

PRESSURE EFFECT ON MICELLAR FORMATION OF SODIUM DODECYL SULFATE IN SATURATED AQUEOUS SOLUTION OF NAPHTHALENE

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Micellar formation of sodium dodecyl sulfate (SDS) in the presence of naphthalene has been measured by the electrical conductivity method up to about 3 kbars. The critical micelle concentration (cmc)-pressure plots show the maximum at about 1.3 kbars, contrary to the increasing cmc with pressure up to 5.5 kbars by Rodriguez and Offen.

Introduction

The fact that the cmc of ionic surface agents determined by the method of the electrical conductivity measurement under high pressure increases up to about 1–1.5 kbars and then decrease, has been generally recognized^{1–6)}. While Rodriguez and Offen⁷⁾ reported that the cmc of SDS increases with pressure up to 5.5 kbars and that does not reverse its behavior above 1.5 kbars from the optical method using naphthalene as a probe. This result is contrary to those of the electrical conductivity measurement and challenges the common explanation of the reverse phenomena of ionic surface active agents under high pressure. In the present study, the micellar formation of SDS in saturated aqueous solution of naphthalene has been measured by the electrical conductivity method up to about 3 kbars in order to clarify whether the cmc in the presence of naphthalene does reverse or not under high pressure.

Experimental

SDS was prepared by the reaction of chlorosulfuric acid and 1-dodecanol, which was fractionally distilled three times and analyzed by gas chromatography. The reaction mixture was neutralized with sodium hydroxide. The crude SDS was extracted three times with petroleum ether in a Soxhlet apparatus for 50 hours, and finally recrystallized from methanol. The cmc value of 8.33×10^{-3} mol

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kg^{-1} is good consistent with those of Hamann ($8.2 \times 10^{-3} \text{ mol kg}^{-1}$)¹⁾ Rehfeld ($8.2 \times 10^{-3} \text{ mol dm}^{-3}$)²⁾, and Nakagaki and Shimabayashi ($8.2 \times 10^{-3} \text{ mol dm}^{-3}$)⁹⁾. Naphthalene (Wako Pure Chemical Co. Ltd.) was recrystallized twice from ethanol and tetrachloroethane, then sublimed once. The conductivity water was prepared by repeatedly distilling water from a mixed-bed deionizing column to be aerated with air free from CO_2 . The specific conductivity of this water was $3.03 \times 10^{-6} \text{ ohm}^{-1}$ at 30°C . Excess naphthalene was added to the detergent solution to keep at room temperature for 2 weeks, then at $30 \pm 0.03^\circ\text{C}$ for 6 hours. The solid naphthalene was filtered from the saturated aqueous solution. The equilibrium of the solubilization was monitored by 275 nm absorption peak.

The apparatus and the procedure used to obtain the electrical conductivity under high pressure have been described in detail elsewhere¹⁰⁾. The cell constant of Teflon cell used was 0.447 cm^{-1} at atmospheric pressure and 30°C .

Results and Consideration

The cmc of SDS solution saturated with naphthalene was $7.6 \times 10^{-3} \text{ mol kg}^{-1}$ at atmospheric pressure and at 30°C , which is inconsistent with $3 \times 10^{-3} \text{ mol kg}^{-1}$ at 25°C of Rodriguez and Offen⁷⁾. The cmc was $6 \times 10^{-3} \text{ mol dm}^{-3}$,¹¹⁾ or $7.5 \times 10^{-3} \text{ mol dm}^{-3}$,¹²⁾ in the presence of benzene. Table 1 shows the data of the cmc of SDS in the presence of naphthalene under high pressure, determined by the plots of the specific conductivity vs. the concentrations of SDS at various pressures as shown in Fig. 1. The logarithm of the cmc can be fitted to the equation containing the maximum, $\log \text{cmc} = A + Bp + Cp^2 + Dp^3$, with $A = -2.11$, $B = 0.729 \times 10^{-4} \text{ bar}^{-1}$, $C = -5.61 \times 10^{-8} \text{ bar}^{-2}$ and $D = 1.44 \times 10^{-11} \text{ bar}^{-3}$, respectively. Applying the eq. (1) to the SDS solution in the presence of naphthalene,

Table 1 The cmc of SDS saturated aqueous solution of naphthalene at various pressures and 30°C .

| Pressure (bar) | cmc (mol kg^{-1}) |
|----------------|-----------------------------|
| 1 (atm) | 7.68 ± 0.25 |
| 385 | 8.30 ± 0.10 |
| 770 | 8.41 ± 0.10 |
| 1155 | 8.50 ± 0.05 |
| 1540 | 8.48 ± 0.05 |
| 1925 | 8.33 ± 0.10 |
| 2310 | 8.26 ± 0.15 |
| 2695 | 8.19 ± 0.20 |
| 3080 | 8.00 ± 0.28 |

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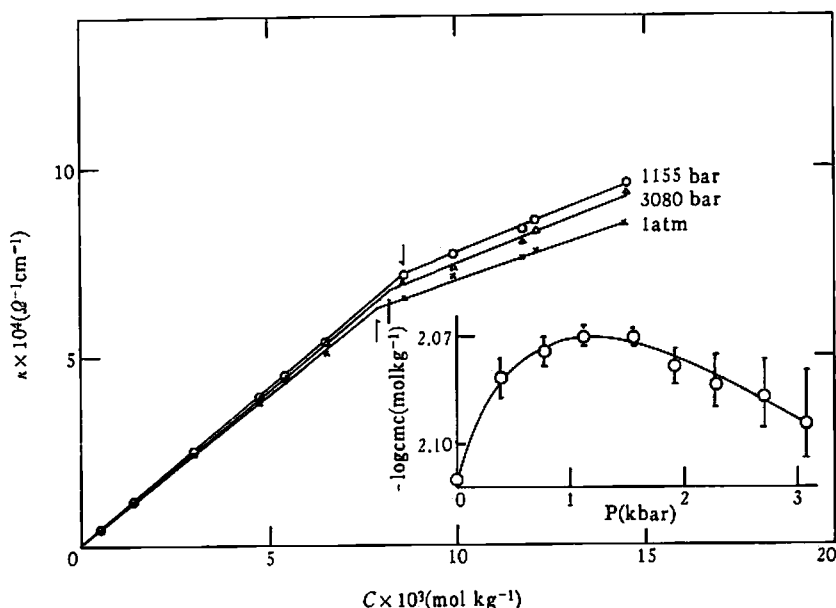


Fig. 1 Relationship between the specific conductivities κ and concentrations of SDS in the saturated aqueous solution of naphthalene at three pressures and 30°C. Inset: $\log \text{cmc}$ vs. pressure plots

$$\Delta V = 2.3 RT (1 + \beta) (\partial \log \text{cmc} / \partial P)_T \text{ at 1 bar} \quad (1)$$

where β is the constant which means the ratio of the number of counterion to that of surfactant ion in micelles. The ΔV value in the case of $\beta = 0.8$ was $7.5 \text{ cm}^3 \text{ mol}^{-1}$ from the initial slope of $\log \text{cmc}$ vs. pressure plots.

Our results that the cmc vs. pressure plots shows the maximum at about 1.3 kbar from the electrical conductivity method is inconsistent with Rodriguez and Offens' data. The error of cmc determined by the electrical conductivity method is less than 2% up to 2 kbar and increases to be 4% at the 2–3 kbar range. As the compression does depress the solubility of naphthalene¹³⁾, the depositing naphthalene may cause the increment of the error at high pressure. These errors are smaller than those of Rodriguez and Offen (about 10% for the 2–5 kbar range). The inversion phenomena of the cmc with the additives such as esters containing the various alkyl chains at the range of 1.0–1.5 kbars is also confirmed by the studies of the hydrolysis reaction of esters in the dodecyl hydrogensulfate micelle (the acid type of SDS)¹⁴⁾ Recently, Nishikido *et al.*¹⁵⁾ have answered to the Rodriguez and Offens' claim through the existence of the maximum at each cmc -pressure plot of dodecylpyridinium bromide determined by both the monitor of the optical probe of the charge transfer band ($\lambda_{\text{max}} \sim 290 \text{ nm}$) accompanying the micellar formation and the electrical conductivity method. This result suggests that there is no essential difference between the optical and electrical conductivity methods

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determining the cmc of surface active agents under high pressure. Therefore, it should be justified that the maximum phenomena of cmc of ionic surface active agents under high pressure is the common sense¹⁶⁾.

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16) There is only one case which the relationship between the pressure and the cmc of decylammonium chloride (DAC) up to 2 kbar does not show any maximum³⁾. Above 2 kbar it is assured to the solidification of DAC (S. D. Hamann, *This Journal*, 35, 109 (1965)).