

Determination of Critical Micelle Concentrations of Some Surfactants by Keto-Enol Tautomerism of Benzoylacetone

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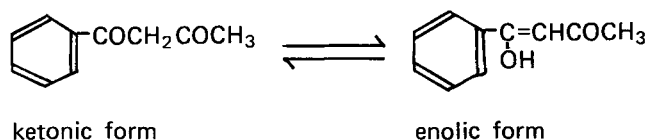
ABSTRACT

Benzoylacetone, keto-enol tautomer, was dissolved in aqueous solutions of sodium dodecyl sulfate, dodecyl trimethyl ammonium chloride, hexaethyleneglycol dodecyl ether, polyoxyethylene tert-octyl phenyl ether, and polyoxyethylene nonyl phenyl ether, respectively. The effect of surfactants on this keto-enol equilibrium was examined by measuring the intensity of two spectral bands at ca. 250 nm and 315 nm due to ketonic and enolic form of this compound. The existence of keto-enol equilibrium of the benzoylacetone was indicated by an isosbestic point among the two bands. The absorbances of the two bands showed hardly any change in the range of surfactant concentrations below the critical micelle concentration (cmc) but, in the concentration range above the cmc, the absorbance of the enolic form increased and that of the ketonic form decreased abruptly. These changes at cmc were very noticeable in the case of ionic surfactant solution. The concentrations corresponding to abrupt change of the spectra used for the determination of cmc were in fair agreement with data obtained by other methods. However, in the case of nonionic surfactant solutions, the absorbance due to the enolic form increased gradually with increase of the surfactant concentration, and the distinct break point was not observed at cmc.

INTRODUCTION

The critical micelle concentrations (cmc's) of surfactants in aqueous solutions have so far been determined by various methods such as surface tension, electroconductivity, and dye absorption spectral measurements (1-8). Recently, it has also been shown that the absorption spectra of organic compounds incorporated into the micelles provide some information about the micellar properties (9-12).

Benzoylacetone, keto-enol tautomer, according to R.A. Morton et al., is more enolized in both polar and nonpolar organic solvents than in water, as shown in the following keto-enol equilibrium (13):



They established that absorption spectra of benzoylacetone dissolved in various solvents show two absorption bands, near 250 nm and 315 nm corresponding to ketonic and enolic form, respectively; the percentage of enolic form is much higher in organic solvents than in water. Accordingly, when benzoylacetone is dissolved in an aqueous surfactant solution, its enolization would be expected to proceed rapidly in the micelles.

In this paper, the cmc's of sodium dodecyl sulfate and dodecyl trimethyl ammonium chloride, two typical ionic surfactants, are determined on the basis of the spectral changes of dissolved benzoylacetone in the aqueous surfactant solutions. These measurements are also compared with

those obtained from surface tension and electroconductivity measurements. On the other hand, micellar properties of hexaethyleneglycol dodecyl ether, polyoxyethylene tert-octyl phenyl ether, and polyoxyethylene nonyl phenyl ether as nonionic surfactants are estimated by the similar method.

EXPERIMENTAL PROCEDURES

Materials

Benzoylacetone used here was prepared by the condensation of acetophenone with acetic anhydride using the Claisen method (14). The product thus obtained was purified by vacuum distillation and by repeated recrystallization from n-hexane to give a purity above 99.9%. Sodium dodecyl sulfate (SDS) was synthesized from pure dodecyl alcohol above 99.9% by the usual method (15). Dodecyl trimethyl ammonium chloride (DTAC1) obtained from Tokyo Kasei Co., Ltd. (Tokyo, Japan) was extra-pure-grade and purified by repeated recrystallization from acetone. Hexaethyleneglycol dodecyl ether $C_{12}H_{25}O(CH_2CH_2O)_6H$ ($C_{12}E_6$) was supplied from Nikko Chemicals Co., Ltd. (Tokyo, Japan) and confirmed to have homogeneous polyoxyethylene chain length by thin layer chromatography and gas-liquid chromatography. Polyoxyethylene tert-octyl phenyl ether (Triton X-100) was obtained from Wako Pure Chemical Industries Ltd. (Tokyo, Japan), and polyoxyethylene nonyl phenyl ether (NP-10) was supplied by Nikko Chemicals Co., Ltd. These two surfactants were found to have, on the average, 10 ethylene oxide units. Since the surface tension values for each surfactant showed no minimum near the cmc in the surface tension-concentration curves, these surfactants were assumed to be very pure. The water used here was prepared by distillation of an alkaline permanganate solution made up from distilled ion-exchanged water. The specific conductivity of purified water used was always ca. $1.0 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25 C.

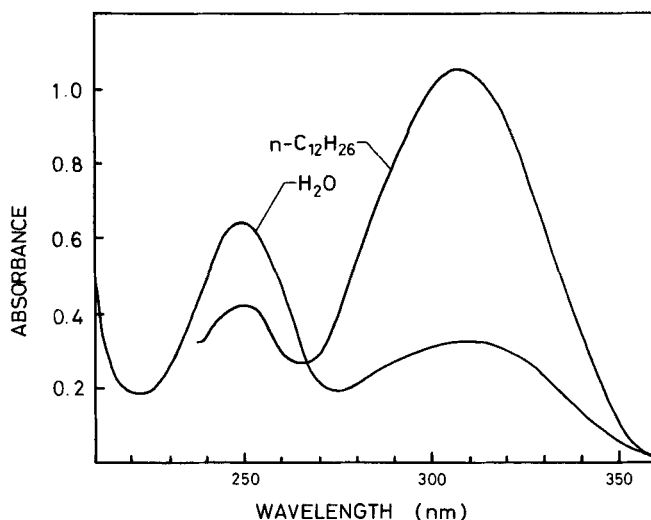


FIG. 1. Absorption spectra of benzoylacetone dissolved in water and n-dodecane.

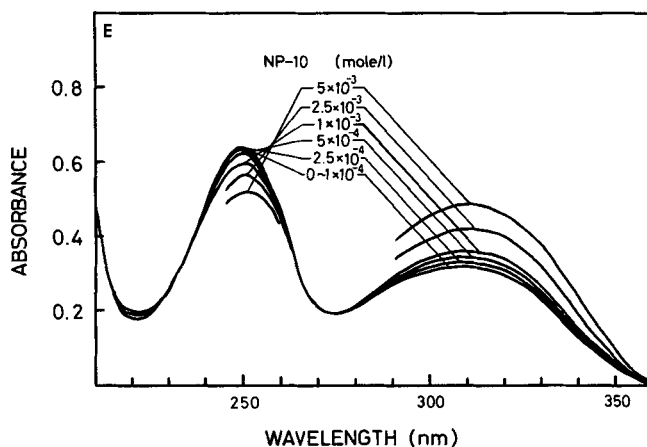
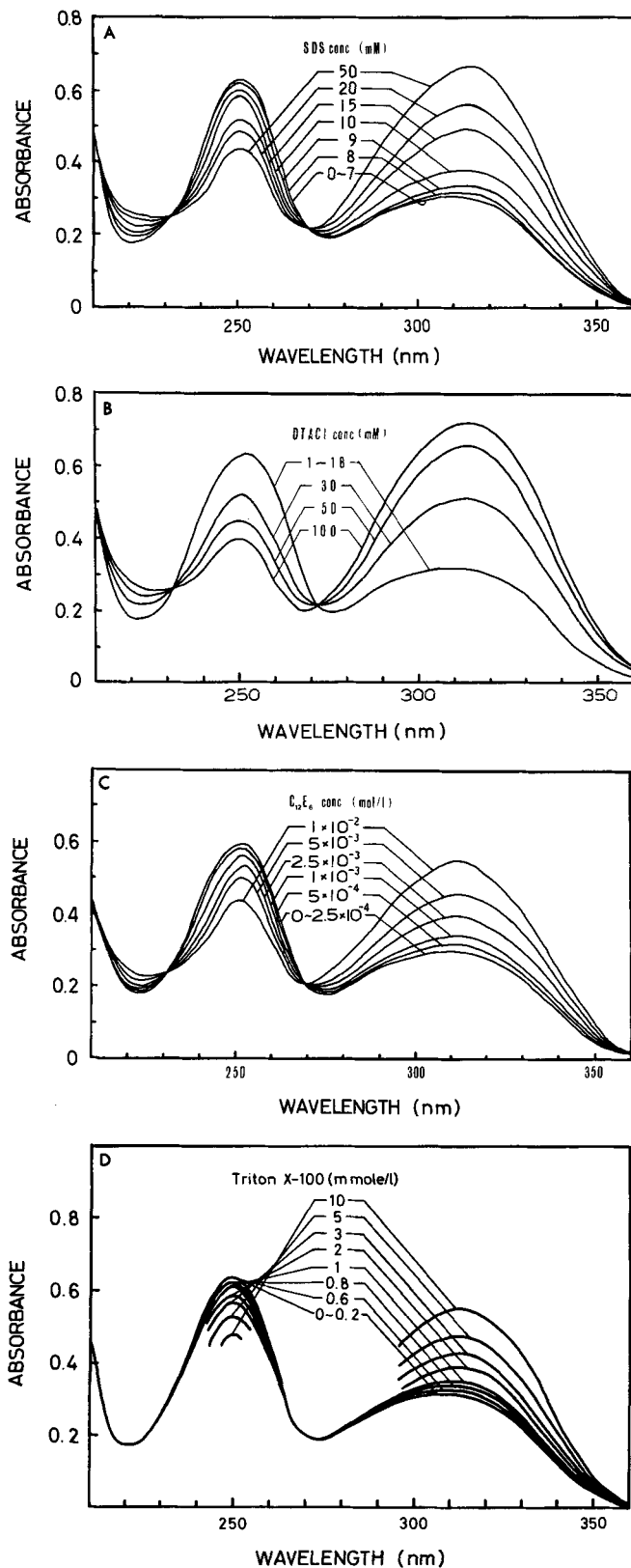


FIG. 2. Absorption spectra of benzoylacetone dissolved in aqueous solution of surfactants. (a) Sodium dodecyl sulfate, (b) dodecyl trimethyl ammonium chloride, (c) hexaethyleneglycol dodecyl ether, (d) polyoxyethylene tert-octyl phenyl ether, (e) polyoxyethylene nonyl phenyl ether.

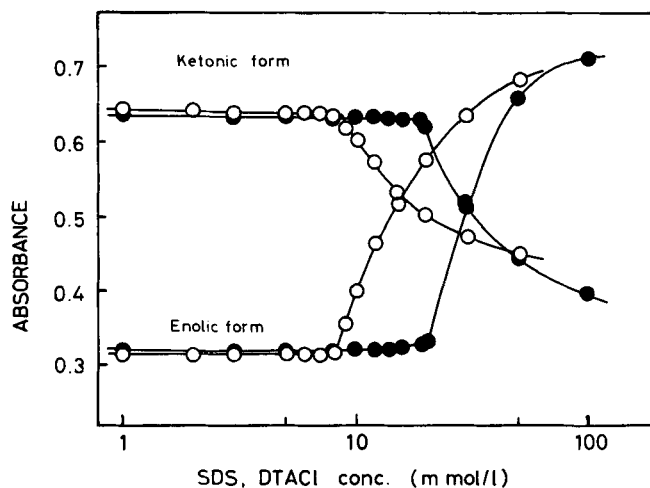


FIG. 3. Absorbance vs. concentration of ionic surfactants. (a) Sodium dodecyl sulfate ($-\circ-$), (b) dodecyl trimethyl ammonium chloride ($-\bullet-$).

from 5.5 and 6.5. The absorption spectra were almost unaffected in this pH range.

Spectral Measurements

The absorption spectra of benzoylacetone in the aqueous surfactant solution were measured in 1.0 cm quartz cells by using a recording spectrophotometer (Hitachi EPS-3T) at 25 C.

Surface Tension Measurements

The surface tensions of the solution were measured by using a Wilhelmy-type surface tensiometer (Shimadzu ST-1) at 25 C. The values of cmc of SDS, DTACI, $C_{12}E_6$, Triton X-100, and NP-10 obtained by this method were found to agree with those of the published data. (16-18).

RESULTS AND DISCUSSION

It is well known that benzoylacetone is more enolized in organic solvent than in water (13). To confirm this, benzoylacetone was dissolved in dodecane, and the absorption spectrum is shown in Figure 1 together with the analogous spectrum in water for comparison. This figure showed two absorption bands at ca. 252 nm and 313 nm, due to ketonic and enolic forms, respectively; and the absorbance for the

Procedure

Benzoylacetone was dissolved in an aqueous surfactant solution by the following procedure: 10 mg benzoylacetone was added to 1 liter of distilled water. After the solution had been shaken for 48 hr, the compound had gone completely in solution. The solution was then used as the solvent for the preparation of the surfactant solutions at various concentrations. The pH value of the solution ranged

enolic form was greater in dodecane than in water and, inversely, that for the ketonic form was smaller than that in water. This suggests that benzoylacetone can be more easily enolized in more nonpolar solvent than in water, as pointed out by R.A. Morton (13). Therefore, the spectra of benzoylacetone dissolved in surfactant solutions would be different from those in water solution due to its incorporation in the surfactant micelle, the core of which can be considered to be nonpolar like liquid dodecane.

The changes in the absorption spectra with varying concentration of surfactants in aqueous solutions containing 10 mg/liter of benzoylacetone are shown in Figure 2 a, b, c, d, and e for SDS, DTACl, C₁₂E₆, Triton X-100, and NP-10, respectively. Here some curves in Figures d and e are discontinuous due to solvent interference.

The abrupt changes in absorbance for SDS and DTACl were distinctly observed by plotting the absorbance at 251.5 nm and 315 nm against the concentration of surfac-

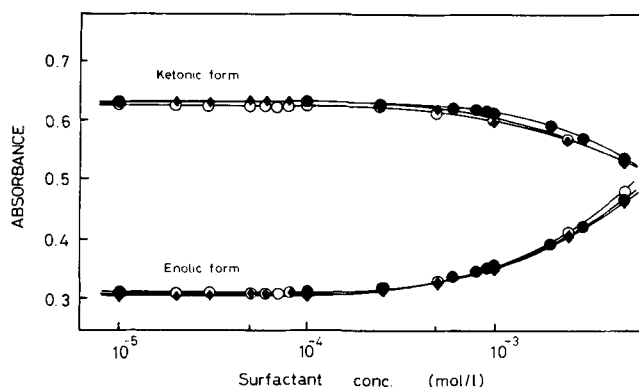


FIG. 4. Absorbance vs. concentration of nonionic surfactants. (a) Hexaethyleneglycol dodecyl ether (—○—), (b) polyoxyethylene tert-octyl phenyl ether (—●—), (c) polyoxyethylene nonyl phenyl ether (—◆—).

TABLE I

Critical Micelle Concentration of the Surfactants by Keto-Enol Tautomerism of Benzoylacetone and Surface Tension Method and Published Data

Surfactant ^a	cmc by surface tension (mol/liter) (25 C)	cmc by published data (mol/liter) (25 C)	cmc by keto-enol tautomerism of benzoylacetone (mol/liter) (25 C)	
			By ketonic form	By enolic form
SDS	8.1 X 10 ⁻³	8.1 X 10 ⁻³ (16)	8.0 X 10 ⁻³	8.1 X 10 ⁻³
DTACl	1.8 X 10 ⁻²	1.6 X 10 ⁻² (17) (30 C)	1.9 X 10 ⁻²	2.0 X 10 ⁻²
C ₁₂ E ₆	6.8 X 10 ⁻⁵	6.8 X 10 ⁻⁵ (18)	1.5 X 10 ⁻⁴	1.0 X 10 ⁻⁴
Triton X-100	9.0 X 10 ⁻⁴	9.0 X 10 ⁻⁴ (19)	1.5 X 10 ⁻⁴	1.0 X 10 ⁻⁴
NP-10	8.0 X 10 ⁻⁵	7.5-9.0 X 10 ⁻⁵ (2)	1.5 X 10 ⁻⁴	1.0 X 10 ⁻⁴

^aSDS = sodium dodecyl sulfate, DTACl = dodecyl trimethyl ammonium chloride, C₁₂E₆ = hexaethyleneglycol dodecyl ether, Triton X-100 = polyoxyethylene tert-octyl phenyl ether, NP-10 = polyoxyethylene nonyl phenyl ether. Triton X-100 and NP-10 were found to have, on the average, 10 ethylene oxide units.

tants as shown in Figure 3.

It is noticed that a remarkable enhancement of enolic absorption occurs at a concentration just above cmc. The concentrations corresponding to break points for SDS and DTACl are tabulated in the first and second columns of Table I, in which the values for SDS and DTACl are in fairly good agreement with the published data of the cmc of each surfactant listed for comparison. The results show that this method is satisfactory for the determination of the cmc of both the anionic and cationic surfactants as shown in Table I.

The absorbances for the three nonionic surfactants almost coincide with each other in the studied range of concentrations of the surfactants, and, although there is a gradual change above the concentrations of 1-1.5 x 10⁻⁴ mol/liter of three surfactants, the curves showed no break point such as those in Figure 4. The concentrations corresponding to a change in curvature for the three nonionic surfactants almost coincide with each other as shown in Table I and are larger than cmc of the published data listed for comparison (18). This suggests that benzoylacetone might be only partially enolized by the ethylene oxide chains located on the micelle surface, regardless of the type of nonionic surfactant, in similarity to enolization in ethyl ether as reported by R.A. Morton (13). Therefore, these findings show that, in general, this method of keto-enol tautomerism is not applicable to the determination of the cmc of nonionic surfactants.

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