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

NORIHITO SHOJI, MINORU UENO, and KENJIRO MEGURO, Department of Chemistry, Science University of Tokyo, Kagurazaka Shinjuku-ku, Tokyo, Japan

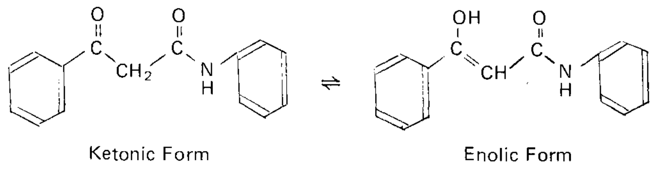
ABSTRACT

The absorbances of benzoylacetoanilide, keto-enol tautomer, dissolved in aqueous solution of several nonionic and ionic surfactants were measured in the concentration ranges below and above the CMC of the incorporating surfactants. Below the CMC, the absorbance of the band at 250 nm due to the ketonic form showed hardly any change and that of the band at 320 nm due to the enolic form could not be observed. In contrast, above the CMC, the spectral band of the enolic form appeared, and the absorbance increased abruptly and that due to the ketonic form decreased gradually. The changes at the CMC in absorbance for these nonionic surfactants were distinctly observed by plotting the absorbance at 250 and 320 nm as a function of the concentration of surfactants. These changes at the CMC were very noticeable with nonionic surfactants as well as with ionic surfactants. The concentrations corresponding to break points for these surfactants were in fairly good agreement with the published data of the CMC of each surfactant. This method of keto-enol tautomerism using benzoylacetoanilide has been confirmed to be more applicable to the determination of the CMC for most anionic, cationic, and nonionic surfactants.

INTRODUCTION

It has been shown recently that the absorption spectra of organic compounds incorporated into the micelles provide some information about the micellar properties (1-4). In a recent paper (5), we have reported that the critical micelle concentration (CMC) values of several ionic surfactants can be determined from abrupt changes of two absorption bands of dissolved benzoylacetone, keto-enol tautomer, in aqueous surfactant solutions, in which the enolic form of benzoylacetone increases and that of the ketonic form decreases above the CMC and are in fair agreement with data obtained by other methods. In contrast, with nonionic surfactants, for example, absorption spectra of benzoylacetone in aqueous solution, regardless of the type of nonionic surfactant, showed no abrupt change from the ketonic to the enolic form at the CMC. Thus, the CMC values for nonionic surfactants could not be determined by this spectral method using benzoylacetone.

In this paper benzoylacetoanilide was selected as the tautomer, and was found applicable to the determination of the CMCs of most nonionic surfactants. This tautomer is sparingly soluble in water but more insoluble in water than benzoylacetone. It is more enolized in both polar and nonpolar solvents except ethyl ether than in water as shown in the following keto-enol equilibrium:



As the benzoylacetoanilide is not enolized in ethyl ether in contrast to benzoylacetone, this tautomer can be expected to be more enolized in the hydrocarbon core of the micelle of nonionic surfactants than in the ethylene oxide chains on the micelle surface, and then precise values for CMCs can be expected to be obtained. These results are also compared with those of cationic and anionic surfactants obtained by this method and also with those obtained from spectral changes of benzoylacetone.

EXPERIMENTAL PROCEDURE

Materials

Benzoylacetoanilide obtained from Tokyo Kasei Co., Ltd. (Tokyo, Japan) was extra-pure grade and was purified by repeated recrystallization from n-hexane to give a purity above 99%. Homogeneous nonionic surfactants, polyethylene glycol dodecyl ethers $C_{12}H_{25}O(CH_2CH_2O)_nH$ ($C_{12}E_n$, n=6, 7 and 8) were highly pure samples obtained as kind gifts from Nikko Chemicals Co., Ltd. (Tokyo, Japan). The samples were confirmed to have homogeneous polyoxyethylene chain lengths by the results of IR spectra, elemental analysis, 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 average ten ethylene oxide units and were used without further purification. The anionic surfactant used here was sodium dodecyl sulfate (SDS) which was synthesized from pure dodecyl alcohol with a purity above 99.9% by the modified method of Dreger et al. (6). Instead of using acetic acid as a solvent for dodecyl alcohol, chloroform was

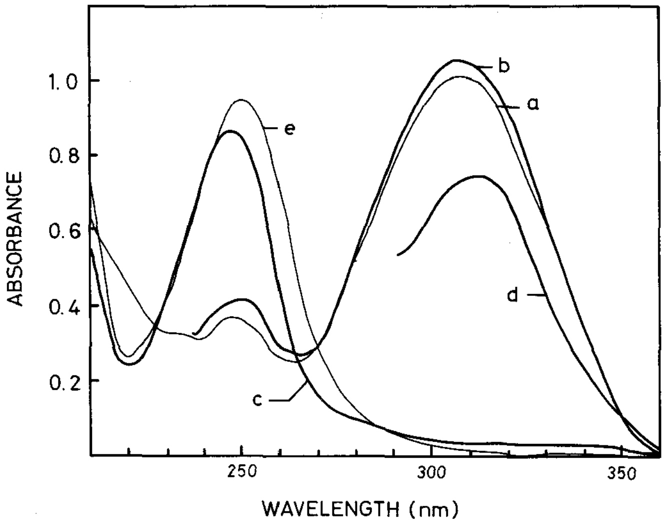


FIG. 1. Absorption spectra of benzoylacetone and benzoylacetoanilide dissolved n-dodecane, ethyl ether, and water; (a) benzoylacetone in ethyl ether, (b) benzoylacetone in n-dodecane, (c) benzoylacetoanilide in ethyl ether, (d) benzoylacetoanilide in n-dodecane, (e) benzoylacetoanilide in water.

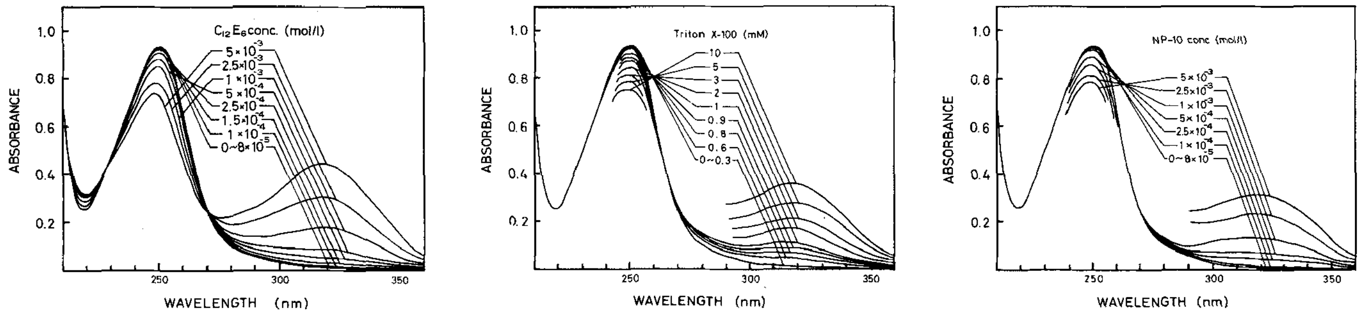


FIG. 2. Absorption spectra of benzoylacetoanilide dissolved in aqueous solution of surfactants; (a) hexaethylene glycol dodecyl ether, (b) polyoxyethylene tert-octyl phenyl ether, (c) polyoxyethylene nonyl phenyl ether.

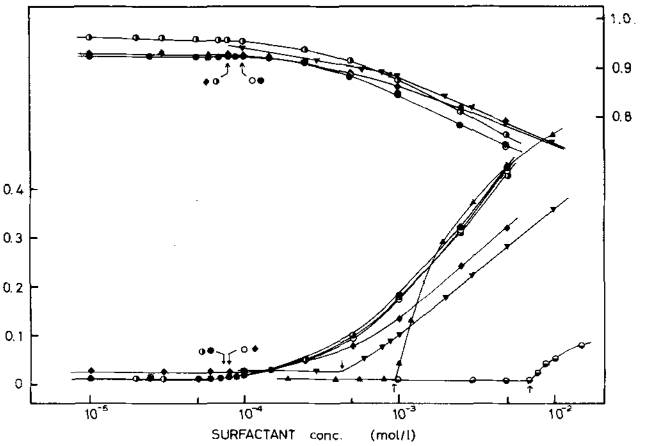


FIG. 3. Absorbance vs. concentration of surfactants; (a) hexaethylene glycol dodecyl ether (-○-), (b) heptaethylene glycol dedecyl ether (-◐-), (c) octaethylene glycol dodecyl ether (-●-), (d) polyoxyethylene tert-octyl phenyl ether (-▼-), (e) polyoxyethylene nonyl phenyl ether (-◆-), (f) sodium dodecyl sulfate (-⊖-), (g) cetyl trimethyl ammonium bromide (-▲-).

used. The crude product was purified by five recrystallizations from either ethanol- or isopropanol water-mixed solutions followed by extraction with ethyl ether. The cationic surfactant used here was cetyl trimethyl ammonium bromide (CTAB) obtained from Tokyo Kasei Co., Ltd. It was extra-pure grade and was purified by repeated recrystallization from acetone. These surfactants have no minimum near the CMC in the surface tension-concentration curves. Thus, these surfactants were assumed to be very pure.

The water used in all the experiments was prepared by distillation of an alkaline permanganate solution made up from distilled ion-exchanged water in a Pyrex glass vessel. The specific conductivity of purified water used was always ca. 1.0 x 10^{-6} ohm^{-1}cm^{-1} at 25 C.

Procedure

Keto-enol tautomers were dissolved in an aqueous surfactant solution by the following procedure: 10 mg of keto-enol tautomers were added to 1 liter of distilled water. After the solution has been shaken for over 72 hr, the tautomers had gone completely in solution. The solution was then used as the solvent for the preparation of the surfactant solutions at various concentrations.

Spectral Measurements

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

Surface Tension Measurements

The surface tension of the solution was determined by a modified Wilhelmy type digital surface tensiometer (Shimadzu ST-1 Mark II).

RESULTS AND DISCUSSION

It is well known that benzoylacetone, keto-enol tautomer, is more enolized in most organic solvents than in water, as reported by Morton et al. (7) and others. Recently, we determined the CMC values of various anionic and cationic surfactants from abrupt changes of absorption spectra of benzoylacetone incorporated into the micelles (5). However, the CMCs for nonionic surfactants could not be determined by this method because benzoylacetone was only partially enolized in the ethylene oxide chains located on

TABLE I

Critical Micelle Concentration (CMC) of the Surfactants by Keto-Enol Tautomerism of Benzoylacetoanilide and Surface Tension Method and Published Data

Surfactant[a]	CMC by surface tension (mole/l) (25 C)	CMC by published data (mole/l)	CMC by keto-enol tautomerism of benzoylacetoanilide (mole/l) (25 C)	
			By ketonic form	By enolic form
$C_{12}E_6$	6.8x10^{-5}	6.6x10^{-5} (8)	1x10^{-4}	8.0x10^{-5}
$C_{12}E_7$	6.9x10^{-5}	6.8x10^{-5} (8)	8x10^{-5}	7.5x10^{-5}
$C_{12}E_8$	7.2x10^{-5}	7.0x10^{-5} (8)	1x10^{-4}	7.5x10^{-5}
Triton X-100	9.0x10^{-4}	9.0x10^{-4} (9)	9x10^{-5}	5.0x10^{-4}
NP-10	8.0x10^{-5}	7.5-9.0x10^{-5} (10)	8x10^{-5}	8.0x10^{-5}
SDS	8.1x10^{-3}	8.1x10^{-3} (11)	7x10^{-5}	7.8x10^{-3}
CTAB	---	1.0x10^{-3} (60 C) (12)	---	9.5x10^{-4}

[a] $C_{12}E_6$ = hexaethylene glycol dodecyl ether, $C_{12}E_7$ = heptaethylene glycol dodecyl ether, $C_{12}E_8$ = octaethylene glycol dodecyl ether, Triton X-100 = polyoxyethylene tert-octyl phenyl ether, NP-10 = polyoxyethylene nonyl phenyl ether, SDS = sodium dodecyl sulfate, CTAB = cetyl trimethyl ammonium bromide.

the micelle surface at concentrations above the CMC. Consequently, the abrupt changes in absorbance for nonionic surfactants could not distinctly be observed.

Benzoylacetoanilide, keto-enol tautomer, differs from benzoylacetone. It was found to be easily enolized in n-dodecane but not in ether as shown in Figure 1, in which the absorption spectra for benzoylacetone enolized by both solvents are shown for comparison.

The changes in the absorption spectra with varying concentrations of nonionic surfactants in aqueous solutions containing 10 mg/l of benzoylacetoanilide are shown in Figure 2, a, b, and c for $C_{12}E_6$, Triton X-100, and NP-10, respectively. As the absorption spectra for $C_{12}E_7$ and $C_{12}E_8$ give the same spectra as that of $C_{12}E_6$, those figures are not shown here.

The changes at the CMC in absorbance for these nonionic surfactants were distinctly observed by plotting the absorbance at 250 nm and 320 nm against the concentration of surfactants as shown together with those of anionic and cationic surfactants in Figure 3.

A remarkable enhancement of enolic absorption for benzoylacetoanilide occurs at a concentration just above the CMC. This phenomenon could not be observed on the spectra for benzoylacetone (5).

The concentrations corresponding to break points for these nonionic surfactants are listed in the third and last columns of Table I. The values for these nonionic surfactants are in fairly good agreement with the published data of the CMC of each surfactant listed for comparison.

This suggests that benzoylacetoanilide dissolved in nonionic surfactant solutions is easily enolized in the liquid dodecane core of the micelle without enolization in ether-like ethylene oxide chains on the micellar surface in forming the micelle, and then can be employed on the CMC determination for nonionic surfactants.

This feature can be supported by the fact that in the case of ionic surfactants as shown in Figure 3, the changes in absorbance of dissolved benzoylacetoanilide in ionic surfactant solutions occur abruptly at the CMC.

Consequently, these findings suggest that, in general, this method of keto-enol tautomerism using benzoylacetoanilide is more applicable to the determination for the CMC of anionic, cationic, and nonionic surfactants than that using benzoylacetone.

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