

O/W Emulsion of *n*-Alkylbenzene/Ionic Surfactant/Water Systems

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The maximum additive concentration of benzene, toluene, ethylbenzene, *n*-propylbenzene, *n*-butylbenzene, and *n*-pentylbenzene into two kinds of ionic micelles, 1-dodecanesulfonic acid and *n*-tetradecyltrimethylammonium bromide micelles, was determined at 298.2 K, where these volatile solubilizes were solubilized, not by direct contact of the liquid solubilize with micellar solution but by molecular transfer through their own gaseous phase. The aggregation number of micelles is ca. 60 and their size is 5 nm in diameter in the aqueous solution in the case of no solubilize in the system. In the presence of the above solubilizes, however, the micellar aggregates greatly grow in size up to more than 150 nm in diameter for 1-dodecanesulfonic acid micelle and 200 nm for *n*-tetradecyltrimethylammonium bromide micelle, where the micelles or the aggregates accommodate the volatile solubilizes as much as possible or the maximum additive concentration. The solubilization was analyzed by partition equilibrium of the solubilizes between aqueous phase and micellar phase, because the micelles are so large in size. The contribution per ethylene group in the alkyl chain to the Gibbs energy change was calculated to be -2.35 and -2.78 kJ mol $^{-1}$ for 1-dodecanesulfonic acid and *n*-tetradecyltrimethylammonium bromide micelles, respectively. The larger negative value for the latter is due to more hydrophobic solubilization site by hydrocarbon head of the latter.

Introduction

Aqueous solubility of organic substances increases by their incorporation into micelles in surfactant solutions. The phenomenon is called solubilization.^{1,2} If an organic solubilize is gaseous, it is not easy to accurately determine the solubilized amount of gaseous molecules into surfactant solutions, because a complex apparatus such as a vacuum line combined with an accurate pressure gauge is commonly employed for the purpose.^{3,4} As far as the maximum additive concentration (MAC) is concerned, an excess of pure solid solubilize phase coexists with a surfactant solution phase, and the chemical potential of the solubilize molecule in the excess phase can be kept constant at a definite temperature and pressure, because the degree of freedom is two for the solid phase by the Gibbs phase rule. This is the reason the concentration of monomeric solubilize is kept constant in the surfactant solutions at a specified temperature and pressure. If the excess solubilize phase is liquid, the liquid solubilize is easily emulsified through its direct contact with surfactant solution. Then, separation of the surfactant solution from emulsion droplets becomes quite difficult. To solve this problem, a simple apparatus for the solubilization of liquid solubilize into surfactant solution was developed in the previous study.⁵

The chemical potential of any component should be the same throughout phases in equilibrium from the restriction of thermodynamics. This condition can be effectively applied to produce identical chemical potential of a gaseous solubilize molecule against surfactant solutions of various concentrations. The apparatus shown in Figure 1 can meet this condition, where a gaseous phase is in contact with eight surfactant solutions of

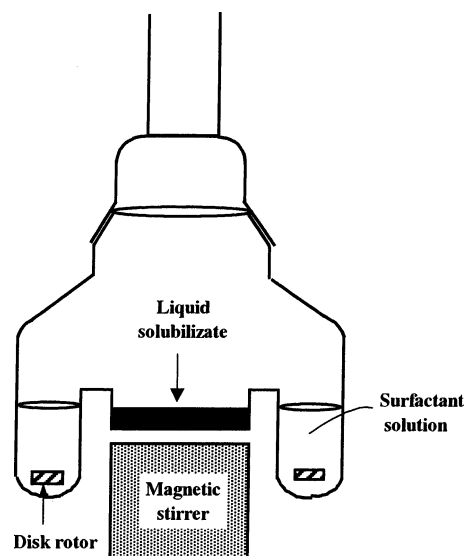


Figure 1. Solubilization apparatus for volatile solubilizes.

different concentrations. Inside the apparatus, the chemical potential of the gaseous solubilize molecule is kept constant throughout the phases, or the concentration of monomeric solubilize can be set identical in the separate eight solutions.

In the preceding studies,^{6–8} the apparatus was used for the solubilization study of volatile solubilize, *n*-alkylbenzene into 1-dodecanesulfonic acid micelle, lithium 1-perfluoroundecanoate micelle, and bile salt micelle. In these studies, (i) the amount of solubilize was controlled so that the solubilizes may obey the Poisson distribution among micelles,⁹ and (ii) the surfactant concentration was less than 4-fold cmc. The above two conditions are quite important in order to treat micelles as chemical species from thermodynamic point of view. On the

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other hand, to remove the two conditions is very interesting for formation of an emulsion system which is thermodynamically stable. In addition, to make it clear whether an emulsion droplet is a chemical species or a separate phase is quite important for colloid and surface chemistry. An interface can be defined only between two macrophases, and an interfacial tension can locate just for such interface. This study is then aimed to examine if a size of an emulsion droplet and an interfacial tension between the droplet and surrounding bulk can be related by the Kelvin equation.¹⁰ In other words, if an interfacial tension exists, the droplet can be regarded as a separate macrophase of O/W type.

In this study, the authors have used two kinds (anionic and cationic) of ionic micellar solutions, 1-dodecanesulfonic acid and *n*-tetradecyltrimethylammonium bromide solutions, over a wide concentration range up to 10-fold cmc and *n*-alkylbenzene as a volatile solubilize at 298.2 K. The size of molecular aggregates or emulsion droplets was found to be quite large, and therefore, the solubilization of *n*-alkylbenzene was studied as a partition equilibrium between aggregate phase and aqueous phase.

Experimental Section

Materials. 1-Dodecanesulfonic acid (C12-acid) solution was synthesized from silver 1-dodecanesulfonate, where the silver salt was synthesized by double decomposition of sodium 1-dodecanesulfonate and AgNO₃ in aqueous suspension. Silver ion of the silver salt was exchanged with hydrogen ion by introducing an equivalent amount of HCl solution into the silver salt suspension.⁶ The precipitated AgCl was separated from the acid solution by ultracentrifugation. The purity was checked at the stages of sodium and silver salts by the elemental analysis: C 52.39 (52.91), H 9.26 (9.25)% for sodium salt; C 40.62 (40.34), H 7.11 (7.05)% for silver salt, where the values in parentheses are the calculated values. *n*-Tetradecyltrimethylammonium bromide (TTAB) was purchased from Tokyo Kasei Kogyo, Co. and purified by repeated ether extractions. The purity was also checked by the elemental analysis: C 60.66 (60.69), H 11.37 (11.38)%. The concentration of C12-acid in aqueous solution was determined by acid–base titration with NaOH solution. The cmc value of C12-acid determined by electric conductivity was 8.9 mmol dm⁻³ at 298.2 K, which was equal to the previous value within experimental error.⁶ On the other hand, the value of TTAB was determined to be 3.8 mmol dm⁻³ at 298.2 K by the same method, which is very close to the reference value, 3.75 mmol dm⁻³.¹¹

Benzene, toluene, ethylbenzene, *n*-propylbenzene, *n*-butylbenzene, and *n*-pentylbenzene of guaranteed reagent grade from Nacalai tesque were washed three times with concentrated sulfuric acid, one time with dilute NaOH solution, and finally three times with a large amount of water. The water used was distilled twice from alkaline permanganate solution.

Solubilization. Eight surfactant solutions of different concentrations were filtrated using a membrane filter of pore size of 0.1 μm (Millipore MILLEX VV) to remove dusts, and then, separately poured into eight tubes of the solubilization apparatus. An excess amount of liquid *n*-alkylbenzene was placed in the hollow place in the middle of the glass apparatus. The whole glass vessel with its cover was kept in a thermostat at 298.2 ± 0.1 K for 24 h, but in the case of *n*-butylbenzene and *n*-pentylbenzene it was kept for 48 h for the complete equilibration, while the surfactant solutions were agitated with rotors in the tubes (Figure 1). Inside the apparatus, the volatile solubilizes easily evaporate because of their high volatility, and the

chemical potential of the gaseous solubilize molecules becomes constant throughout the phases, or the concentration of monomeric solubilize can be set identical in the eight solutions. After the equilibration, each surfactant solution was separately drawn into each photocell through an injection needle, which was immediately capped. The concentrations of solubilizes in the surfactant solutions were determined spectrophotometrically by the optical density of the solutions.

Dynamic Light Scattering. The hydrodynamic diameter of aggregates was measured by DLS spectrophotometer (Otsuka Electronics, PAR-II). The light source employed was a 5 mW He–Ne laser of wavelength 633 nm. The solution in a 10-mm square cell was thermally controlled at 298.2 ± 0.1 K in contact with a built-in heater.

The average hydrodynamic diameters were automatically obtained by analyzing the normalized second-order exponential autocorrelation functions (i.e., scattered light intensity–time autocorrelation function fitting) according to the method of cumulants. The accumulations were performed 50 times, and the residuals for two-exponential curve fitting were held within ±0.03. Then, the distributions of particle size were analyzed and presented in due form of a histogram by the Otsuka Electronic software, where the viscosity used was that of water for all the solutions. Unfortunately, the emulsion droplets less than 150 nm in diameter were less than the detection limit of the apparatus due to small scattered light intensity.

Results and Discussion

Maximum Additive Concentrations of *n*-Alkylbenzene.

The molar extinction coefficients (ε) were those in the previous study,⁶ where the surfactant and the solubilizes were identical with those of the present study. The ε values at 260 nm were 232 for toluene, 216 for ethylbenzene, 201 for *n*-propylbenzene, 211 for *n*-butylbenzene, 222 mol⁻¹ dm³ cm⁻¹ for *n*-pentylbenzene and the one at 254 nm for benzene is 188 mol⁻¹ dm³ cm⁻¹.

The changes of maximum additive concentration with surfactant concentration are illustrated in Figures 2a and 2b for C-12 acid and TTAB solutions, respectively. Solubilize concentrations below the cmc remain almost constant for all the solubilizes except benzene, which indicates the constancy of chemical potential of the solubilize molecule throughout the phases inside the glass apparatus. The mean value of the solubilize concentration below the cmc gives the value of the monomer concentration in aqueous bulk [R] of the solubilize molecules. A steep increase in solubilize concentration or the maximum additive concentration above the cmc is brought about by the incorporation of solubilize into micellar aggregates. At further high surfactant concentrations, say more than 40 mmol dm⁻³ for C12-acid (Figure 2a), the solubility deviates upward from the initial linear increase below the concentration. A similar change was also the case for TTAB (Figure 2b). The maximum additive concentration decreased in the order of benzene > toluene > ethylbenzene > *n*-propylbenzene > *n*-butylbenzene > *n*-pentylbenzene, which is the same order in the aqueous solubility. In other words, as the alkyl chain of the solubilize becomes shorter, the maximum additive concentration increases more. Especially in the case of benzene, the maximum additive concentration was quite large, and the solution became slightly turbid. The present results agree well with the fact that the solubilized amount in the aggregates becomes larger for more soluble solubilize in an aqueous bulk.

Size Distribution of Aggregates. The size distribution of aggregates is illustrated as a histogram vs hydrodynamic

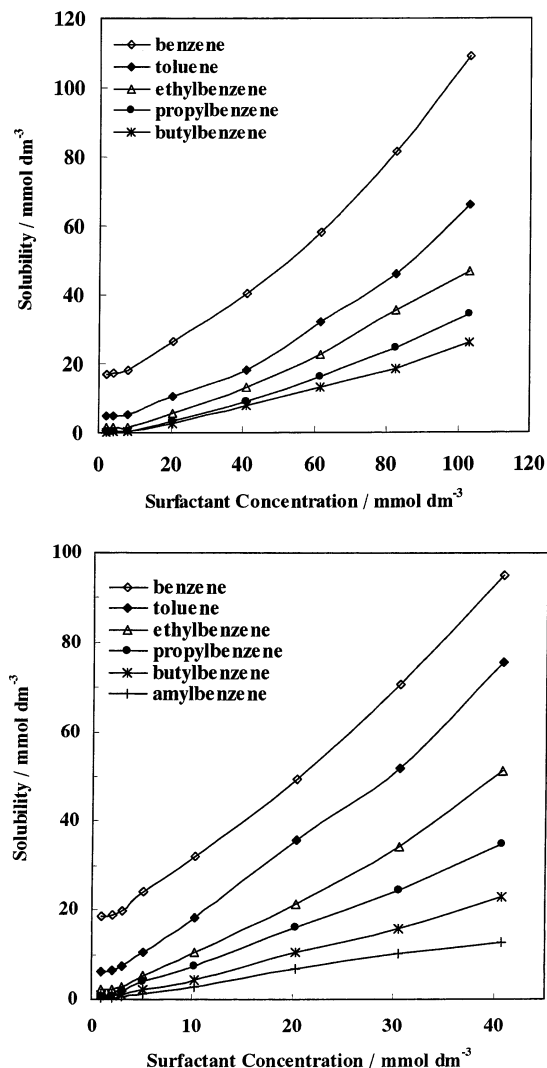


Figure 2. (a) Changes of maximum additive concentration of *n*-alkylbenzene with C12-acid concentration. (b) Changes of maximum additive concentration of *n*-alkylbenzene with TTAB concentration.

diameter for toluene/1-dodecanesulfonic acid system in Figure 3. As is clear from the figure, there exist two maxima in the distribution at lower surfactant concentrations; one is for normal micelles with a diameter of molecular size of surfactant, and the other is for swollen micelles incorporated with many solubilize molecules. However, the smaller size distribution shifts to the larger one with increasing surfactant concentration. At the maximum surfactant concentration (Figure 3e), there remains only the larger size distribution whose maximum is located at 320 nm. The diameter of the aggregates is longer by more than sixty times than that of micelle just in water of ca. 5 nm.^{11,12} Plots of the hydrodynamic diameter of the aggregates against surfactant concentration are shown in Figures 4a and 4b. For all the solubilizes, the aggregates grew in size with increasing surfactant concentration, although increasing rate in the size growth becomes less with decreasing aqueous solubility of the solubilizes. The following findings can be derived from the results of Figures 2 and 4; (i) larger size of molecular aggregates is accompanied by higher maximum additive concentration, (ii) surfactant concentration becomes a crucial factor to specify the solubilization system, and (iii) a system including such large molecular aggregates can be regarded as a thermodynamically stable emulsion.

Gibbs Energy Change for Transfer. Now that the size of aggregates was found quite large, the partition equilibrium was

adopted for the Gibbs energy change for transfer of solubilize molecules from aqueous bulk to a large molecular aggregate or an emulsion droplet. In other words, the large molecular aggregates were regarded as a separate phase to see if the partition equilibrium was reasonable to obtain the Gibbs energy change. The mole fractions of the solubilizes in aggregate phase and aqueous phase are given as eqs 1 and 2, respectively:

$$X_R^A = ([R_t] - [R]) / \{ [C - \text{cmc}] + ([R_t] - [R]) \} \quad (1)$$

$$X_R^W = [R] / (55.5 + [R] + \text{cmc}) \quad (2)$$

where $[R_t]$ is the total equivalent concentration of solubilize, C is the total surfactant concentration, and cmc is the concentration at which solubility started to increase steeply. The mole fractions are easily available from Figure 2. The subscript R refers to solubilize, and the superscripts A and W refer to the aggregate phase and the aqueous phase, respectively. The chemical potential in each phase is expressed as follows under temperature T and pressure P :

$$\mu_R^A = \mu_R^{0,A}(T, P + \Delta P) + RT \ln X_R^A \quad (3)$$

$$\mu_R^W = \mu_R^{0,W}(T, P) + RT \ln X_R^W \quad (4)$$

where ΔP is the difference in pressure between aqueous phase and aggregate phase, and μ^θ is the standard chemical potential at infinite dilution. There results the following relationship for the solubilize molecule under equilibrium:

$$RT \ln(X_R^A/X_R^W) = -\{ \mu_R^{0,A}(T, P + \Delta P) - \mu_R^{0,W}(T, P) \} = -\Delta G^0 \quad (5)$$

From this equation, we can determine the Gibbs energy change for transfer of a solubilize molecule from aqueous phase to aggregate phase. The Gibbs energy changes (ΔG^0) were plotted against the number of carbon atoms in alkyl chains of the solubilizes at different surfactant concentration in Figure 5 for C12-acid aggregates. Quite similar changes in ΔG^0 values were also obtained for TTAB aggregates. From the figure, the Gibbs energy change decreases or the transfer becomes more stabilized with increasing alkyl chain length of the solubilize. The contribution per ethylene group in *n*-alkyl chain to the Gibbs energy change ($\Delta G_{\text{CH}_2}^0$) is calculated to be -2.35 and -2.78 kJ mol⁻¹ for the former and the latter aggregates, respectively, from the slope in the figures. The former value is less in magnitude than -2.81 and -2.59 kJ mol⁻¹ in the previous studies,^{6-8,13} where the transfer from aqueous bulk into micelle was investigated. On the other hand, the latter value is close to the lowest value. The larger negative value is due to more hydrophobic solubilization site by hydrocarbon head of the latter. In Figure 6a, the energy changes are plotted against C12-acid concentration. The slopes of the changes are all negative, which strongly suggests the presence of pressure effect due to the Laplace equation, because the aggregates grow in size with increasing surfactant concentration. In other words, extra energy seems to be dissipated for intrusion of solubilize into an inside of the aggregate phase of higher pressure or smaller diameter, as is suggested by eq 3. Namely, the higher the surfactant concentration becomes, the more favorable the transfer becomes as for the C12-acid aggregates. On the contrary, the slopes of ΔG^0 against surfactant concentration do not have a definite sign for TTAB aggregates; some have positive slope and others have a negative one (Figure 6b).

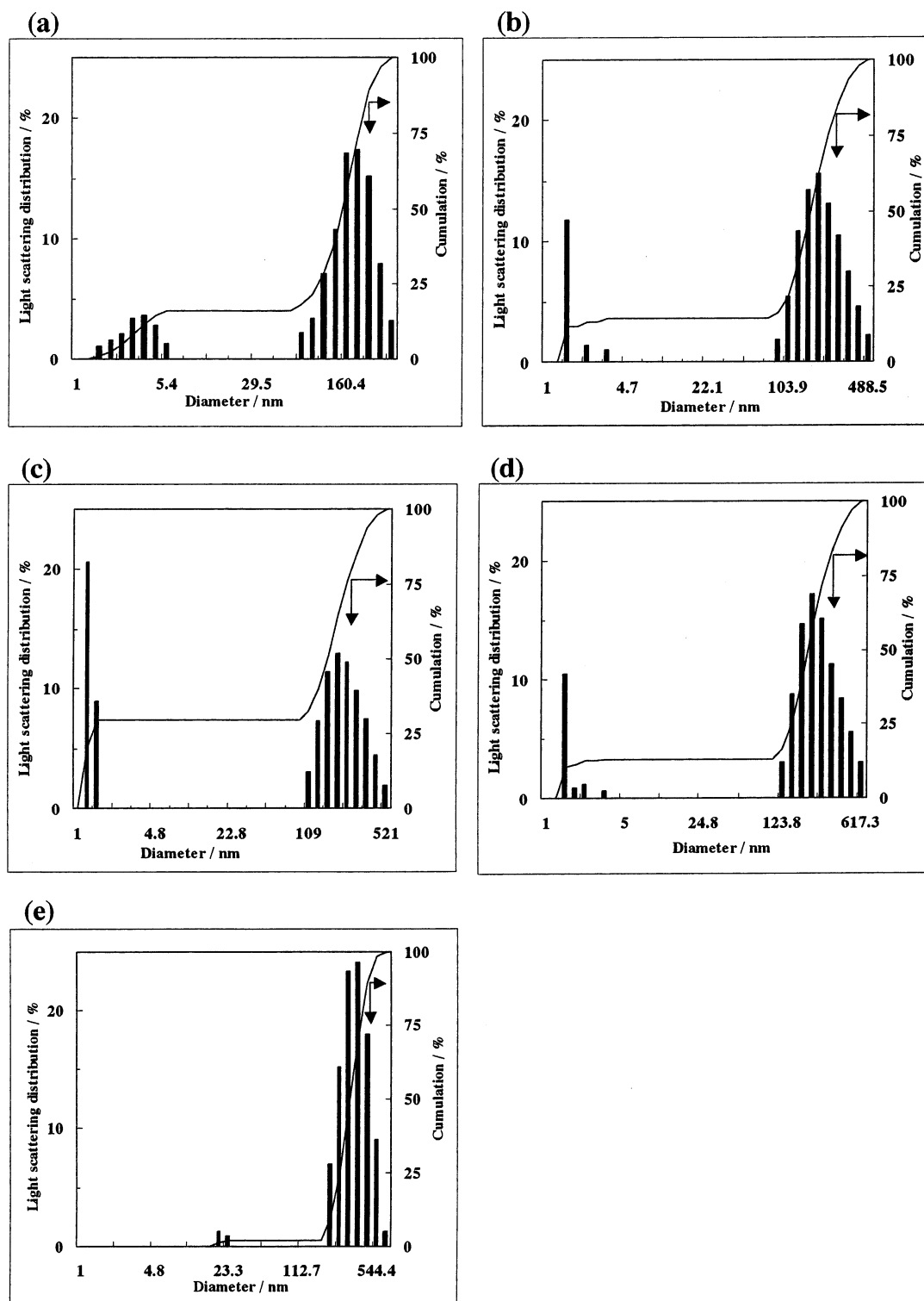


Figure 3. Histogram of size distribution of molecular aggregates for toluene. Concentration of C12-acid is 20.6 (a), 41.2 (b), 61.8 (c), 82.4 (d), and 103.0 mmol dm⁻³ (e).

Examination of Interfacial Tension between Aggregate Phase and Aqueous Phase. As shown in Figure 4a, the diameter of C12-acid aggregates is now available. In addition, the difference in the transfer energy between aggregate sizes has already been obtained (Figures 6a and 6b). These two can lead to evaluation of interfacial tension between both phases.

When two kinds of homogeneous fluid form a spherical interface in-between, the difference in pressure between both fluids appears across the interface. In the case of a sphere of radius (*r*), internal pressure is higher than external pressure by

ΔP . This difference is called the Laplace pressure ($\Delta P = 2\gamma/r$), where γ is an interfacial tension. Now, eq 5 can be rewritten in a more concrete form using the pressure difference:

$$\begin{aligned} RT \ln(X_R^A/X_R^W) &= -\{\mu_R^{0,A}(T,P) - \mu_R^{\theta,W}(T,P)\} - V\Delta P^A \\ &= -\{\mu_R^{0,A}(T,P) - \mu_R^{\theta,W}(T,P)\} - V\left(\frac{2\gamma}{r}\right) = -\Delta G^0 \quad (6) \end{aligned}$$

where *V* is a partial molar volume of solubilize. When eq 6 is

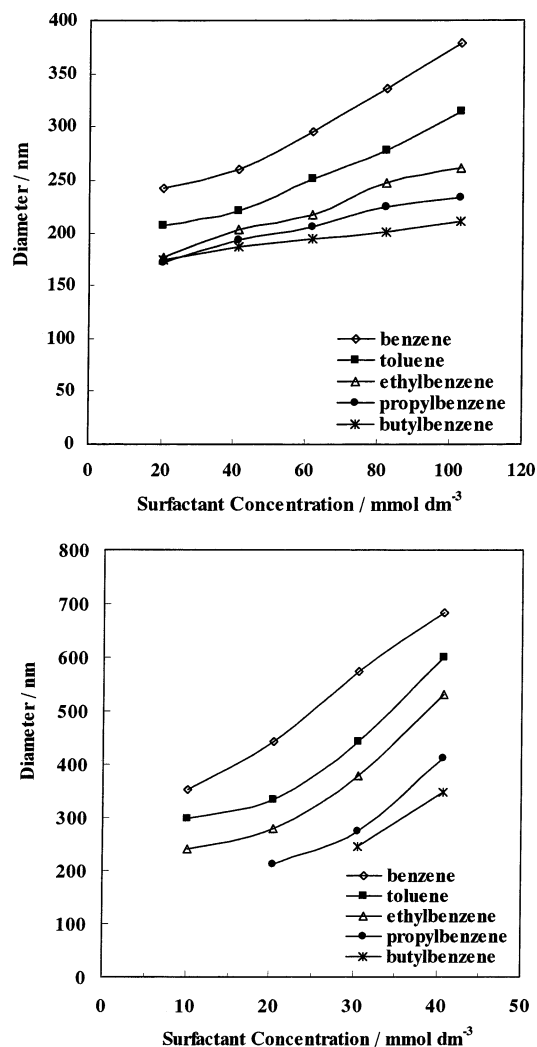


Figure 4. (a) Change of the aggregates diameter with C12-acid concentration at the MAC. (b) Change of the aggregates diameter with TTAB concentration at the MAC.

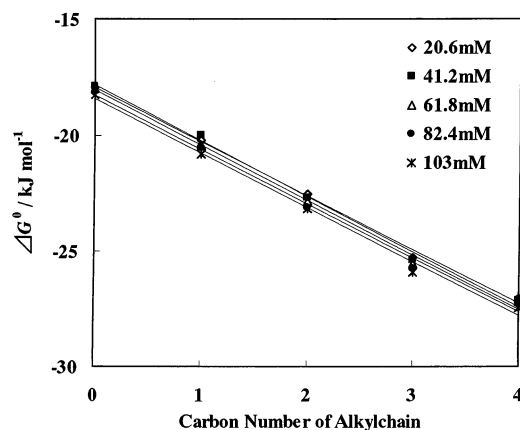


Figure 5. The Gibbs energy change for transfer of the solubilizes against carbon number of the alkyl chain of the solubilizes for the C12-acid system.

applied to the transfer energy at two surfactant concentrations (1 and 2), there result the following relationships:

$$RT \ln(X_R^A/X_R^W)_1 - RT \ln(X_R^A/X_R^W)_2 = -\Delta G_1^0 + \Delta G_2^0 = 2V\gamma \left(\frac{1}{r_2} - \frac{1}{r_1} \right) \quad (7)$$

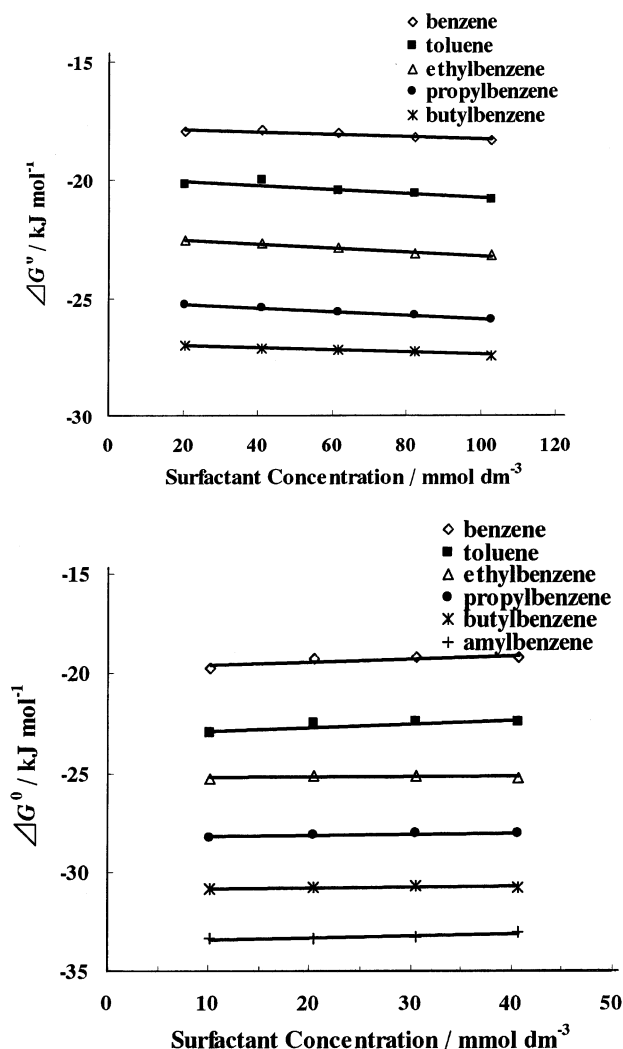


Figure 6. (a) The Gibbs energy change for transfer against C12-acid concentration. (b) The Gibbs energy change for transfer against TTAB concentration.

where the first term of the right-hand side of eq 6 is canceled out for the two concentrations. The γ values were determined from the difference in ΔG^0 between 20.6 and 103 mmol dm⁻³ of C12-acid concentration for every solubilize, where the molar volume used is 89.40, 106.85, 123.08, 139.59, and 156.78 cm³ for benzene, toluene, ethylbenzene, *n*-propylbenzene, and *n*-butylbenzene, respectively. The interfacial tensions thus obtained from the difference in ΔG^0 are found to be several hundreds of mNm⁻¹ for all the solubilizes, which is quite unreasonable judging from reference data, say less than 1 mNm⁻¹, on interfacial tension between an emulsion droplet and its surrounding surfactant solution.^{14,15} The extraordinary surface tension results from the experimental values within the experimental errors, as is clear from the values on TTAB aggregates. That is, the Gibbs energy changes remain almost constant for TTAB aggregates irrespective of the concentration change. The TTAB aggregate was examined to see if the similar extraordinary interfacial tension as above could be also observed. Fortunately, however, a definite interfacial tension could not be calculated from the Gibbs energy change, because there was not a reliable or definite slope in Figure 6b, as mentioned above. That is, the slope was very near to zero, which suggests that the interfacial tension is quite small, as is the case of emulsion droplet. However, it is highly possible that there exists an interface of very low tension between an emulsion droplet and

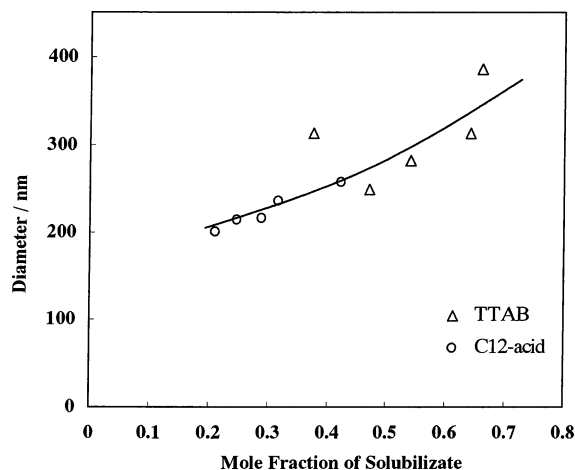


Figure 7. Change of droplet size on mole fraction of solubilize in droplet at the same solubilized amount (20 mmol dm^{-3}).

its surrounding solution phase, because a large number of such droplets give rise to a turbidity as is the case for benzene solubilization. The presence of an interface between the aggregate phase and the aqueous phase strongly suggests that the present aggregates or the emulsion droplets can be regarded as a separate phase. This is also substantiated by the reasonable $\Delta G_{\text{CH}_2}^0$ values.

Dependence of Drop Size on Solubilize Species. The relationship between the size of droplets and the solubilized amount of solubilizes can be derived from the results of Figures 2 and 4. The maximum additive concentration (MAC) does not mean the maximum capacity for micelles to accommodate a solubilize at all, but is determined only by an aqueous solubility of the solubilize. The above dependence was

examined at the same solubilized amount (20 mmol dm^{-3}). Dependence of the size on the mole fraction of solubilize in the droplets is illustrated in Figure 7, in which the droplet sizes increase monotonically with the mole fraction irrespective of the surfactants used, except one point probably due to the experimental error. More surfactant concentration is required for solubilizes of smaller aqueous solubility, because the mole fraction of the solubilizes becomes less in the droplets. Therefore, the droplets grow more in size for solubilizes of higher aqueous solubility, resulting in larger mole fraction. This is quite reasonable. However, it is very interesting that the relation between the droplet diameter and the mole fraction can be expressed roughly by one curve irrespective of both solubilize species and surfactant species (Figure 7).

References and Notes

- (1) McBain, M. L. E.; Hutchinson, E. *Solubilization and Related Phenomena*; Academic Press: New York, 1955.
- (2) Elworthy, P. H.; Florence, A. T.; Macfarlane, C. B. *Solubilization by Surface-Active Agents and Its Application in Chemistry and Biological Sciences*; Chapman & Hall: London, 1968.
- (3) Tucker, E. E.; Christian, S. D. *J. Chem. Thermodyn.* **1979**, *11*, 1137.
- (4) Matheson, I. B. C.; King, A. D., Jr. *J. Colloid Interface Sci.* **1979**, *66*, 464.
- (5) Moroi, Y.; Morisue, T. *J. Phys. Chem.* **1993**, *97*, 12668.
- (6) Take'uchi, M.; Moroi, Y. *Langmuir* **1995**, *11*, 4719.
- (7) Take'uchi, M.; Moroi, Y. *J. Colloid Interface Sci.* **1998**, *197*, 230.
- (8) Sugioka, H.; Moroi, Y. *Biochim. Biophys. Acta* **1998**, *1394*, 99.
- (9) Moroi, Y. *J. Phys. Chem.* **1980**, *84*, 2186.
- (10) Defay, R.; Prigogine, I.; Bellemans, A.; Everett, D. H. *Surface Tension and Adsorption*; Longmans: London, 1966; Chapter 15.
- (11) Aguiar, J.; Molina-Bolivar, J. A.; Peula-Garcia, J. M.; Ruiz, C. C. *J. Colloid Interface Sci.* **2002**, *255*, 382.
- (12) Matsuoka, K.; Moroi, Y.; Saito, M. *J. Phys. Chem.* **1993**, *97*, 13006.
- (13) Moroi, Y.; Matuura, R. *J. Colloid Interface Sci.* **1988**, *125*, 463.
- (14) Shah, D. O.; Schechter, R. S., Ed.; *Improved Oil Recovery by Surfactant and Polymer Flooding*; Academic Press: New York, 1977.
- (15) Kunieda, H.; Shinoda, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1777.