Properties of Ampholytic Surfactant, *N*-Alkyl-β-alanine

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Ampholytic surfactant, *N*-alkyl-β-alanine, was synthesized and its infrared absorption spectra, surface tension, isoelectric points and critical micelle concentrations of aqueous solutions were measured at various electrolyte concentrations, pH and temperature. The measurements of isoelectric points and infrared spectra confirmed a zwitterionic sructure of *N*-alkyl-β-alanine. The critical micelle concentrations determined by surface tension measurements are 1.3×10^{-2} and 9×10^{-4} mol/l respectively for the decyl and dodecyl homologs at 30 °C, the values decreasing with the increase in pH, electrolyte concentration and temperature.

Although considerable information is available concerning the properties of aqueous solutions of ionic and nonionic surfactants, little is known about those of ampholytic surfactants. Studies on *C*-alkyl betaine[1] and *N*-alkyl betaine[2-4] give information on the ampholytic surfactant. Properties of a number of other ampholytic surfactants have been investigated by Herrmann.[5] However, only a few papers have appeared on ampholytic *N*-alkyl-β-alanines.[6-8]

We have studied the effect of pH, temperature and electrolyte concentration on the critical micelle concentration (CMC) of *N*-alkyl-β-alanine by surface tension measurements. Zwitterion formation and micelle formation were discussed. A phase diagram was constructed in order to study the phase transition.

Experimental

Materials. *N*-Alkyl-β-alanine was prepared by the reaction of *n*-alkylamine with β-propiolactone in acetonitrile at 25—30 °C for one hour according to the method of Gresham *et al.*[9] The purity of *n*-alkylamine was better than 99.5% as confirmed by gas chromatography. A crude product was purified by repeated recrystallization from a mixture of acetone and ethanol (1:1) followed by drying in a vacuum. Thin layer chromatography confirmed the absence of unreacted materials in the purified sample. The result of elementary analysis agreed with the theoretical composition within experimental error.

Surface Tension Measurements. The surface tension was measured by a drop-weight method in a thermostated air-bath and the CMC value was determined from the surface tension *vs.* log concentration curve at different pH and temperature.

Phase Diagram. A phase diagram was constructed for the binary system consisting of surfactant and water, covering the concentration range 0—0.7 by weight fraction of the surfactant and the temperature range 0—100 °C. The transition temperature was determined by observing visually or microscopically the phase change caused by heating or cooling the sealed test-tubes containing the solutions of known concentration in a water bath.

Infrared and Proton Magnetic Resonance Spectrometry. Infrared (IR) spectra were measured with a Hitachi EPI-2 infrared spectrometer. The proton magnetic resonance (PMR) spectra in deuteriochloroform solutions were measured with a Nihon Denshi JNM PS-100 spectrometer at 100 MHz, and the chemical shifts are given by ppm, using tetramethylsilane as an external standard.

Results and Discussion

IR and PMR Spectrometry. IR spectra of the decyl homolog in aqueous solutions are given in Table 1. The absorption bands due to COO^- and N^+H_2 in a neutral solution (pH=6) confirm the zwitterionic structure of *N*-decyl-β-alanine. The IR spectra in an acid solution (pH=1) give the absorption bands due to COOH and the characteristics of the quaternary ammonium salts. This confirms the cationic structure in an acid solution. The spectra in an alkaline medium (pH=12) lack the absorption bands due to N^+H_2 but retain the bands due to COO^-, indicating the anionic structure. Similar results have also been obtained for the dodecyl homolog.

Table 1. IR spectra of *N*-decyl-β-alanine in aqueous solutions

N-Decyl-β-alanine	COOH	COO^-	N^+H_2[a)]	N^+H_2[b)]
in neutral (pH 6)	—	1560 cm^{-1} 1400	2300 cm^{-1} 1650	—
in acid (pH 1)	1740 cm^{-1}	—	—	2400–2800 cm^{-1}
in alkaline (pH 12)	—	1560 cm^{-1}	—	—

a) zwitterion b) quaternary ammonium ion

The numbers of protons obtained from the measurements of PMR spectra are in agreement with those expected from the molecular structure. Thus PMR spectra also confirm the zwitterionic structure of *N*-alkyl-β-alanine.

Isoelectric Points. Isoelectric point (pH_i) of ampholytic surfactants was determined from pH titration[10] and dissociation constant measurements. The titration curves of 0.1 M hydrochloric acid solution with 0.1 M sodium hydroxide solution were plotted in the presence and also in the absence of surfactant. The common point of intersection was obtained for three such curves which gave pH_i's 7.0—7.2 and 6.8—7.0 for the decyl and dodecyl homologs, respectively.

Dissociation constant as a weak acid or base is calculated from the pH change of an acid or alkaline solution caused by the addition of a given amount of the ampholyte. The values of pK_a and pK_b thus determined for *N*-decyl-β-alanine are 3.3—3.5 and 3.1—3.2, respectively. The pH_i calculated from pK_a and pK_b for the decyl homolog is 7.0—7.2 agreeing with

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Table 2. CMC values of several ampholytic surfactants in aqueous solutions (mmol/l)

Surfactant	Decyl	Dodecyl	Reference
N-alkyl-β-alanine	13(30 °C)	0.9(30 °C)	Present work
C-alkyl betaine	13(30 °C)	1.3(27 °C)	1
N-alkylbetaine	18(23 °C)	1.8(23 °C)	3
trimethylamino-alkaneimide	—	1.3(25 °C)	11

those determined by pH titration.

Critical Micelle Concentrations. The CMC values determined from the plot surface tension *vs.* log concentration at 30 °C are given in Table 2 together with those of other ampholytic surfactants.[1,3,11] We see that the CMC values of *N*-alkyl-β-alanines are nearly equal to those of the same alkyl chain length.

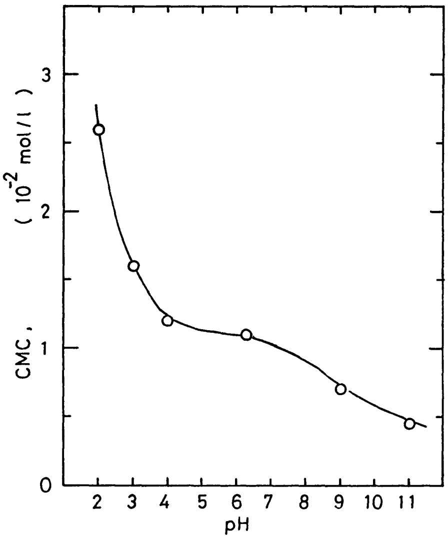

Fig. 1. Effect of pH on the CMC of *N*-alkyl-β-alanine at 30 °C.

The effect of pH on the CMC of *N*-decyl-β-alanine in 0.1 M sodium chloride solution is shown in Fig. 1. The CMC values decrease with increasing pH of the solution. The decrease is rapid in acid region, slow in alkaline side and imperceptible around pH 5—7. Corkill *et al.*[11] reported that CMC of *N,N,N*-trimethylaminododecaneimide decreased with increasing pH of the solution. This is due to the suppression of ionization of amino group, which can explain the rapid decrease of CMC of the decyl homolog in acid region but not the slow decrease of CMC in alkaline side since the enhanced dissociation of carboxyl group prevents the micelle formation. The position of the ionized group would be taken into account to explain the phenomena.

As is evident from the molecular structure, cationic ionization takes place in the inner position, while anionic ionization occurs at the end of the molecule. Thus the steric hindrance against micellization is less for the latter which acts to decrease the CMC with increasing pH. Such a steric hindrance has been studied in detail by Hartley.[12] The high CMC values in acid region show the instability of micelles in a low pH region.

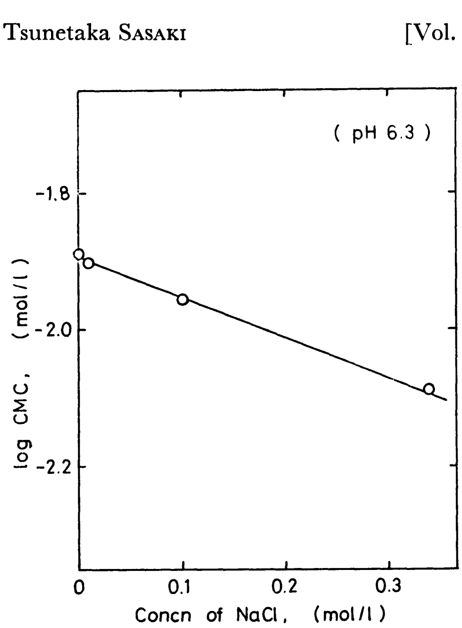

Fig. 2. Effect of electrolyte on the CMC of *N*-decyl-β-alanine at 30 °C.

The effect of sodium chloride on the CMC of *N*-decyl-β-alanine in a nearly neutral solution (pH=6.3) at 30 °C is shown in Fig. 2. The logarithm of the CMC decreases linearly with increasing concentration of added salt as in the case of nonionic surfactants.[13] In the case of ionic surfactants the plot log-log instead of that semi-log proves to be linear.[14] The difference can be explained by the zwitterionic property of *N*-alkyl-β-alanine in the isoelectric region where the ionic charges are neutralized in a molecule and the surfactant is considered to be nonionic.

In the plot of log CMC against $1/T$ at various pH for the decyl homolog (Fig. 3), at pH 11 the CMC increases slightly with increasing temperature in accordance with other ionic surfactants, while at pH 6.3, it decreases with increasing temperature as in the case of nonionic surfactant.[15] At pH 2, the CMC remains unchanged with temperature.

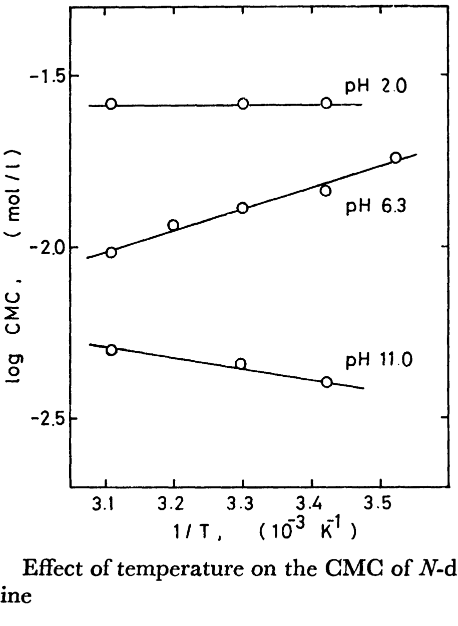

Fig. 3. Effect of temperature on the CMC of *N*-decyl-β-alanine

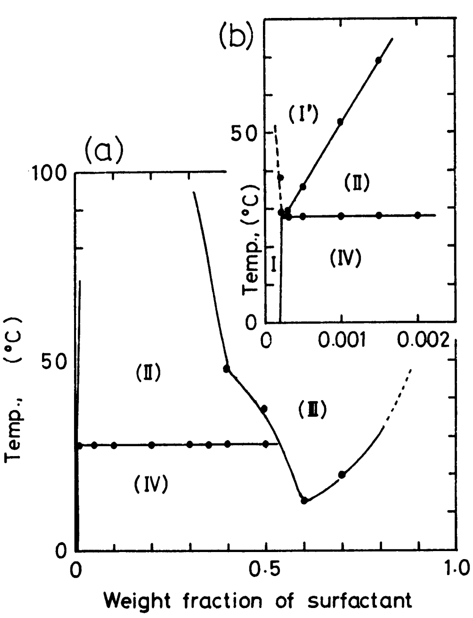

Fig. 4. Phase diagram of N-dodecyl-β-alanine/water system.

(a) system as a whole, (b) system in a dilute surfactant region; (I), (III): homogeneous region; (II), (IV): heterogeneous region.

Phase Diagram. The phase diagram of N-dodecyl-β-alanine/water system in (a) isoelectric region as a whole and (b) dilute surfactant region is shown in Fig. 4. (I) is a clear and homogeneous isotropic liquid phase consisting of surfactant monomers and water, (I′) a similar phase consisting of surfactant monomers, micelles and water, (II) a region of the heterogeneous system which separates into two clear liquid phases when left standing, one rich and the other poor in surfactant, (III) a clear and homogeneous liquid phase, and (IV) a region of heterogeneous suspension consisting of a so called hydrated solid surfactant, dilute surfactant solution and (III). The line separating regions (I) and (I′) shows the temperature dependence of CMC. The line separating regions (II) and (IV) is parallel to the composition axis showing the melting point of the hydrated solid surfactant determined by the differential scanning calorimetry. The cloud points usually observed in the nonionic surfactant could not be detected in the aqueous solution of N-decyl- and N-dodecyl-β-alanine in isoelectric region at temperatures 0—100 °C. The phase diagram for the decyl homolog and water system was also constructed for the concentrations 0—0.5 (weight fraction of surfactant) and temperatures 0—100 °C. Only one isotropic liquid phase without phase change was observed.

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