instead of SDS. To the first sample was added a small amount (approximately 0.5 mL) of 1 N KOH for the SDS/HCl systems to prevent hydrolysis, i.e., the protonation of SDS by H_3O^+ ions.

A small amount (approximately 0.5 mL) of 1 N HCl for the DTAB/KOH systems was added to prevent hydrolysis, i.e., a reaction of DTAB with OH^- ions.

Results and Discussion

Starting at the CMC, the solution's light-scattering ability (turbidity) rises sharply. These facts indicate that above the CMC a substantial portion of the solute ions are aggregated to form units of colloidal size. Such aggregates are micelles. Dilution of the solution below the CMC eliminates the micelles, and so micelle formation is reversible.

The plots of pH vs. surfactant concentration [C] at different temperatures (Figures 1-4) are characterized by an intersection of two straight lines at a concentration that corresponds to the CMC. For SDS/HCl, the CMC is 25 mM; for SDS/KOH, 23 mM; increasing the temperature caused a decrease in CMC. For DTAB/HCl, the CMC is 30 mM; for DTAB/KOH, 25 mM. The CMCs of solutions also decreased systematically as temperature increased for these systems.
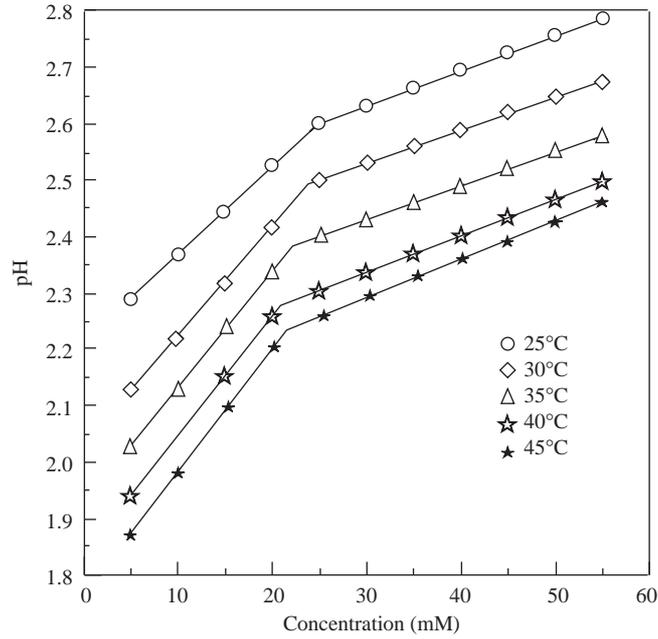
Figure 1. Variation of pH as a function of surfactant concentration for the sodium dodecyl sulfate (SDS)/HCl system in water at different temperatures.
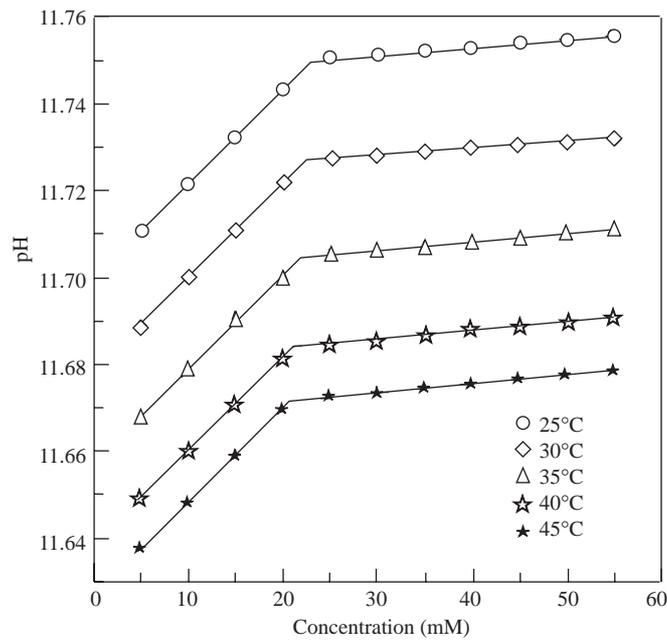
Figure 2. Variation of pH as a function of surfactant concentration for the SDS/KOH system in water at different temperatures.
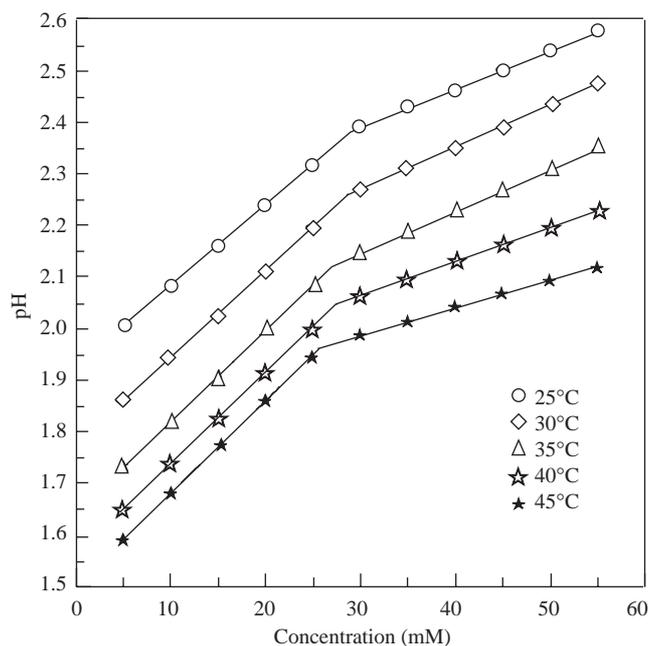
Figure 3. Variation of pH as a function of surfactant concentration for the dodecyltrimethylammonium bromide (DTAB)/HCl system in water at different temperatures.
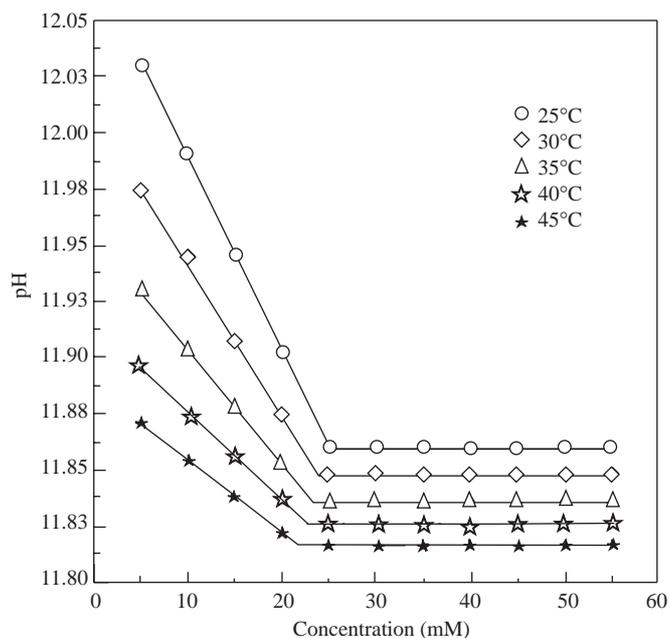
Figure 4. Variation of pH as a function of surfactant concentration for the DTAB/KOH system in water at different temperatures.

As shown in Figure 1, pH values increase continuously up to 25 mM at 25 °C and increase slightly above this concentration. In this process, the addition of 1 N HCl ensured that a small fraction of the SDS molecules became protonated to form dodecyl sulfonic acid (DSA)[18]. Under these conditions, SDS and DSA combined to form 1:1 acid-surfactant crystals[18,19], which added an additional phase to the system.

The SDS/HCl results (Figure 1) can be explained on the basis of the reaction of hydrogen ions with negative SDS micelles, as can be seen in Scheme 1.

$$CH_3—(CH_2)_{11}—O—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}—O—Na + HCl \longrightarrow CH_3—(CH_2)_{11}—O—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}—O—H + NaCl$$

Sodium dodecyl sulfate (SDS) Dodecyl sulfonic acid (DSA)
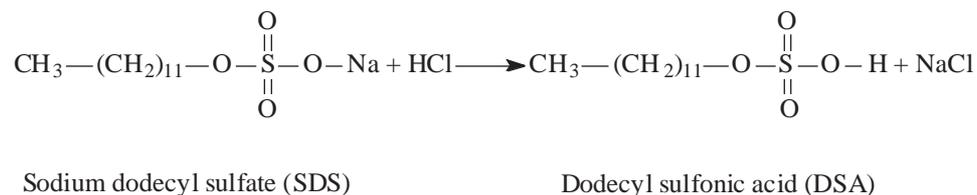
Scheme 1.

In Figure 1, a concentration range between 20 and 35 mM of SDS around the CMC is the concentration range at which SDS/DSA crystals precipitated. Here, the Na^+ and Cl^- ions can be found in the aqueous solution. This was observed qualitatively, not quantitatively, as a white turbidity near the CMC; above the CMC, small particles began to form.

In Figure 2, pH values increase continuously and gradually below and above 23 mM. The SDS/KOH results (Figure 2) can be explained by a simple dilution effect according to Scheme 2.

$$CH_3—(CH_2)_{11}—O—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}—O—Na + KOH \longrightarrow CH_3—(CH_2)_{11}—O—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}—O—K + NaOH$$

Sodium dodecyl sulfate (SDS) Potassium dodecyl sulfate (PDS)
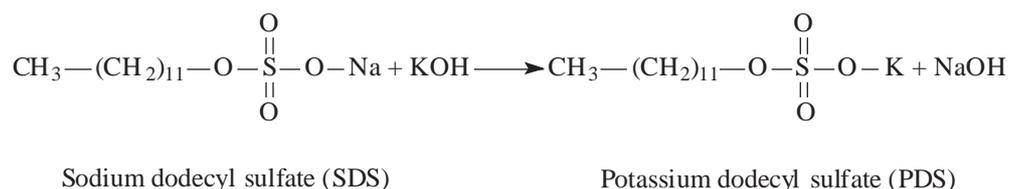
Scheme 2.

As can be seen from Scheme 2, a sodium ion replaces the potassium ion. Since the sodium ion has more activity than the potassium ion, i.e., $a_{Na^+} > a_{K^+}$, the pH values increase gradually and continuously as the concentration of the SDS/KOH system increases.

Gradual and continuous changes were also observed for the DTAB/HCl system in Figure 3 as in Figure 2. The DTAB/HCl results (Figure 3) can be explained by a simple dilution effect as shown in Scheme 3.

$$CH_3—(CH_2)_{11}—\overset{+}{N}—CH_3 \; Br^- + HCl \longrightarrow CH_3—(CH_2)_{11}—\overset{+}{N}—CH_3 \; Cl^- + HBr$$

Dodecyltrimethylammonium bromide
(DTAB) Dodecytrimethylammonium chloride
(DTAC)
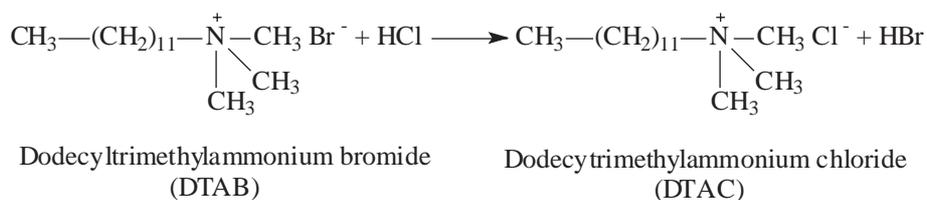
Scheme 3.

Here, the bromide ion replaces the chloride ion and $a_{Cl^-} > a_{Br^-}$; therefore, pH values increase gradually and continuously.

For the DTAB/KOH system, pH values decrease continuously up to 25 mM and remain constant above 24 mM (Figure 4). Here, the addition of 1 N KOH allowed a small fraction of the DTAB molecules to become hydroxylated to form dodecyltrimethylammonium hydroxide (DTAH). Therefore, it can be said that DTAB and DTAH combine to form 1:1 base-surfactant crystals, which add an additional phase to the system.

The DTAB/KOH results (Figure 4) can be explained on the basis of an exchange of a hydroxide ion by the positive DTAB micelle as shown in Scheme 4.

$$CH_3—(CH_2)_{11}—\overset{+}{N}—CH_3 \, Br^- + KOH \longrightarrow CH_3—(CH_2)_{11} \quad \overset{+}{N}—CH_3 \, OH^- + KBr$$

Dodecyltrimethylammonium bromide
(DTAB)

Dodecytrimethylammonium hydroxide
(DTAH)
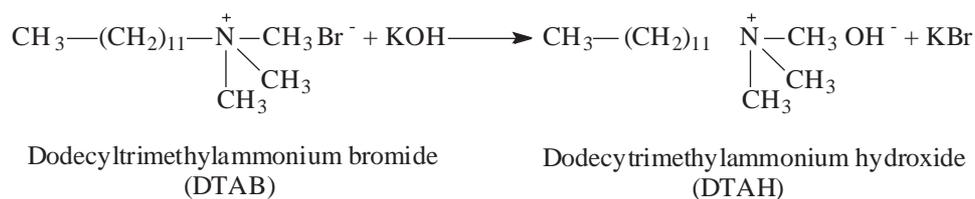
Scheme 4.

In contrast, in the systems shown in Figures 2 and 3, the properties of the micellar phase could have changed with temperature as a function of concentration at different temperatures, giving rise to inhomogeneity and polydispersity.

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