MICELLE-COUNTERION INTERACTION, I. CRITICAL MICELLE CONCENTRATIONS OF SDS UNDER THE INFLUENCE OF COPPER COUNTERION

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Key Words Index—Micelle-counterion interaction.

We investigated the effect of counter ion (Cu^{2+}) adsorption on Sodium Dodecylsulfate and Sodium Tetradecylsulfate micelle by three different techniques: surface tension decrease, copper-selective electrode and electric conductivity. The effect of added copper ion on critical micelle concentration (CMC) was determined. The effectiveness of these three techniques was critically evaluated. It is concluded that copper ions are able to strongly displace Sodium ions from the micellar surface.

The critical micelle concentration (CMC) of sodium dodecyl sulfate (SDS) has been reported to be influenced strongly by the presence of positive counter-ions[1,2]. It has been investigated by conductivity[3] and ion-selective electrode[4] techniques. The amount of data available in the literature is limited, however. Furthermore, there is a general lack of critical comparisons of the results obtained by different techniques. In this paper, we investigate the effect of copper ion (Cu^{2+}) on the CMC values of SDS at various concentrations by surface tension, conductivity and Cu^{2+} ion activity measurements. We will compare the results and critically discuss the relevant procedures.

The surface tension generally shows a large decrease near the CMC and, with the presence of Cu^{2+} ion, it also shows a minimum instead of a simple flat line above the CMC. This minimum will be explained by a positive adsorption of counterion on the double-layer near the water-air surface. An extrapolating procedure for determining the CMC is proposed and compared with other techniques.

The CMC value can also be measured by monitoring Copper ion activity by a selective ion membrane electrode. The procedure is essentially a titration of two solutions, one containing fixed concentration of copper nitrate and the other being the SDS solution. The CMC is detected as a sharp break in the plot of [Cu^{2+}] versus SDS concentration.

Finally, we also measure the change of conductivity of the SDS+Cu^{2+} solution as the SDS concentration is increased. All the results give CMC values of SDS ranging from 8×10^{-3} mole dm^{-3} before the addition of the Cu^{2+} ion to 2×10^{-3} mole dm^{-3} after addition of the ion. This indicates that copper ions are able to displace sodium ions from the micelle surface and probably finally saturate the micelle surface.

EXPERIMENTAL METHODS

Surface tensions were measured by the capillary method. The capillaries were of precision tubing. They were cleaned with n-hexane and distilled water and their

bores then determined to an accuracy of $\pm 0.1\%$ by measuring the length of mercury thread with a traveling microscope accurate to $\pm 0.01\,mm$. After calibration, a $10\,cm$ length was cut and cleaned as before to make the measuring apparatus. The capillary radius was double-checked by measuring the surface tension of pure water, the agreement was within 0.1%. Three capillary tubes of radius $0.02022\,cm$, $0.01596\,cm$, $0.01681\,cm$ were used.

Surface tension was calculated by using capillary formula to the fourth power approximation in the radius. All the necessary density corrections were made.

The copper-selective electrode was constructed according to the procedure of Chang[5]. The solid state electrode is a mixed coppor sulfide/silver sulfide pellet. The electrode potential follows the Nernst equation over a $[Cu^{2+}]$ range of $10^{-3}\,M$ to $10^{-6}\,M$. The potential was measured with a Tacussel ISIS 20000 potential meter. A silver/silver chloride wire was used as the reference electrode. One should note that a waiting period of several minutes is necessary for the potential to be stabilized for measurements in surfactant system. One should also avoid any gas bubbles adhering to the electrode surface.

Electric conductivity was measured by using a Leads & Northrup AC conductivity bridge operated by a HP model 201c. Audio oscillator at $10\,KHz$. The electrodes are made of platinized platinum. Three cells of cell constants 0.0407, 0.432 and $12.05\,cm^{-1}$ were used. The conductivity cell assembly was thermostated at $25.00\pm0.01°$ controled by a Mueller temperature bridge and platinum resistance thermometer. Steady readings were obtained in about ten minutes.

SDS and STDS (Merck) were recrystalized twice from water and extracted from ether. The samples show no minimums in surface tension versus concentration plot. They show a single peak in HPLC analysis (C-18μ-Bonadack), the purity was estimated to be 99.5% or

higher.

All the measurements for SDS were done at $25.00\pm0.05°$. For STDS a temperature of 35° was used because of the solubility problem. Water was double-distilled in an quartz column.

RESULTS

Surface tension

Since the 1930's many investigators[4] have measured the surface activity of aqueous SDS in terms of the lowering of the surface tension. The precise data differ in two aspects, the purity of the surfactant used and the technique of surface tension measurement. So direct comparison is difficult, but it is generally agreed that the surface tension should show no minimun in the concentration plot. Our results are shown in Fig. 1, 2, 3 and 4. Figures 1 and 2 show the surface tension data for pure SDS and STDS solution with no copper ion added. They show no minimums. CMC values were determined by intesection of two nearly linear lines. The CMC for sodium dodecyl sulfate (SDS) at 25° is $7.0\times10^{-3}\,M$ and for sodium tetradecyl sulfate (STDS) at 35° is $1.8\times10^{-3}\,M$. The results for SDS agree fairly well with most of the other determinations as reviewed recently[6]. Figure 3 shows the effect of adding small amount of copper ion, the solid lines are best fits to experimental data. They show minimums and furthermore the CMC
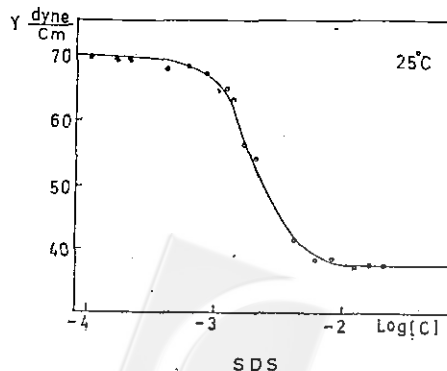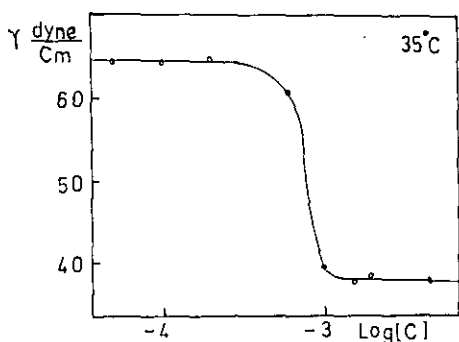

Fig. 1. Surface tension of pure SDS at 25°.

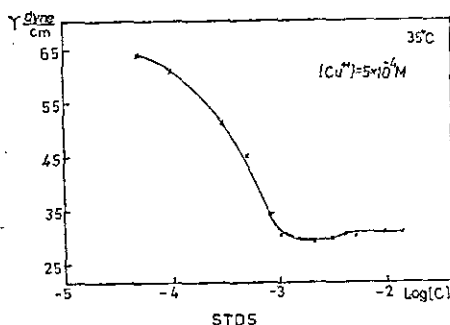Fig. 2. Surface tension of pure STDS at 35°.

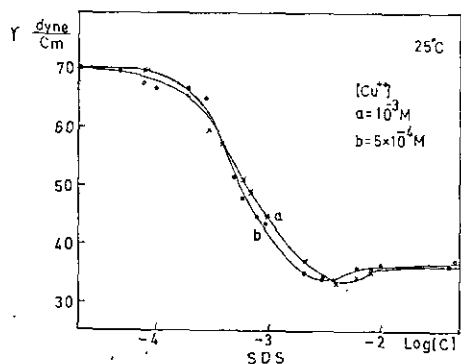Fig. 4. Surface tension of STDS under the influence of Copper ion.

Fig. 3. Surface tension of SDS under the influence of Copper ion.

extrapolate the flat portion at large C back to intersect the solid line to obtain the CMC. The results are listed in Table 1. The minimum is due to the "positive" adsorption of coppor ion on to the double layer at the air-water interface. We discuss this in terms of Gibbs adsorption isotherms in next section.

One should note here that the determination of the surface tension is difficult because it changes with time, the so called "age effect". This age effect is of complicated origin. In our experiment we found that a waiting period of several hours is necessary to obtain reproducible results.

values shift to lower concentrations. Our procedure for determining the critical micelle concentration (CMC) is to use these τ vs. $\log C$ plot in the following way:

Copper-selective electrode potential

These sets of experiments were run to directly measure the decrease of copper ion activities in the presence of micelles.

Table 1a. CMC values of SDS solution at vaaious copper concentrations (25°)

[Cu²⁺] Method	0	$1\times10^{-4}\,M$	$5\times10^{-4}\,M$	$1\times10^{-3}\,M$
Sursace tension	$7.0\times10^{-3}\,M$	—	$2.5\times10^{-3}\,M$	$3.5\times10^{-3}\,M$
Copper-selective electrode	—	$6.5\times10^{-3}\,M$	$2.4\times10^{-3}\,M$	$3.0\times10^{-3}\,M$
Conductivity	$8.0\times10^{-3}\,M$	$6.0\times10^{-3}\,M$	$3.0\times10^{-3}\,M$	$2.5\times10^{-3}\,M$

Table 1b. CMC values of STDS solution at various copper concentrations (35°)

[Cu²⁺]₀ Method	0	$5\times10^{-4}\,M$	$1\times10^{-3}\,M$
Surface tension	$1.8\times10^{-3}\,M$	$1.0\times10^{-3}\,M$	$1.0\times10^{-3}\,M$
Copper-selective electrode	—	$1.2\times10^{-3}\,M$	$1.1\times10^{-3}\,M$

A typical result is shown in Fig. 5 where $[Cu^{++}]_0$ represents the stochiometric concentration of copper ion and $[Cu^{++}]$ is obtained from the ion-selective electrode response and a standard calibration curve (following the Nernst law). No activity coefficient corrections are necessary at these low ionic strengths.
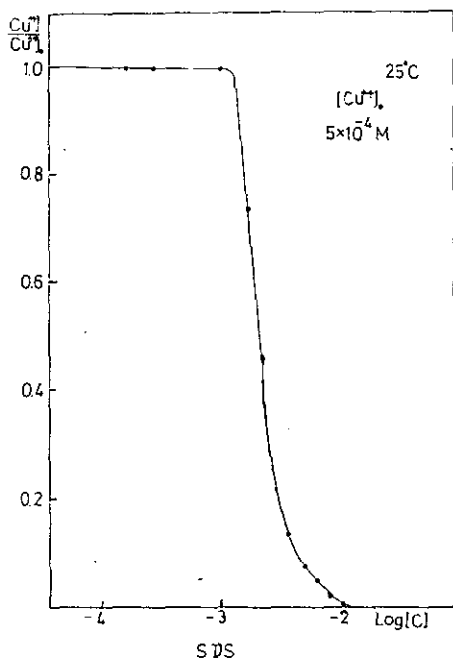

Fig. 5. Copper ion activity change under the influence of SDS.

One can see from Fig. 5 that there is a precipitous drop in Cu^{2+} ion activity at the CMC of SDS. The value of the CMC can thus be unambiquously determined at the point of discontinuity. Figure 5 is for $[Cu^{2+}]_0=5\times10^{-4}\,M$, other results are summarized in Table 1. This method gives a CMC value very close to that found using the surface tension method.

Similarly, Fig. 6 shows the change of Cu^{2+} ion activity under the influence of the STDS micelle.

Conductivity measurements

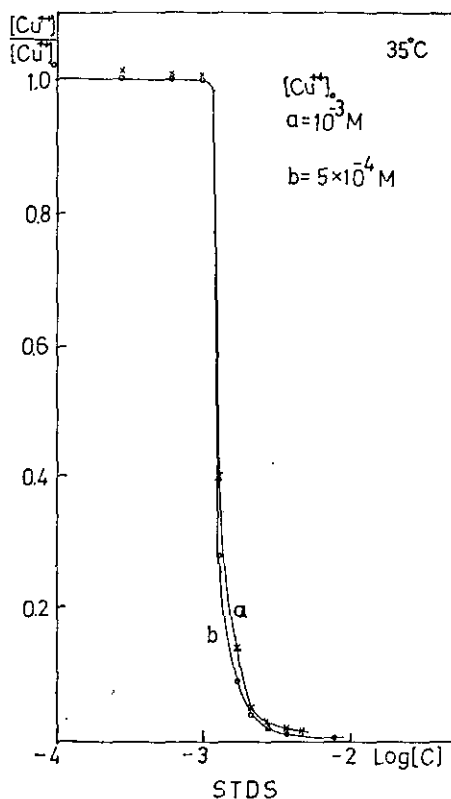We used a plot of conductivity k vs. surfactant concentration C to present the data

Fig. 6. Copper ion activity change under the influence of STDS.

$$k=\frac{C\Lambda}{1000}$$

where Λ is the equivalent conductance. The data is fairly well represented by two straight lines. The break point in the slope is identified as the critical micelle concentration. The plots are shown in Fig. 7. We note here that such a procedure seems to be superior to that of using a Λ vs. $\sqrt{C}$ plot as usually done. Equivalent conductance loses its usual physical significance in the presence of micelles since it includes the effect of counter ion adsorption.

DISCUSSIONS

From Table 1 we can see all three methods give comparable results. This verifies that the critical micelle concentration is a valid, well-defined point to within
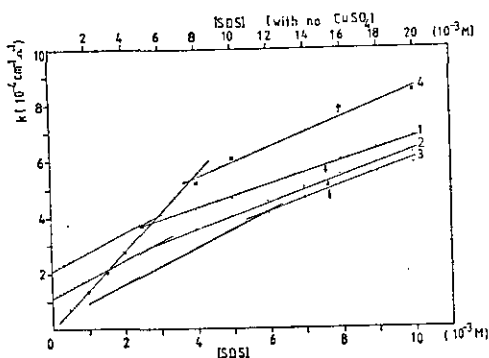
Fig. 7. Conductivity versus concentration of SDS under the influence of Copper ion.

$[Cu^{2+}]=1$, $1\times10^{-3}\,M$　2, $5\times10^{-4}\,M$
3, $1\times10^{-4}\,M$　4, 0

15% certainty. Different techniques give slightly different values of the CMC, this is probably due to uncertainties in the extrapolating procedures and different probes of physical properties. STDS has smaller CMC values than SDS because of a stronger hydrophobic interaction. This is consistent with many previous investigations and theoretical expectations[7]. The range of CMC values for STDS is however small. This is because for STDS the hydrophobic interaction dominates the electrostatic interaction.

The surface tension data can be rationalized with the use of the Gibbs adsorption equation

$$-d\gamma=\Sigma\Gamma_i d\mu_i \qquad (1)$$

where γ is surface tension, Γ_i is surface excess of ith component and μ_i its chemical potential. Take the SDS system as an example. Let C_T be the toatl surfactant concentration, one then has

$$-\frac{\partial\gamma}{\partial\ln C_T}=\Gamma_{DS^-}\frac{\partial\mu_{DS^-}}{\partial\ln C_T}+\Gamma_{Na^+}\frac{\partial\mu_{Na^+}}{\partial\ln C_T}$$
$$+\Gamma_{Cu^{2+}}\frac{\partial\mu_{Cu^{2+}}}{\partial\ln C_T}+\Gamma_{NO_3^-}\frac{\partial\mu_{NO_3^-}}{\partial\ln C_T}$$
$$+\Gamma_m\frac{\partial\mu_m}{\partial\ln C_T} \qquad (2)$$

Here, Γ_m represents the surface excess of the micelle species. Due to the adsorption behavior of the surfactants on the air/water surface Γ_{DS^-} and Γ_m are positive; $\Gamma_{Cu^{2+}}$ and Γ_{Na^+} also become positive due to adsorptions on the electric double layer. Since

$$\mu_i=\mu_i^o+RT\ln C_i \qquad (3)$$

we conclude that the first, second and the final terms on the right hand side of Eq. (2) are always positive. $\Gamma_{NO_3^-}$ should be negative due to electric repulsion from a negatively charge air/water surface, however $\mu_{NO_3^-}$ should be influenced only slightly upon addition of SDS, the fourth term in Eq. (2) should be of secondary importance. $\Gamma_{Cu^{2+}}$ is always positive, and from our copper-selective potential data we see that $\mu_{Cu^{2+}}$ decreases as C_T increases; therfore $\Gamma_{Cu^{2+}}\frac{\partial\mu_{Cu^{2+}}}{\partial\ln C_T}$ is always negative.

Immediately above CMC, $\left|\frac{\partial\mu_{Cu^{2+}}}{\partial\ln C_T}\right|$ becomes very large so that the third term in Eq. (2) dominates; this can qualitatively explain the minimum and positive slopes in the γ vs. C_T plots. A quantitative explaination is, however, more difficult because surface excesses are not easy to measure. One can, nontheless, approach the problem by using electric double layer theory to calculate the Γ_i theoretically. This will be the subject of a future paper.

The CMC determinations by copper-selective electrode are of curse applicable only in the presence of copper ion. But this method is the easiest and the most rapid one. Qualitatively, one can see a rapid decrease of copper ion activity that comes about by the ion exchange mechanism between bulk ion and micelle surface ions. Due to the stronger coulombic attraction of divalent ion and micelle, the copper ions displace sodium ions from the micelle surface. This effect reduces the surface charge at the micelle surface and stabilizes the micelle structure. Hence, one observes a lower CMC value. From Table 1, one also observes that CMC values seems to approach constant values at higher copper ion concentrations. This is probably due to a saturation effect of

the surface counterion, that is, the counterion in the stern layer will approach a kind of saturation of the monolayer. One should note that different divalent ions should give somewhat different results due to the specific interaction at the stern layer in addition to the coulombic forces. For example, Newbery[4] measured the CMC values of SDS under the effect of Nickel ion. The CMC values change from $8 \times 10^{-3} M$ to $4 \times 10^{-4} M$ over the concentration range of the Nickel ion.

As for general the relation between the CMC and salt concentration (M), Corrin and Harkins[3] suggested an equation of the form

$$\log (CMC) = a \log M + b \qquad (3)$$

This equation is satisfied by many univalent salts. Hower, Newberry[4] reported Eq. (3) is not satisfied for Nickel ion. From our data, Eq. (3) does not apply to copper/SDS system. We do not advocate any simple formula for divlent ions. It seems that for divalent ions each type of ion is an individual case due to specific chemical interactions.

For the conductivity data, a quantitative intepretation of the concentration dependence is not possible due to the lack of a suitable theory. The usual Onsager theory will not apply due to the strong ion-pair formation in micellar systems. There is a need of a satiafical mechanical theory of ionic conductivity for micellar solutions. In this paper, we can however simply identify the break in slope as the CMC according to the usual intepretation.

In summary, we have compared three experimental techniques for measuring the CMC for ionic micelles under the influence of an added copper salt. The change in the CMC is due to the replacement of micellar surface ions and the resulting change in the electrostatic-hydrophobic balances.

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