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Self-Association of Cyclohexylamine in Water

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The self-association of cyclohexylamine (CHA) in water at 25 °C was investigated by measuring the fluorescence spectrum and intensity of ammonium 8-anilino-1-naphthalenesulfonate as a fluorescent probe. The surface tension of an aqueous solution of CHA was also measured with a Du Nöuy tensiometer at 25 °C. CHA formed self-association in water, and the association was micellar. The critical micelle concentration of CHA in water at 25 °C was estimated as 0.5—0.6 M by the fluorescence method, and this value coincided with that of 0.54 M obtained by the surface tension method.

Key words cyclohexylamine; micelle; fluorescent probe; surface tension

It is generally known that compounds without distinct hydrophobic and hydrophilic moieties do not easily form micelles. In contrast to a large number of studies on the surface activities of aliphatic compounds,[1] only a few have been made on the surface activities of aromatic compounds (especially simple aromatic compounds). For instance, it has been reported[2] that morpholine, (tetrahydro-1,4-oxazine) does not form micelle, and we have found[3] that piperidine, (hexahydropyridine) also does not form micelle. It is, therefore, interesting to know how much hydrophobicity is necessary to form micelle, and is also of interest to investigate the surface activities of simple aromatic compounds from the viewpoint of structure–activity correlation. Morpholine and piperidine have four and five methylene units, respectively, in their molecular structures. For systematic study of the surface activity of simple aromatic compound, we chose cyclohexylamine (CHA) which has six methylene units in its molecular structure. CHA is used in many organic syntheses, however, few studies on its surface activity of CHA have been made except on the adsorption of CHA on an iron sheet.[4] The surface tension of aqueous solution of the fatty acid salt of CHA (cyclohexylamine caprate) has been measured,[5] although there have been no reports on the surface tension of CHA and the self-association of CHA in water.

The self-association of CHA in water was measured by the fluorescence method and the surface tension method, and the critical micelle concentration (cmc) of CHA obtained by the two methods was compared.

Experimental

Materials CHA purchased from Wako Pure Chemical Industries, Ltd. was of guaranteed reagent grade and was used without further purification. Ammonium 8-anilino-1-naphthalenesulfonate (ANS) as a fluorescent probe was the same as that used in the previous study.[6] Deionized and twice-distilled water was used throughout this study.

Measurement of Fluorescence Intensity ANS as a fluorescent probe was freshly dissolved in water before use by sonication at about 25 °C for 5 min as previously described.[7] The concentration of ANS was maintained at 1×10^{-5} M, and CHA was dissolved in the ANS aqueous solution. ANS is located closer to the polar field than to the nonpolar field, so it is believed to be located at the surface of micelle. The fluorescence spectra and intensities were measured with a Hitachi F-4000 spectrofluorometer as previously described.[8] The temperature was maintained at 25±0.2 °C during the fluorescence measurement by circulating water through the cuvette holders. The fluorescence spectra and intensities were determined after temperature of the sample solution had reached the measurement temperature. The wavelength of excitation was 360 nm; the fluorescence intensity was measured at emission wavelength 490 nm.

Measurement of Surface Tension The surface tension was measured with a Du Nöuy tensiometer. A platinum ring with a diameter of 19 mm was heated by an oxidizing flame before use. The thermostat temperature was maintained at 25±0.1 °C. To calculate the surface tension of aqueous solutions, the value of 71.96 mN m^{-1} was used as the surface tension of pure water at 25 °C. The experimental determination of the surface tension was precise to ±0.1 mN m^{-1}.

Results and Discussion

Self-Association of CHA in Water by Fluorescence Method Changes in the λ_{max} of ANS excited at 360 nm by varying the concentration of CHA from 0 to 2 M are shown in Fig. 1. ANS in water at 25 °C had a λ_{max} at 520 nm, but λ_{max} shifted gradually to a lower wavelength as the concentration of CHA was increased to approximately 0.4 M. At 0.4—0.6 M of CHA λ_{max} shifted sharply to a shorter wavelength, and λ_{max} became constant, 490 nm, at concentrations of CHA above 0.6 M. The decrease in λ_{max} at concentrations below about 0.4 M is due to the increase in viscosity of the solution surrounding ANS by the addition of CHA. The relationships between the λ_{max} of dyes and the micro-viscosity have been reported by several researchers.[9] The decrease in λ_{max} at concentrations of 0.4—0.6 M is thought to be due to the penetration of ANS from the bulk phase to the CHA micellar phase. The cmc of CHA in water is regarded as 0.5—0.6 M. The value of λ_{max} of ANS located at the micellar surface of general surfactant was 480 nm,[8] so the

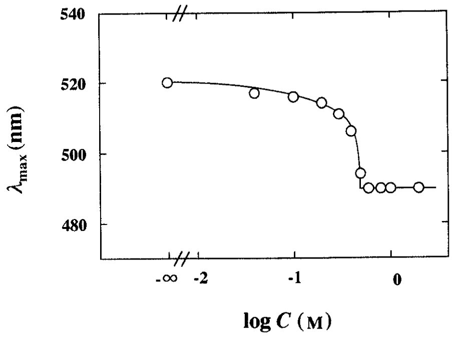

Fig. 1. Variation of λ_{max} of ANS with Increasing Concentration of CHA in Water at 25 °C

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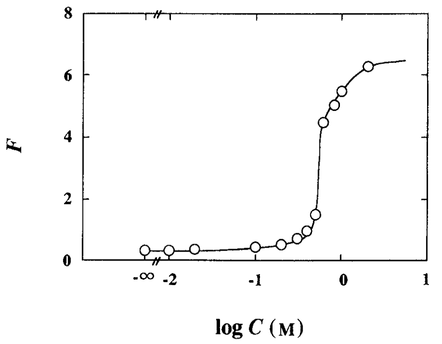

Fig. 2. Relationship between Fluorescence Intensity of ANS at 490 nm and Concentration of CHA in Water at 25 °C

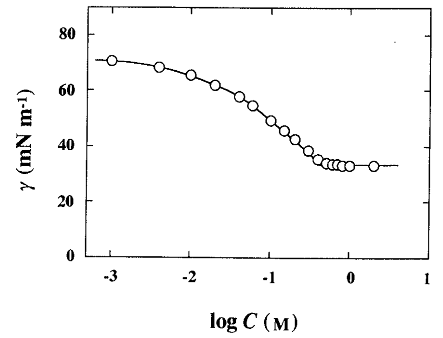

Fig. 3. Surface Tension of CHA in Water at 25 °C

value of 490 nm for CHA micelle is believed to be adequate.

Changes in the fluorescence intensity of ANS at 490 nm by varying the concentration of CHA are shown in Fig. 2. As seen, the value of *F* was small at concentrations of CHA below 0.2 M, *F* increased gradually at 0.3—0.5 M, and then greatly at concentrations above 0.6 M. This suggests that the CHA micelle begins to form at a concentration of 0.5—0.6 M. The micellar aggregation number of CHA is thought to be relatively small because of the six-membered ring structure of CHA and the large value of cmc. In general, the micellar aggregation number of aromatic compounds is small: equal to the micellar aggregation numbers of dibucaine hydrochloride, [2-butoxy-*N*-{2-(diethylamino)ethyl}-4-quinolinecarboxamide hydrochloride],$^{10)}$ and piperidolate hydrochloride, [*N*-ethyl-3-piperidyl diphenylacetate hydrochloride],$^{11)}$ are 9 and 12, respectively.

Surface Tension of Aqueous Solution of CHA To confirm the micellization of CHA shown by the fluorescence method, the surface tension (γ) of CHA in water was measured, and the result is presented in Fig. 3. As can be seen, γ decreased with increasing concentration of CHA and became nearly constant above 0.6 M. This indicates that the CHA micelles are indeed formed. If the cmc is estimated from the inflection point in the γ *vs.* log *C* curve, cmc is obtained as 0.54 M. This value exactly coincides with that obtained by the fluorescence method.

The cmc of sodium octanoate in water at 20 °C is reported as 0.36 M.$^{12)}$ The cmc of sodium ω-cyclohexylethanoate, sodium ω-cyclohexylpropanoate and sodium ω-cyclohexylbutanoate in water at 25 °C are 1, 0.53, and 0.26 M, respectively.$^{13)}$ The cmc of CHA is larger than that of sodium octanoate$^{12)}$ and is nearly equal to that of sodium ω-cyclohexylpropanoate.$^{13)}$

In conclusion, CHA formed micelle in water, although the hydrophobic and hydrophilic parts in the CHA molecular structure are not so clear. The cmc of CHA in water at 25 °C was 0.5—0.6 M (0.54 M). The concentration of CHA when the substance is used as a material for synthesis or as a solvent thus may be of importance.

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