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Effects of Temperature and Alkyl Chain Length on the Associations of *n*-Fatty Acids in 1,2-Dichloroethane

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The association of saturated fatty acid (FA) with carbon number (*n*) of 12—18 has been investigated in 1,2-dichloroethane by measuring the fluorescence spectrum and intensity of ammonium 8-anilino-1-naphthalenesulfonate as a fluorescent probe at 25, 40, 50 and 60 °C, and the effects of *n* and temperature on the association of FA were also studied. A simple phase diagram of octadecanoic acid in 1,2-dichloroethane was constructed.

The critical concentration at which the dimers or the trimers of FA began to appear, C_1, was approximately the same for all cases; C_1 did not depend on *n* or temperature. On the contrary, the critical concentration at which the reversed micelles of FA were formed, C_2, decreased regularly as *n* increased. The relationship between $\log C_2$ *vs.* *n* thus indicated a linearity.

Keywords fatty acid; 1,2-dichloroethane; association; reversed micelle; phase diagram; fluorescent probe

The effect of temperature on the critical micelle concentrations (cmc) of aqueous solutions of surfactants have been reported[1]: in general, the value of cmc increases as temperature rises, though in the lower temperature regions, cmc decreases as temperature rises. For example, sodium dodecyl sulfate shows a minimum in the cmc-temperature profile at 25 °C,[1a] the cmc of 3-(4-heptylbenzoyl) benzoic acid decreases with temperature initially, shows a minimum at 40—45 °C, and then increases with temperature rise.[1c] On the other hand, it is well known that the cmc of the aqueous solution of surfactant decreases with increasing alkyl chain length.[2] No "odd–even effect" is found in the cmc-alkyl chain length behavior,[3] although melting points,[4] Kraft points,[5] saturated adsorption amount at air–water interface,[3] and surface tensions at cmc[6] indicate zigzag patterns against alkyl chain lengths.

In contrast to a large number of studies on aqueous micellar systems, a few have been made on the formation of reversed micelles in nonaqueous solvents. Formation of reversed micelles has been reported for calcium xylylstearate and calcium xenylstearate in benzene,[7] and alkyl ammonium propionate in dichloromethane[8] and in other solvents.[9] In addition, the cmc of alkyl ammonium propionates in benzene and dichloromethane have been found[9] to decrease with increase in carbon number (*n*) in the alkyl chain. Regarding the dimerization of alkanoic acids in nonaqueous solvents, there have been two kinds of reports: that they are independent of *n*[10] and that they are somewhat dependent on *n*.[11,12] In organic solvents, associations for heptane solutions of 1-pentanol and 3-pentanol have been reported,[13] and fatty acid (FA) reportedly forms trimer in benzene.[12] Association of FA in other organic solvents or its association with an aggregation number of more than 3 has not been reported excepting our own previous short essay.[14] Namely, octadecanoic acid (C18) formed aggregates in 1,2-dichloroethane[14]: at 40 °C, C18 began to associate at a concentration of 1.0—1.2×10^{-2} mol dm^{-3}, the aggregation number increased with concentration of C18 up to approximately 4×10^{-2} mol dm^{-3} above which the reversed micelles were formed.

Against this background, we studied the associations of FA with varying alkyl chain lengths in 1,2-dichloroethane, and the effect of *n* on these associations. The effect of *n* on the dimerization, trimerization or reversed micellization was of particular interest, as was whether the "odd–even effect" would be visible. Temperature effect on the association of FA in 1,2-dichloroethane was investigated, and a simple phase diagram of C18 in 1,2-dichloroethane was constructed.

Experimental

Materials Dodecanoic acid (C12), tridecanoic acid (C13), tetradecanoic acid (C14), pentadecanoic acid (C15), hexadecanoic acid (C16), heptadecanoic acid (C17) and octadecanoic acid (C18) purchased from P-L Biochemicals, Inc. were of guaranteed reagent grade and used without further purification. 1,2-Dichloroethane of guaranteed reagent grade was purchased from Kokusan Chemical Works, Ltd., 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.[14]

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 as previously described.[14] The concentration of ANS was maintained at 1.5×10^{-5} mol dm^{-3}. FAs were dissolved in the 1,2-dichloroethane solution of ANS. Since ANS is not easily dissolved in 1,2-dichloroethane, most of the ANS was believed to be incorporated into the reversed micelles: ANS is located near the polar head of the reversed micelles.

The fluorescence spectra and intensities were measured with a Hitachi F-4000 spectrofluorometer as previously described.[14,15] Measurements were carried out at 25, 40, 50 and 60 ± 0.2 °C, and each tempepature was maintained during the 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 365 nm at four temperatures, and the wavelength of emission was 485—488 nm in the temperature range 25—60 °C.

Results

Maximum Wavelength of Emission Changes in the maximum wavelength of the emission spectrum ($\lambda_{\max}$) of ANS excited at 365 nm by varying the concentration of C16 from 0 to 8×10^{-2} mol dm^{-3} are shown in Fig. 1. ANS in 1,2-dichloroethane at 25 °C had a $\lambda_{\max}$ at 471 nm, but this shifted gradually to a lower wavelength as the concentration of C16 was increased to approximately 1×10^{-2} mol dm^{-3}. This was due to the change in viscosity of the solution surrounding ANS by the addition of C16.[14] At concentrations of C16 above about 1×10^{-2} mol dm^{-3} $\lambda_{\max}$ shifted sharply to a longer wavelength, and $\lambda_{\max}$ became nearly

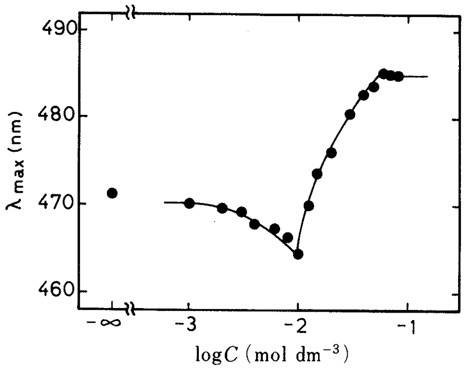

Fig. 1. Variation of λ_{max} of ANS with Increasing Concentration of FA

FA: C16. Temperature: 25 °C.

constant, 485 nm, at concentrations of C16 above about 6×10^{-2} mol dm^{-3}. In accord with a previous report,[14] C16 is believed to begin to associate at a concentration of 1.0—1.25×10^{-2} mol dm^{-3} and the reversed micelle to be formed at above 6×10^{-2} mol dm^{-3}. This assumption is based on the mechanism[16] proceeding as monomer $\rightleftharpoons$ dimer $\rightleftharpoons$ trimer $\rightleftharpoons$ n-mer in nonaqueous solvent, in contrast with the associations in aqueous micellar systems as monomer $\rightleftharpoons$ n-mer equilibria.[17] A similar pattern as that shown in Fig. 1 was observed for the other FA, although those results are not shown here.

The value of λ_{max} was smaller at lower temperature, and the value of λ_{max} became slightly larger as the temperature rose. At the same temperature, no difference in λ_{max} was found among seven FA. This is due to ANS being located near the polar head of the FA reversed micelle and the value of λ_{max} being constant unless the microenvironment surrounding ANS is changed, so that the difference in the alkyl chain length of FA does not affect the value of λ_{max}.

Fluorescence Intensity The changes in the fluorescence intensity of ANS at 485 nm and 25 °C by varying the concentration of C16 are shown in Fig. 2. As can be seen, the fluorescence intensity decreased slightly as the concentration of C16 increased to approximately 1×10^{-2} mol dm^{-3}. At concentrations of C16 above about 1×10^{-2} mol dm^{-3} the fluorescence intensity increased gradually, and then greatly at concentrations above about 6×10^{-2} mol dm^{-3}. It is suggested[14] that C16 begins to associate at a concentration of 1.0—1.25×10^{-2} mol dm^{-3} and that the reversed micelle begins to be formed at a concentration of 5—6×10^{-2} mol dm^{-3}. ANS fluoresces strongly when adsorbed on the micelle.[14,15] Above the C_2 concentration, the reversed micelle increases with the concentration of FA, leading to an increase in fluorescence intensity. Quenching was not found, perhaps due to the small aggregation number of the reversed micelles. A similar pattern was observed for the other FAs, although those results are not shown.

Relationship between FA and Temperature The first and second break points shown in Fig. 1 were denoted as the critical concentrations C_1 and C_2, respectively, and C_1 and C_2 are plotted against temperature in Fig. 3 using triangles and circles, respectively. The prior and after points for the break points are also indicated by bars. Moroi and Matuura[18] pointed out that the cmc is not a point but a range. Our results also suggest that it is better to express cmc as a concentration range.

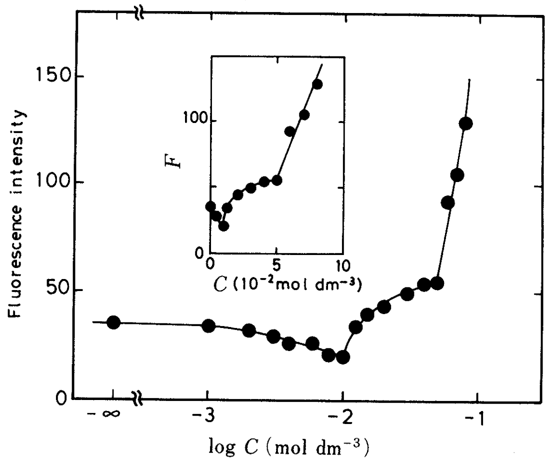

Fig. 2. Relationship between Fluorescence Intensity of ANS at 485 nm and Concentration of FA

FA: C16. Temperature: 25 °C.

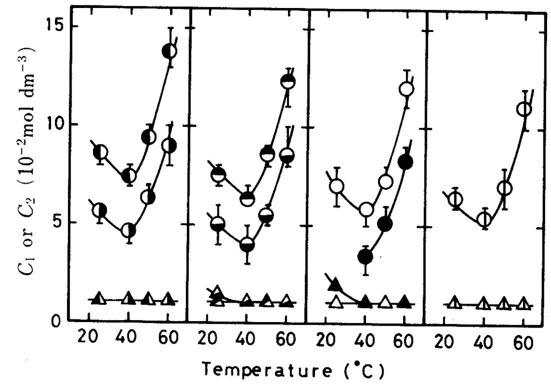

Fig. 3. Relationship between C_1 (Triangles) or C_2 (Circles) and Temperature

FA: ◐, ◭, C12; ◓, ◬, C13; ○, △, C14; ⦶, △, C15; ◑, ◮, C16; ◒, ▲, C17; ●, ▲, C18.

It was found that the critical concentration C_1, at which FA begins to associate, was independent of n. This phenomenon is consistent with the report by Goodman[11] that the dimerization of FA in nonaqueous solvents is independent of n. This is because the moiety of –COOH contributes dominantly to the dimerization of FA. In our results, no significant variation in C_1 was found either by changing n or temperature, except for the values of C17 and C18 at 25 °C. It has been reported that the dimerization and trimerization of 1-decanol is independent of temperature,[19] while, on the contrary, the critical concentration C_2, at which FA begins to form the reversed micelle, depended on n; C_2 decreased with increasing n. At 25 °C, C18 could not form the reversed micelle. This is considered to be due to the Kraft point. Except for C18, the other FAs formed the reversed micelles at 25—60 °C, and the relationship between C_2 and temperature was minimum at 40 °C.

Discussion

Relationship between C_2 and n The value of C_2 was found to depend on the alkyl chain length, so C_2 were plotted against n and are shown in Fig. 4. C_2 can be seen to decrease as n becomes large. This phenomenon in which

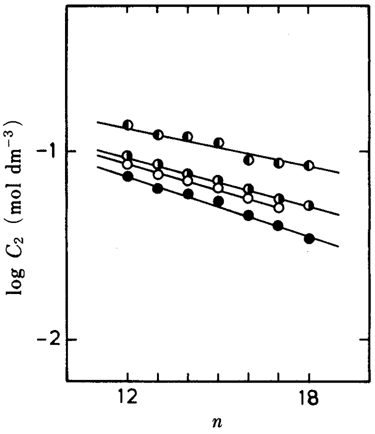

Fig. 4. Relationship between Alkyl Chain Length and C_2
Temperature: ○, 25 °C; ●, 40 °C; ◑, 50 °C; ◐, 60 °C.

Table I. Relationship between C_2 and n

Temperature (°C)	$\log C_2 = An + B$ (mol dm^{-3})
25	$\log C_2 = -0.04600n - 0.5158$
40	$\log C_2 = -0.05208n - 0.5126$
50	$\log C_2 = -0.04274n - 0.5238$
60	$\log C_2 = -0.03333n - 0.4792$

aggregation tendency increases with increasing chain length is well known for other surfactants.[9,12] In general, the relationship between cmc and n is expressed by Eq. 1[20]:

$$\log \text{cmc} = An + B \tag{1}$$

As shown in Fig. 4, good linearity was obtained for each case. So, the relationship between C_2 and n was expressed by the equation, and summarized in Table I. The equations show that the value of C_2 increases 1.112-, 1.127-, 1.103-, and 1.080-fold with every single reductive methylene unit at 25, 40, 50 and 60 °C, respectively. The change in C_2 with n variation was largest when the value of C_2 was smallest, *i.e.* at 40 °C.

The cmc of alkyl ammonium propionates in benzene or dichloromethane decreased with increasing alkyl chain length, and the relationship between log cmc and n indicated a linearity.[9a] The slopes for the plots of log cmc *vs.* n for alkyl ammonium propionate at 30—35 °C are -0.125 and -0.0654 in benzene and dichloromethane, respectively.[9a] These values are affected by the polarities of solvents. Incidentally, the slopes of ionic surfactants in aqueous solutions are about -0.29.[20] A comparison between these values and our value shown in Table I shows that of FA in 1,2-dichloroethane to be slightly smaller than that of alkyl ammonium propionate in dichloromethane. The values obtained in this paper are therefore considered reasonable. The following tendency was also found[9]: alkyl ammonium alkanoate with a lower cmc has a larger slope for the plots of log cmc *vs.* n. Our results are in agreement with this tendency.[9]

As shown in Fig. 4, C_2 indicated a linearity against n. There was no difference between even-numbered FA and odd-numbered FA. In aqueous micellar systems, the "odd–even effect" has not been found in cmc.[3] We found a similar tendency in an organic micellar system.

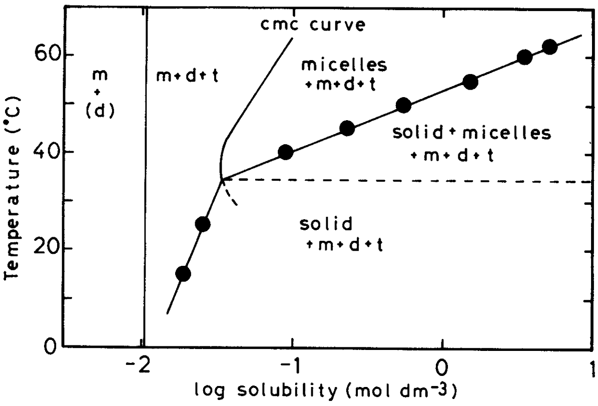

Fig. 5. Phase Diagram for the 1,2-Dichloroethane Solution of C18
m, monomer; d, dimer; t, trimer.

Phase Diagram for the Solution of C18 A simple diagram for C18 in 1,2-dichloroethane was constructed based on the results of association and solubility at various temperatures, and is shown in Fig. 5.

Conclusion

The critical concentration C_2 of FA in 1,2-dichloroethane decreased with increasing n, and the plots of $\log C_2$ *vs.* n indicated a linearity. The relationship between C_2 and temperature was minimal at 40 °C.

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