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Light Scattering Study of Local Structure in Solution. Double-Layered Structure Formation in Chloroform Solution of Surfactant

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Light scattering spectra have been observed for binary solutions of chloroform–tetrabutylammonium chloride (TBACl) and chloroform–hexadecyltrimethylammonium chloride (HTACl) at various concentrations. The Rayleigh intensities have been reduced to concentration fluctuations. The observed concentration dependence of the concentration fluctuation was explained in terms of the existence of aggregates which were composed of a few surfactant molecules and several decades of chloroform molecules. Using the infrared data, the structures of the aggregates were demonstrated to be double-layered. In HTACl solution, a singular concentration dependence of concentration fluctuation was observed in the concentration range below 0.004 mole fraction.

In previous reports,[1,2] quantitative analysis of the infrared absorption intensities of some water soluble surfactants in chloroform solutions has been reported. In these reports it has been postulated that those surfactants dissolve in chloroform by forming hydrogen bonds with several solvent chloroform molecules. As the hydrogen bonds were not of the 1 : 1 type, an investigation to elucidate the structure of these complexes was undertaken.

Recently, a method has been reported for determining the local structures existing in binary solutions by observing the concentration fluctuation at different concentrations. This has been applied to various liquid mixtures.[3–7] In the present study, the light scattering method has been applied in chloroform solutions of the surfactants. Hexadecyltrimethylammonium chloride (HTACl) and tetrabutylammonium chloride (TBACl) were chosen since their specific refractive index incriments are large enough to measure the concentration fluctuation accurately and reliable infrared data are available for thier chloroform solutions. Elucidation of the double-layered structures may be determined by the complementary use of vibration spectra and light scattering spectra for these solutions. The experimental part of the light scattering study on HTACl–chloroform solution has been published already.[8]

Experimental

All chemicals used in the present study were commercial products. Chloroform was purified by column chromatography on alumina in order to eliminate water and ethanol. HTACl and TBACl were dried over P_2O_5 under vacuum for several days. The sample solutions were made dust-free by the use of a millipore filter FG of 0.2 μm pore size.

Light scattering spectra were observed by the use of a spectrometer designed and constructed in the laboratory.[3] The refractive indices of the sample solutions were measured by means of an Abbe refractometer (Atago). All the measurements were performed at 24±0.5 °C for CTACl solution and 21±0.5 °C for TBACl solution.

Results and Discussion

Light Scattering Spectra and Concentration Fluctuation. Figure 1 illustrates the light scattering spectra for chloroform solutions of TBACl in the concentration range of 0—0.036 mole fractions (for the spectra of HTACl, see Ref. 8). After separating the Rayleigh part from the observed spectra, the Rayleigh intensity was expressed relative to the Rayleigh intensity of pure chloroform. Then, the concentration fluctuation of the surfactants, $N\langle(\Delta x)^2\rangle$, was calculated from the equation[4]

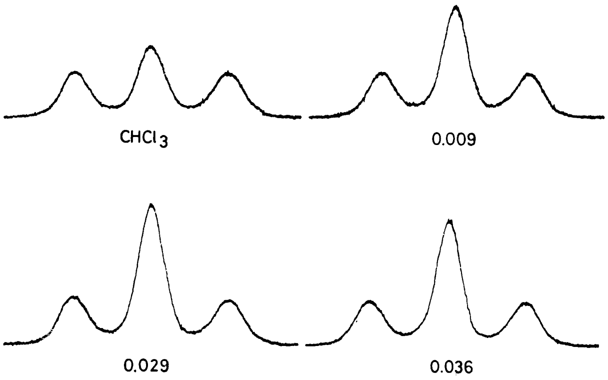

Fig. 1. Observed light scattering spectra for TBACl–chloroform system at 21 °C. Concentration is expressed in terms of mole fraction of TBACl.

$$N\langle(\Delta x)^2\rangle = \frac{RT^2}{M(\partial n/\partial x)^2_{P,T}}\left[\frac{S}{S_0}\left(\frac{n_0}{n}\right)^2\frac{\rho}{\rho_0}\frac{(\partial n_0/\partial T)^2_{P,x}}{C_{P\mathrm{g}}{}^0} - \frac{(\partial n/\partial T)^2_{P,x}}{C_{P\mathrm{g}}}\right], \quad (1)$$

where R is the gas constant, M the mean molecular weight, T the absolute temperature, n the refractive index, ρ the density, $C_{P\mathrm{g}}$ the specific heat per gram, N the total number of molecules of the field within which the concentration fluctuation is considered, and (S/S_0) is the intensity ratio of Rayleigh lines. The suffix zero specifies quantities related to pure chloroform.

In Fig. 2, the concentration fluctuation thus obtained was plotted as a function of mole fraction, $\bar{x}$, of the surfactants. The broken line in Fig. 2 corresponds to the concentration fluctuation expected for an ideal binary solution. From the figure the observed concentration flutuation is seen to take larger values than those of an ideal binary solution at low concentration and smaller values as the concentration increases. Therefore, the concentration fluctuation of each system has a maximum value. The concentration at which the concentration fluctuation of TBACl takes a maximum value is higher than that of HTACl. In the region

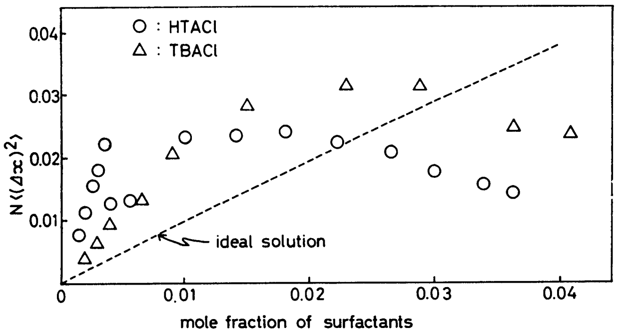

Fig. 2. Observed concentration fluctuation for TBACl-chloroform system.

where $\bar{x}$ is smaller than 0.004, the concentration fluctuation of HTACl increases rapidly with increasing $\bar{x}$, and decreases sharply at $\bar{x}=0.004$. In the concentration range of $\bar{x}>0.004$, it again increases gradually with increasing $\bar{x}$. The concentration flutuaction of TBACl, however, does not exhibit such singular concentration dependence in the low concentration region. These results suggest that the surfactant molecules aggregate with each other, in addition to the aggregation with chloroform molecules. The infrared data, on the other hand, suggests that these surfactant molecules form strong hydrogen bonds with chloroform molecules. Therefore, it is expected that an aggregate of the type A_lB_{ln} exist in these solutions, where l is the aggregation number of surfactants and n is the solvation number of chloroform per one surfactant molecule, where A and B refer to surfactant and chloroform molecules, respectively.

Analysis of $N\langle(\Delta x)^2\rangle$. Analysis of the observed concentration fluctuation employed the so-called association complex model.[5,6] From the discussion in the preceding paragraph, it may be assumed that an aggregate of the type A_lB_{ln} and a free chloroform molecule, B_1, behave as independent molecules in the solution. Aggregates of the type A_l may be assumed negligible since the analysis of infrared absorption intensity has shown that all surfactant molecules form hydrogen bonds with chloroform molecules in this concentration range. Aggregates of the type B_l may be assumed negligible since the hydrogen bonding between chloroform molecules is very weak in comparison with that between chloroform and surfactant molecules.[9]

Assuming that A_lB_{ln} and B_1 behave as independent molecules in the solution, the probability, $f(N_A)$, of finding N_A numbers of A molecules within the region which contains a constant number, N, of molecules may be expressed as[6]

$$f(N_A) = \frac{(N_1+N_2)!}{N_1!N_2!}P^{N_1}(1-P)^{N_2}, \qquad (2)$$

with

$$N_1 = N - nN_A$$
$$N_2 = N_A/l$$
$$P = \bar{N}_1/(\bar{N}_1+\bar{N}_2)$$

where N_1 and N_2 are molecular numbers of aggregates, B_1 and A_lB_{ln}, respectively. Then, the number fluctuation of A molecules in the region considered may be calculated thus

$$\begin{aligned}\langle(\Delta N_A)^2\rangle_N &= \frac{-1}{(\partial^2\ln f(\bar{N}_A)/\partial\bar{N}_A{}^2)_N}\\ &= \frac{\bar{N}_A}{N^2}[N-(n+1)\bar{N}_A]\\ &\quad\times[lN-\{l(n+1)-1\}\bar{N}_A]. \qquad (3)\end{aligned}$$

Therefore, the concentration fluctuation may be expressed as:

$$\begin{aligned}N\langle(\Delta x_A)^2\rangle &= \bar{x}_A[1-(n+1)\bar{x}_A]\\ &\quad\times[l-\{l(n+1)-1\}\bar{x}_A]. \qquad (4)\end{aligned}$$

Figure 3 demonstrates the concentration dependence of the concentration fluctuation calculated from Eq. 4 for $l=2$ and for various n-values, together with the observed concentration fluctuation values for TBACl solution. The figure demonstrates that the concentration fluctuation decreases in magnitude as n increases. The theoretical curve for $n=10$ best explains the curve in the sence that the concentration fluctuation takes a maximum value at $\bar{x}\approx0.03$. Figure 4 demonstrates the concentration dependence of the concentration fluctuation calculated from Eq. 4 for $n=10$ and various l-values. The figure demonstrates that the concentration fluctuation increases in magnitude as l increases

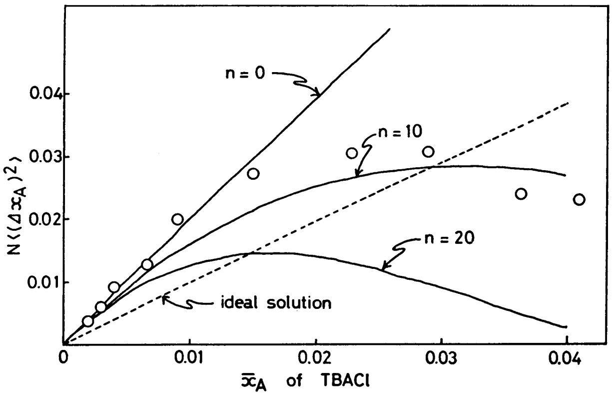

Fig. 3. Theoretical values of concentration fluctuation calculated from Eq. 4 for $l=2$ and $n=0$, 10, and 20. The open circles correspond to observed values for TBACl-chloroform system.

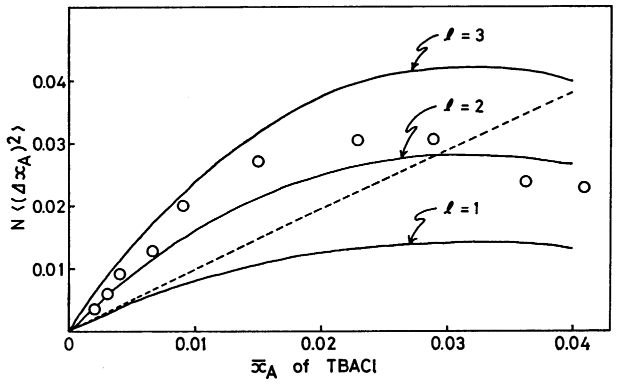

Fig. 4. Theoretical values of concentration calculated from Eq. 4 for $n=10$, and $l=1$, 2, and 3.

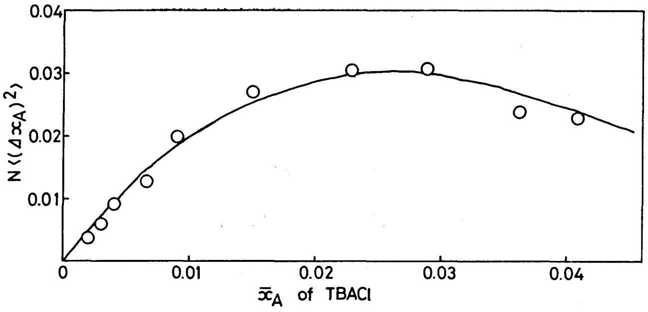

Fig. 5. Final results of theoretical calculation for TBACl-chloroform system ($l=2.6$, $n=12$).

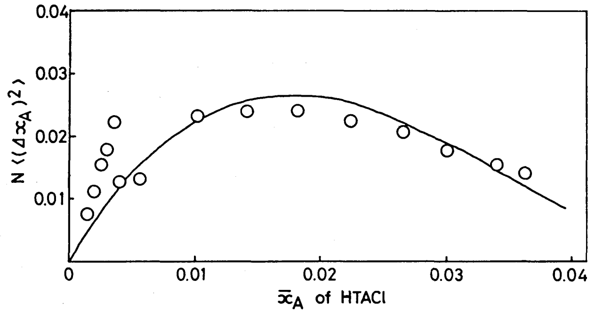

Fig. 6. Final results of theoretical calculation for HTACl-chloroform system ($l=3.4$, $n=18$).

without change in function, *i.e.*, the concentration at which the concentration fluctuation takes a maximum value is almost independent of l-values. The best fit between the calculated and the observed concentration fluctuation curves was obtained by setting $l=2.6$ and $n=12$ for TBACl solution and $l=3.4$ and $n=18$ for HTACl solution. The theoretical calculations are shown in Figs. 5 and 6.

Local Structure in the Solution. The present results may be summarized as follows. The surfactants studied dissolve in chloroform by forming an aggregate which is made up of a few surfactant molecules and several decades of chloroform molecules. This conclusion is in apparent contrast to the conclusion drawn from the infrared analysis, in that there, the indication is that the surfactants dissolve in chloroform by forming complexes which are made up of several chloroform molecules and one surfactant molecule.$^{1)}$ Table 1 shows the value of l and n obtained from the present study, together with the n-values obtained from the infrared study, n_{IR}. It was to be expected that the n and n_{IR} values would not agree and the difference is thought to be real. From the intensity ratio of the infrared absorption bands corresponding to the free and the bonded chloroform molecules, the number ratio of free and bonded chloroform molecules may be determined. Therefore, the infrared result affords rigorous information about the number of chloroform molecules which are directly attached to the surfactant molecules by hydrogen bonds. In the light scattering study, however, the molecular aggregate which behaves as a single molecule in solution is important, since concentration fluctuation is determined by the spatial distribution of component molecules in solution.

TABLE 1. l AND n VALUES OBTAINED IN THE PRESENT STUDY AND n_{IR} VALUES OBTAINED FROM THE INFRARED ABSORPTION STUDY FOR CHLOROFORM SOLUTIONS OF TBACl AND HTACl

	TBACl	HTACl
l	2—3	3—4
n	12	18
$n_{\mathrm{IR}}$$^{a)}$	2	4—4.5

a) See Ref. 1.

Combining results obtained from these light scattering and infrared absorption studies indicate a double-layered aggregate structure formed in the solutions; l numbers of surfactant molecules make a core of the aggregate and the core is surrounded by $(l\times n)$ numbers of chloroform molecules. Among the $(l\times n)$ numbers of chloroform molecules in one aggregate, $(l\times n_{\mathrm{IR}})$ numbers of chloroform molecules form hydrogen bonds directly with the surfactant molecules and make a first shell. The remaining $l(n-n_{\mathrm{IR}})$ numbers of chloroform molecules envelope the first shell by weak intermolecular interactions.

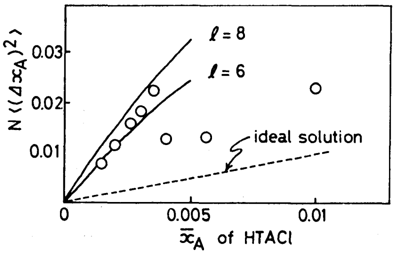

Fig. 7. Observed and calculated concentration fluctuation for HTACl-chloroform system in the region of $x_A\leq 0.01$.

The singular behavior of the concentration fluctuation observed for HTACl solution at low concentration is of some interest. Figure 7 shows the observed and calculated concentration fluctuation in the region where x_A is smaller than 0.01. As can be seen from Eq. 4, concentration fluctuation is only marginally affected by n for small values of x_A, that is, it is largely dependent on l. Therefore, a dummy number of 18 was set for the n-value in the theoretical calculation. From the figure the number of the surfactant molecules making an aggregate was determined to be 6—8 for HTACl. In TBACl solution, on the other hand, such singular concentration dependence of concentration fluctuation was not observed. This difference may arise from the molecular structure of HTACl which favors the aggregation of HTACl in chloroform.$^{10)}$

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10) The refree's comment has been against the experimental result itself. It says that this singular behavior of the concentration fluctuation may arise from the existence of "impurity" in the observed system. We think this may or may not be so, because we could not recognize the existence of any impurities by the use of our experimental technique. We feel it is more important to report the fact that the *l*-value of 6—8 was obtained from our experimental result and from our theoretical analysis, because it suggests the fact that the aggregation number in the low concentration range is larger than that in the high concentration range.