Association of 1-Octadecanoic Acid in 1,2-Dichloroethane

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The association of 1-octadecanoic acid (C18) in 1,2-dichloroethane at 40 °C has been investigated by measuring the fluorescence spectra and intensities of ammonium 8-anilino-1-naphthalenesulfonate as a probe.

As a result, it has been found that C18 begins to associate at a concentration of 1.0—1.2 × 10^{-2} mol·dm^{-3} and that the aggregation number is small and constant in the concentration region above about 4 × 10^{-2} mol·dm^{-3}.

The mechanism for the formation of fatty acid (FA)–thiamine disulfide (TDS) complexes, $(FA)_6(TDS)$, was also discussed.

Keywords 1-octadecanoic acid; 1,2-dichloroethane; association; ammonium 8-anilino-1-naphthalenesulfonate; fluorescence intensity

It has been reported that the solid state complexes composed of higher fatty acids (FA) and thiamine disulfide (TDS) are obtained from 1,2-dichloroethane solutions.[1] The stoichiometry of the complex is expressed as $(FA)_6(TDS)$.[1] It is suggested that FA forms an association similar to a reversed micelle in 1,2-dichloroethane before the complex is formed: (1) TDS is practically insoluble in 1,2-dichloroethane but TDS is dissolved in the presence of FA; (2) the molar ratio of FA to TDS in the complex is 6:1, although approximately 8:1 of FA and TDS were dissolved in 1,2-dichloroethane, suggesting that the concentration of FA which does not participate in the formation of the complex corresponds to the critical micelle concentration (cmc); (3) the complex can not be purified in 1,2-dichloroethane by recrystallization, namely, part of TDS coprecipitates, suggesting that part of FA corresponding to the cmc transfers from the complex to the solvent; (4) the complex can not be obtained from ethanol solution.

In contrast to a large number of studies on aqueous micellar systems, a few studies on the formation of reversed micelles in nonaqueous solvents have been made. The formations of reversed micelles have been reported for calcium xylylstearate and calcium xenylstearate in benzene,[2] α-monoglycerides in benzene and chlorobenzene,[3] and alkyl ammonium propionate in dichloromethane[4] and in the other solvents.[5] For the purpose of the measurements of the formations of reversed micelles in nonaqueous solvents, rhodamine B (RB) had been used as a fluorescent dye.[2,6]

On the other hand, ammonium 8-anilino-1-naphthalenesulfonate (ANS) is known as a fluorescent probe for aqueous systems. ANS has been used for the measurements of cmc[7] and the surface potential of the micelles.[8]

From these points of view, the association of 1-octadecanoic acid (C18) in 1,2-dichloroethane at 40 °C was determined by using ANS. Furthermore, the mechanism for the formation of $(FA)_6(TDS)$ was discussed.

Experimental

Materials C18 and 1,2-dichloroethane purchased from P-L Biochemicals, Inc. and Kokusan Chemical Works, Ltd., respectively, were of guaranteed reagent grade and used without further purification. ANS was the same as that used for the previous studies.[8] RB obtained from Wako Pure Chemical Industries, Ltd. was of guaranteed reagent grade.

Measurement of Fluorescence Intensity ANS as a fluorescent probe was freshly dissolved in 1,2-dichloroethane before use by sonication at about 25 °C for 5 min using a Tsutsui-Chemical UW-15. The concentration of ANS was kept constant at 1.5 × 10^{-5} mol·dm^{-3}. RB[2] as another fluorescent dye was dissolved in 1,2-dichloroethane and the concentration was kept constant at 1 × 10^{-6} mol·dm^{-3}. C18 was dissolved in the 1,2-dichloroethane solution of ANS or RB.

ANS is not easily dissolved in 1,2-dichloroethane, while RB is freely soluble in 1,2-dichloroethane. According to the report[9] that merocyanine dye is not incorporated into the normal micelle because the dye is insoluble in nonaqueous solvents, it is considered that most of the RB is adsorbed on the surface of reversed micelles and part of the RB is dispersed in the solvent. On the contrary, it is considered that most of the ANS is incorporated into the reversed micelles.

The fluorescence spectra and intensities were measured with a Hitachi F-4000 spectrofluorometer as previously described.[8b] The temperature was maintained at 40 ± 0.2 °C during the fluorescence measurement by circulating water through the cuvette holders. The fluorescence spectra and intensities were determined after 7 min that the fluorescence cell contained a sample solution which settled in the fluorometer. The wavelength of excitation and emission are 365 and 486 nm, respectively, for ANS, and 562 and 582 nm, respectively, for RB.

Results and Discussion

Maximum Wavelength of Emission The changes in the maximum wavelength of the emission spectrum (λ_{max}) of ANS excited at 365 nm by varying the concentration of C18 from 0 to 8 × 10^{-2} mol·dm^{-3} are shown in Fig. 1. ANS in 1,2-dichloroethane had a λ_{max} at 472.5 nm, but λ_{max} shifted gradually to the lower wavelength as the concentration of C18 was increased up to approximately 1 × 10^{-2} mol·dm^{-3}. This is considered to be due to the change in the viscosity of the solution surrounding ANS by the addition of C18. Handa *et al.*[10] have reported that the absorption maxima of dyes, dialkyl thiacarbocyanines, are shifted by varying the viscosity of solvents. At concentrations of C18 above about 1 × 10^{-2} mol·dm^{-3} λ_{max} shifted sharply to the longer

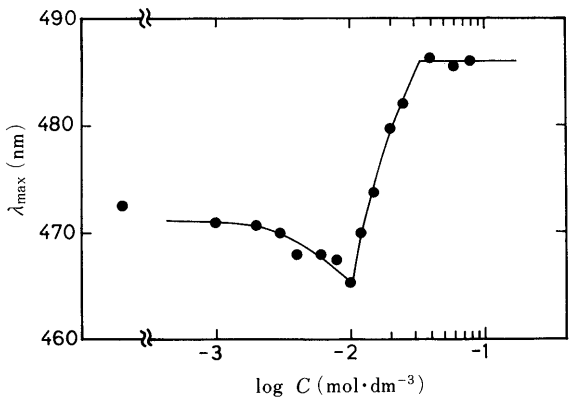

Fig. 1. Variation of λ_{max} of ANS at an Increasing Concentration of C18
Temperature: 40 °C.

wavelength, and λ_{max} became constant, 486 nm, at concentrations of C18 above about 4×10^{-2} mol·dm^{-3}.

The observed shift of λ_{max} toward a longer wavelength at concentrations of C18 above about 1×10^{-2} mol·dm^{-3} is considered to imply that the microenvironment surrounding ANS transfers to a polar environment and ANS is located near the polar head of the C18 association as described by Belletete and Durocher[11] with regard to the relationship between a probe and λ_{max}. This agrees with the expectation that ANS will be located near the core of the reversed micelle because ANS is not easily dissolved in 1,2-dichloroethane.

Furthermore, the value of λ_{max} is constant unless the microenvironment surrounding ANS is not changed.[8a] In addition, ANS in an aqueous solution has a λ_{max} at the neighborhood of 480 nm when ANS is excited at 360 nm.[8] According to the reports,[8,11] the observed shift of λ_{max} toward a longer wavelength is suggested to be caused as C18 begins to associate at a concentration beyond 1×10^{-2} mol·dm^{-3} and that the aggregation number increases with an increasing concentration of C18 up to approximately 4×10^{-2} mol·dm^{-3}. Furthermore, the aggregation number becomes nearly constant at concentrations of C18 above about 4×10^{-2} mol·dm^{-3} because it is cosidered that the increasing aggregation number leads to a shift of λ_{max} beyond the constant value of 486 nm.

The measurement at concentrations above 8×10^{-2} mol·dm^{-3} cannot be carried out because of the solubility limit of C18 in 1,2-dichloroethane at 40 °C.

On the other hand, λ_{max} of RB excited at 562 nm was independent of the concentration of C18 and maintained a constant value of 582 nm. This is considered to be due to the fact that RB is located not in the core but at the surface of the reversed micelle. This is based on the value of λ_{max} of dye adsorbed on the surface of normal micelles being nearly equal to that of dye alone in an aqueous solvent.[8a]

It is found that ANS is useful not only in aqueous solutions but also in 1,2-dichloroethane solution, although ANS has been used in aqueous systems.

Fluorescence Intensity The changes in the fluorescence intensity of ANS at 486 nm by varying the concentration of C18 are shown in Fig. 2. As can be seen in Fig. 2, the fluorescence intensity decreased slightly as the concentration of C18 was increased up to approximately 1×10^{-2} mol·dm^{-3}. This is considered to be because of a larger shift of λ_{max} than of ANS alone solution from 486 nm, at which the fluorerscence intensity is measured, and following the decrease in fluorescence yield. At concentrations of C18 above about 1×10^{-2} mol·dm^{-3} the fluorescence intensity increased gradually, and increased largely at concentrations above about 4×10^{-2} mol·dm^{-3}. ANS fluoresces strongly when adsorbed on micelle.[7,8] Furthermore, it has been found[12] that fluorescence intensity of ANS is increased by the inclusion of ANS into the cyclodextrin host cavity. The increase in fluorescence intensity is, therefore, considered to represent the presence of a C18 aggregate in 1,2-dichloroethane. Namely, it is suggested that C18 begins to associate at a concentration of 1.0—1.2×10^{-2} mol·dm^{-3} and that the aggregation number of C18 becomes constant at a concentration of 2.5—4.0×10^{-2} mol·dm^{-3} as described in the previous section. Additionally, the increase in fluorescence intensity at concentrations of C18 above about 1×10^{-2} mol·dm^{-3} shown in Fig. 2 is considered to be based on the association mechanism[13] proceeding as: monomer $\rightleftharpoons$ dimer $\rightleftharpoons$ trimer $\rightleftharpoons$ *n*-mer in nonaqueous solvents. On the contrary, generally observed associations in aqueous micellar systems proceed as monomer $\rightleftharpoons$ *n*-mer equilibria,[14] because the driving force for the association is mainly hydrophobic interaction.

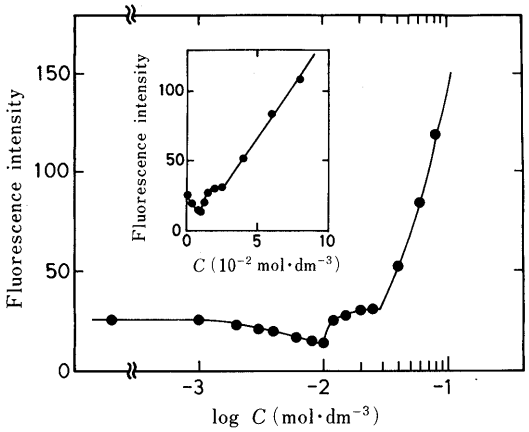

Fig. 2. Relationship between Fluorescence Intensity of ANS at 486 nm and Concentration of C18
Temperature: 40 °C.

It has been reported that carboxylic acids in solutions exist as equilibrium mixtures of monomer and dimer molecules.[15] On the other hand, Armistead *et al.*[16] have indicated by the measurements of heats of a solution of *n*-fatty acids in benzene that *n*-fatty acids in benzene exist as monomeric species only at low solution concentrations. Unfortunately, it is not possible from our fluorescence data only to ascertain whether C18 in 1,2-dichloroethane exists as a monomeric species only or as an equilibrium mixture of monomer and dimer species at concentrations below 1×10^{-2} mol·dm^{-3}. It is, however, at least certain that the aggregation number begins to increase at a concentration of C18 1.0—1.2×10^{-2} mol·dm^{-3}. Furthermore, Armistead *et al.*[16] have reported by infrared spectroscopic measurements that *n*-fatty acids in benzene tend to form hydrogen-bonded dimer at concentrations above about 1×10^{-2} mol·dm^{-3}, indicating an agreement with our observed concentration although there is a difference in solvent. Therefore, it may be considered that C18 in 1,2-dichloroethane exists as a monomeric species only at concentrations below 1×10^{-2} mol·dm^{-3}, what is called "below the cmc."

In the case of RB, also, the fluorescence intensity began to increase at a C18 concentration of 1—2×10^{-2} mol·dm^{-3}. The first break point in the RB system was equal to that in the ANS system. However, detailed information as shown in the ANS system could not be obtained with regard to the changes in fluorescence intensity. This is considered to be due to the fact that the replication point of RB is different from that of ANS. In this study, ANS as a fluorescent probe was more valuable than RB.

It has been reported that the aggregation numbers of alkylammonium carboxylates[5] in various organic solvents are 3—10 and that of dodecylammonium propionate[4] in dichloromethane is 6. In addition, the trimer of *n*-

dodecanoic acid has been found in the benzene solution.[17] The aggregation number of C18 in 1,2-dichloroethane cannot be decided from only the fluorescence data shown in Figs. 1 and 2. However, the aggregation number of C18 in 1,2-dichloroethane is suggested to probably be 6. This suggestion is based on the following: (1) the molar ratio of C18 to TDS in the complex[1] is 6 : 1 and the complex cannot be obtained[1] in benzene or other solvents except 1,2-dichloroethane; (2) the C18–TDS complex is an inclusion compound, that is, guest TDS is included in the cylindrical C18 host structure[18]; (3) assuming that the host structure consists of six molecules of C18, the diameter of host cavity is estimated as 5.1—6.7 Å by using the values[19] of 20—35 Å^2 for the area occupied by a fatty acid molecule, indicating a similar size as the host cavity[20] of α or β-cyclodextrin, 5.5, 7.0 Å, respectively; (4) the internal diameter (d) of hydrogen-bonded hexamer is derived as $d > 5.12$ Å by using the value[21] of 2.56 Å for the distance of hydrogen bond (O–H$\cdots$O) in crystalline 1-dodecanoic acid, also indicating a similar size as the host cavities of cyclodextrins. Furthermore, it has been reported[22] that the reversed micelles with small aggregation numbers are not spherical but platelike. Therefore, probably a platelike reversed micelle of C18 with an aggregation number of 6 might be formed in 1,2-dichloroethane at C18 concentrations above about 4×10^{-2} mol·dm^{-3}. Using the term "reversed micelle" for a hexamer may be questionable, but the phenomena that the λ_{max} of fluorescence spectra and the fluorescence intensities are changed sharply above a critical concentration as shown in Figs. 1 and 2 do represent a micellar characteristic.

Shinomiya[23] has reported the hydrogen-bonded species of alkanols by measurement of dielectric relaxation. According to the reports, (1) 1-decanol in the pure liquid state is in equilibrium among a free monomer, a chain dimer and trimer, a linear hydrogen-bonded chain polymer, and a hydrogen-bonded cyclic polymer, (2) the percentage of linear chain polymer decreases and that of cyclic polymer increases, as the temperature increases from 15 to 40 °C, (3) the percentage of linear chain polymer decreases and that of cyclic polymer increases, as pure 1-decanol is diluted with heptane or cyclohexane; 30 mol% of 1-decanol solution is almost in the state of a cyclic polymer. The cyclic polymer becomes a most stable structure in dilute solutions, although the linear hydrogen-bonded chain polymer is favorable in pure 1-decanol.[23a]

There is, therefore, a possibility of a hydrogen-bonded cyclic polymer for the association of C18 in 1,2-dichloroethane. From the above, the C18 association is described as a platelike, cyclic hexamer-like and reversed micellar aggregate.

In the case where ethanol was used instead of 1,2-dichloroethane, no increase in the fluorescence intensity of ANS was found although the concentration of C18 was increased up to 1 mol·dm^{-3}. This corresponds to the fact[24] that neither a reversed micelle nor a normal micelle are formed in ethanol or methanol solution.

Regarding the mechanism of the formation of $(C18)_6$(TDS) which is obtained as a crystal in 1,2-dichloroethane solution, it is suggested as follows: C18 forms an association similar to a reversed micelle in 1,2-dichloroethane, and TDS is solubilized in the C18 association in the first step, the C18–TDS association similar to a mixed reversed micelle brings about a transformation (probably from a platelike to a cylindrical structure) in the second step, and the solid crystalline $(C18)_6$(TDS) is precipitated in the third step. A similar phenomenon has been reported for the micellar system of sodium dodecyl sulfate (SDS): solubilized alkanols with short alkyl chain cause a breakdown of the SDS micelle.[25] Furthermore, a structual transition has been reported[26] for the SDS micelle–1-dodecanol system, namely the transition from a mixed micellar structure to a complex structure whose stoichiometry is expressed as $(SDS)_2$(1-dodecanol).

In addition, it has been reported[27] that the distance of hydrogen bond (O–H$\cdots$O) is shortened (about 0.15 Å) by crystallization. Therefore, it may be considered that the distances of hydrogen bonds in C18 hexamer are shortened when the C18–TDS association begins to crystallize and that the shortening of the (O–H$\cdots$O) distance leads to a new or strengthened interaction between C18 and TDS (hydrophobic interactions[18] and van der Waals forces[18]) and contributes toward forming the crystalline $(C18)_6$(TDS).

Conclusion

It has been found that C18 begins to associate at a concentration of 1.0—1.2 $\times 10^{-2}$ mol·dm^{-3} and a C18 association with a constant aggregation number is formed at concentrations above about 4×10^{-2} mol·dm^{-3} in 1,2-dichloroethane at 40 °C. Additionally, it is suggested that the aggregation number of the C18 association is small: the aggregation number is probably 6.

It is suggested that the crystalline $(C18)_6$(TDS) obtained from 1,2-dichloroethane solution is formed by passing through a transition from the C18–TDS association structure similar to a mixed reversed micelle to the complex structure.

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