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Solubilization of Alkyl *p*-Hydroxybenzoates in Hexa(oxyethylene) Dodecyl Ether Micelle

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Synopsis. An experimental study was made on the effect of the alkyl-chain length of alkyl *p*-hydroxybenzoates on their solubilization in nonionic micelle. The location of alkyl *p*-hydroxybenzoate in micelle and the change in micelle structure are discussed on the basis of the experimental result.

Two subjects should be considered to elucidate the solubilization mechanism:[1] One is concerned with the variation of the overall distribution coefficient with the concentration of solubilizate in a micelle and with thermodynamic interpretation of its behavior; the other is concerned with the location of solubilizate in a micelle. The latter subject has been investigated spectrophotometrically by a number of workers, but few papers have been published in which the latter is considered in connection with the former. We[2,3] have reported on the concentration dependence for methyl and ethyl *p*-hydroxybenzoates in nonionic surfactant micelles and explained this dependence on the basis of the regular solution theory.

In the present work we have inferred the location of alkyl *p*-hydroxybenzoate in hexa(oxyethylene) dodecyl ether ($C_{12}E_6$) micelle and discussed the inference in terms of the nonideality of distribution and the change in micelle structure.

Experimental

Hexa(oxyethyelene) dodecyl ether[2] ($C_{12}E_6$) and alkyl *p*-hydroxybenzoates (alkyl=methyl, ethyl, propyl, and butyl) were of reagent grade. Gel filtration was carried out at 20 °C in the same way as previously described.[2] The concentration of alkyl *p*-hydroxybenzoates was determined spectrophotometrically[2,3] and that of $C_{12}E_6$ was measured by gas chromatography.[4] Distribution coefficient (K), mole fraction in micelle phase (X_s^m) and that in aqueous phase (X_s^w), cmc, interchange energy (ω), free energy change of solubilization (ΔG), elution volume of micelle (V_m), and cloud point were evaluated in the same way as reported in our previous paper.[2] UV spectra of *p*-hydroxybenzoates in water and aqueous $C_{12}E_6$ solution were measured with a Hitachi EPS-3T spectrophotometer.

Results and Discussion

The apparent distribution coefficients of propyl and butyl *p*-hydroxybenzoates (K_a), X_s^m/X_s^w were measured at 20 °C. Figure 1 shows a plot of K_a values of propyl and butyl esters against X_s^m. The values at $X_s^m=0$ corresponds to the K value.[2] ΔG values for alkyl esters obtained from K values are given in Table 1. They are linearly related with the carbon number of the alkyl group of *p*-hydroxybenzoates, and the slope of the straight line corresponds to the increment of -2.6×10^3 J/mol of ΔG per methylene unit. This value is equal to the reported values for alcohols (-2.6×10^3 J/mol) in sodium dodecyl sulfate (SDS) micelle[5] and *p*-hydroxybenzoates (-2.6×10^3 J/mol) in SDS micelle.[6] It may also be concluded that the alkyl moiety of *p*-hydroxybenzoate is incorporated in the hydrocarbon core of micelle. We[3] reported that the solubilization of ethyl *p*-hydroxybenzoate in $C_{12}E_6$ micelle results from both the enthalpy and entropy effects and that the latter effect might be due to a hydrophobic interaction, which is also compatible with the above conclusion.

A red shift was observed with UV maxima of *p*-hydroxybenzoates in $C_{12}E_6$ micelle; methyl, ethyl, propyl, and butyl esters have UV maxima at 257.9, 258.1, 258.4, and 258.9 nm in 2.0% $C_{12}E_6$ solution, respectively, whereas they all have UV maxima at 256 nm in water. The change of spectra in the nonionic surfactant micelle might be due to the following factors:[7] i) specific interactions such as hydrogen bonding; ii) change in polarity of the environment. Therefore, the above red shift suggests an increase in polarity of the environment and/or specific interactions between $C_{12}E_6$ and *p*-hydroxybenzoate. Nemethy and Ray[8] reported that phenol molecules are located in a polar environment of nonionic surfactant micelle and/or are hydrogen-bonded. Muller and Metcalf[9] described that chloroxyrenol is hydrogen-bonded in poly(oxyethylene) dodecyl ether micelle. Therefore, the hydrogen bond between the phenolic hydrogen of alkyl esters and the etheric oxygen of $C_{12}E_6$ may occupy an important position in the specific interactions. This interaction has also been proved in terms of interchange energy (ω), which is

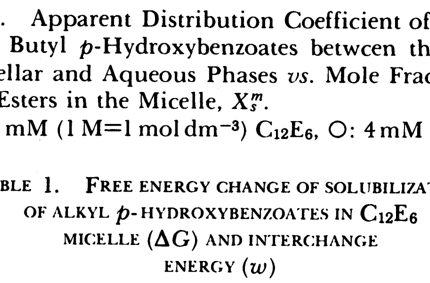

Fig. 1. Apparent Distribution Coefficient of Propyl and Butyl *p*-Hydroxybenzoates between the $C_{12}E_6$ Micellar and Aqueous Phases *vs.* Mole Fraction of the Esters in the Micelle, X_s^m.
●: 2 mM (1 M=1 mol dm^{-3}) $C_{12}E_6$, ○: 4 mM $C_{12}E_6$.

TABLE 1. FREE ENERGY CHANGE OF SOLUBILIZATION OF ALKYL *p*-HYDROXYBENZOATES IN $C_{12}E_6$ MICELLE (ΔG) AND INTERCHANGE ENERGY (w)

p-Hydroxybenzoate	ΔG/J/mol	w/J/mol
Methyl ester[4]	-2.07×10^4	-3700 ± 400
Ethyl ester[5]	-2.26×10^4	-3400 ± 500
Propyl ester	-2.49×10^4	-2800 ± 700
Butyl ester	-2.85×10^4	-3300 ± 500

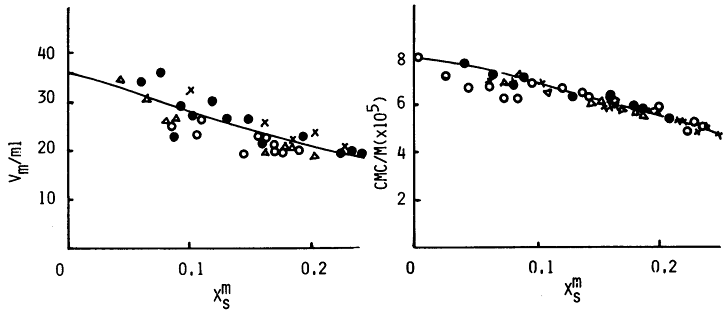

Fig. 2. Variation of the Elution Volumes of the $C_{12}E_6$ Micelles (V_m) and the cmc's of $C_{12}E_6$ Solutions in the Presence of Alkyl *p*-Hydroxybenzoates with Mole Fraction of Alkyl *p*-Hydroxybenzoates, X_s^m.
(●): Methyl ester,[2] (○): ethyl ester, (×): propyl ester, (△): butyl ester.

calculated on the basis of the regular solution theory.[2] These values (ω) are negative as shown in Table 1, corresponding to the ω value of methyl ester in hepta(oxyethylene) dodecyl ether ($C_{12}E_7$) obtained by molar volume measurements.[10] This suggests that $C_{12}E_6$ and alkyl ester in a mixed micelle become thermodynamically stable by mutual attraction. From the above results, it is concluded that solubilized esters are most likely to be located in the area spreading from the inside of hydrocarbon core to the poly(oxyethylene) mantle of micelle. Furthermore, it may also be concluded that the hydrophobic interaction and the specific interaction in a micelle reflect directly the distribution coefficient and that the nonideality of distribution is due mainly to the specific interaction.

Figure 2 shows plots of the retention volume of micelle which is a measure of the hydrated size of micelle[12] and of the cmc against X_s^m. The cmc and retention volume decrease with X_s^m and the pattern of the decrease depends little on the length of the alkyl chain of *p*-hydroxybenzoate. Therefore, Fig. 2 implies that the mixed micelle becomes thermodynamically stable[2,11] by enlarging its size and indicates that the manners of change in cmc and retention volume are nearly the same, suggesting that such a change in micellar structure is due mainly to the specific interaction, *i.e.* the hydrogen bonding between *p*-hydroxybenzoate and $C_{12}E_6$ in the mixed micelle.

Figure 3 shows a plot of cloud points against the concentration of esters added. The longer alkyl chain of *p*-hydroxybenzoates is able to depress the cloud point more deeply because of its denser distribution into the micelle phase. Kuriyama[14] has suggested that increase in micellar weight with increasing temperature is a dominant factor for the cloud formation. Therefore, the depression of cloud point by the ester added is related closely with the increase in micelle size, as shown in Fig. 2a; this effect would result from both the specific interaction favoring the retention of ester in the oxyethylene region of micelle and the structured water supported by the ester in this environment.[13]

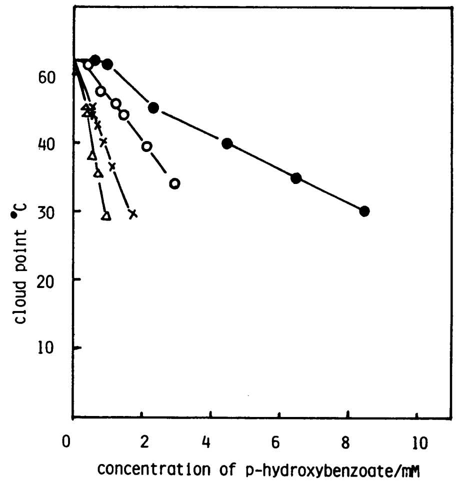

Fig. 3. Cloud Point of Aqueous $C_{12}E_6$ Solution in the Presence of Alkyl *p*-Hydroxybenzoates.
(●): Methyl ester,[2] (○): ethyl ester, (×): propyl ester, (△): butyl ester.

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