

Effects of Concentration and Temperature on SDS Monolayers at the Air–Solution Interface Studied by Infrared External Reflection Spectroscopy

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Infrared external reflection (IER) spectra of sodium dodecyl sulfate (SDS) monolayers at the air–solution interface and infrared transmission spectra of the corresponding aqueous solutions were measured at various SDS concentrations and temperatures. A comparison between the spectra of adsorbed monolayers and bulk solutions revealed that the conformational order of the SDS alkyl-chain at the air–solution interface improved with increasing the SDS concentrations, up until the saturation adsorption, and that the conformational order of the adsorbed SDS monolayer was higher than those of monomers and micelles. In addition, below the Krafft point temperature, the adsorbed SDS was maintained in the liquid crystal state, while SDS in the bulk solution was in the crystalline state. Furthermore, the SDS adsorption density was evaluated based on the IER band intensities of the insoluble monolayer of tridecanoic acid with an identical alkyl chain length to SDS.

Introduction

The monomolecular films at the air–water interface have been a considerable focus of recent model systems for biological membranes and two-dimensional pattern formation, photo-mechanical response, and molecular recognition systems.^{1–8} A number of techniques have been employed to investigate the microscopic structure and morphological properties of insoluble monolayers on water (Langmuir (L) films) such as X-ray diffraction,^{9–11} nonlinear optical spectroscopy,^{12,13} Raman¹⁴ and infrared spectroscopy,^{15,16} and Brewster angle microscopy.^{17,18} On the other hand, the application of these techniques to water-soluble surfactant monolayers adsorbed at the air–solution interface (Gibbs monolayer) is still limited.^{11,12,13,19–22}

Infrared external reflection (IER) spectroscopy¹⁵ is a non-destructive and sensitive method of monitoring molecular conformation, which is widely recognized for its application to Langmuir film systems. Since Dulhy first applied IER to Langmuir films, extensive applications have been developed to elucidate the structural characterization of various Langmuir film systems. Fina et al.²¹ and Ren et al.²² applied this method to sodium dodecylsulfonate Gibbs monolayers and water-soluble polymers, respectively, in an effort to study the adsorption behavior at the air–solution interface.

In a previous paper,¹⁹ an effective method of removing the effect of surfactant molecules dissolved in the water phase on measured IER spectra in a concentrated sodium dodecyl sulfate (SDS) system was reported, and the effect of the SDS concentration on the conformational order of SDS adsorbed at the air–solution interface was demonstrated. In this paper, IER spectra and IR transmission spectra of aqueous SDS solutions are measured, and the relationship between molecular states at the air–solution interface and in the bulk state and the effect of temperature on the adsorbed SDS state at the air–solution interface are discussed.

Experimental Section

SDS and perfluorooctadecanoic acid (PFODA) used in this experiments were identical to those previously described.¹⁹ Guaranteed reagent (GR) grade tridecanoic acid (TDA) and polyallylamine (PAA) cationic polymer with an average molecular weight of about 10 000 were purchased from Nitto Boseki Co., Ltd., and used without further purification. A polyion complex (TDA/PAA) comprised of TDA and PAA was prepared in methanol at a molar ratio of 1:1 (TDA:PAA, monomer units). Twice-distilled deionized water was used.

A particular volume of SDS solution was transferred into a trough, and a waiting time of 30–60 min was allowed in order to reach the adsorption equilibrium, after which the sample was subjected to IER single-beam reflectance (R) at 28 ± 1 °C. An equal volume of the corresponding SDS solution, covered with a PFODA monolayer was used to collect the single-beam background (R_0). The reflection spectrum was defined as $-\log(R/R_0)$. A monolayer of PFODA was spread onto the water surface using a 1.0×10^{-3} M solution of chloroform. Following monolayer compression to 20 mN/m (0.19 nm²/molecule), the desired SDS concentration was achieved by adding 100 mM SDS to the water. Measurements were taken after the concentration of the solution had been equilibrated for more than 30 min. IER spectroscopy with unpolarized radiation was performed using a modified attenuated total reflectance attachment (Spectra-Tech Inc.). The angle of incidence of the beam was 30°.

In the infrared transmission measurements, demountable liquid cells with CaF₂ windows were employed. Mylar spacers, 10, 15, 25, and 35 μ m thick were selected according to the concentration of the particular solution. The spectra of SDS in aqueous solution were obtained by subtracting the spectra of water recorded under the same conditions.

All infrared spectra were obtained using an FT-IR spectrophotometer (Nicolet 510M) equipped with a narrow band Hg–Cd–Te detector. Interferograms were accumulated 500–2000 times at a resolution of 4 cm⁻¹. Interpolation of data using a zero-filling technique resulted in accuracy of peak positions of ca. 0.2 cm⁻¹.

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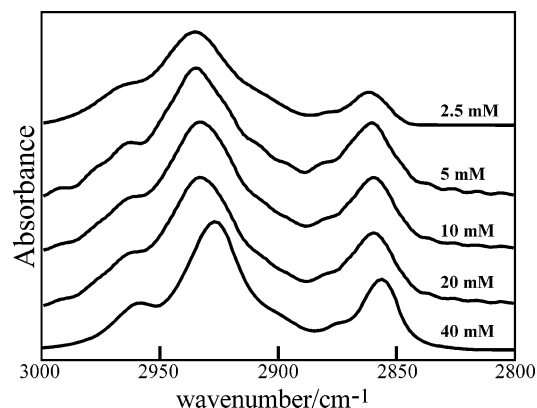


Figure 1. Infrared transmission spectra in the CH stretching region of aqueous SDS at various concentrations, after subtraction of the water spectrum. The ordinate is normalized for the largest peak-height at each concentration.

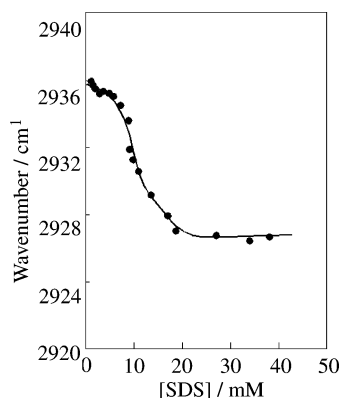


Figure 2. Concentration dependence of the wavenumber of the SDS $\nu_a(\text{CH}_2)$ band.

Water from a circulating bath was pumped through the jacket of cell holders. Sample temperatures were monitored using a thermocouple placed at the edge of CaF_2 windows for transmission measurements and inserted into the solutions for IER measurements.

Formation of Micelle in Bulk Solution. Figure 1 shows the IR transmission spectra of aqueous SDS solution in the CH stretching region at various concentrations. The two strong bands at about 2930 and 2860 cm^{-1} were assigned to the antisymmetric and symmetric CH_2 stretching modes, $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$, of the methylene chain of SDS, respectively. These bands are conformation sensitive and can be empirically correlated with the conformational order (trans/gauche ratio) of alkyl chains.^{23,24} That is, lower wavenumbers are characteristic for highly ordered conformations with preferential all-trans conformations, while higher wavenumbers are characteristic of gauche conformers. The peak positions of $\nu_a(\text{CH}_2)$ band were then plotted against the SDS concentration. As shown in Figure 2, the wavenumbers showed a drastic decrease at SDS concentrations above 8 mM, and reached 2926 cm^{-1} at higher concentrations.

Since the reported value for the critical micellar concentration (CMC) of SDS is 8.1 mM at room temperature,^{25,26} this drastic decrease observed, starting at a concentration of 8 mM, was thought to be due to the formation of micelles. Below the CMC the monomer band is the only band present, while above the CMC the band is composed of overlapping monomer and micelle bands. Therefore, as the SDS concentration increases, micelle bands become dominant, and then the peak of the absorption band shifts from that typical for a monomer to that typical of a micelle. The spectra taken at an SDS concentration of 6 and 40 mM revealed absorption bands for $\nu_a(\text{CH}_2)$ monomer

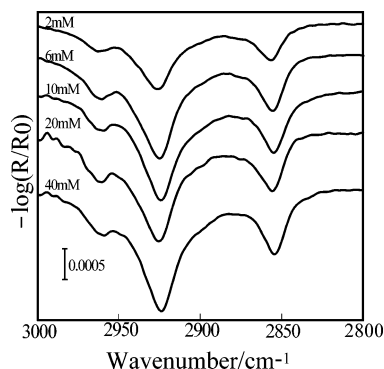


Figure 3. IER spectra in the CH stretching region of aqueous SDS at 25 °C.

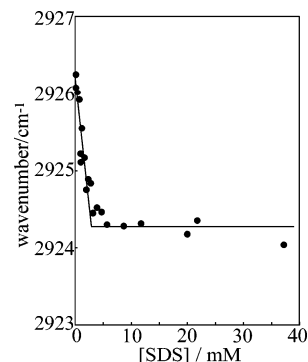


Figure 4. Wavenumber shift of the $\nu_a(\text{CH}_2)$ band of SDS adsorbed at the air-solution interface at various concentrations.

and micelle bands at 2935 and 2927 cm^{-1} , respectively. The decrease in the wavenumber was thus attributed to the differences in the conformation and the environment of the alkyl chains of the monomer and the micelle.

The State of SDS at the Air-Solution Interface and in Bulk Solution. Figure 3 shows the IER spectra of the CH stretching region of SDS monolayer at the air-solution interface, where the strongest absorption bands are the $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$ at about 2925 and 2850 cm^{-1} , respectively. The peak positions of the $\nu_a(\text{CH}_2)$ were plotted against the SDS concentration, as shown in Figure 4. The wavenumber decreased drastically with increasing concentration, but no significant change was observed at concentrations higher than 3 mM.

This decrease in wavenumber indicated that there was an increase in the conformational order of the alkyl chain, such as a decrease in gauche conformers due to an increase in surface density caused by the addition of SDS, whereas the constant wavenumber observed at concentrations above 3 mM occurred when the solution reached a constant conformational state, as described previously.¹⁹ At an SDS concentration of 3 mM, the amount of SDS adsorbed at the air-solution interface was considered to reach saturation, as verified by the constant $\nu_a(\text{CH}_2)$ band intensities observed above 3 mM.

The observed saturation concentration of 3 mM is in good agreement with the results obtained on the same system using radioisotope tracer measurements.²⁵ Thus, the improvement of the conformational order of the alkyl chain, up until 3 mM, was concluded to be caused by the increased density of SDS, the packing density of the alkyl chains, at the air-solution interface. The SDS saturation at the air-solution interface was clearly complete at a concentration much lower than the CMC, 8.1 mM.^{25,26} The phenomenon of saturation prior to the micelle formation is confirmed by the fact that the IER intensity, which depends on the surface density of SDS, is constant above 3 mM, as shown in Figure 5 in the next section.

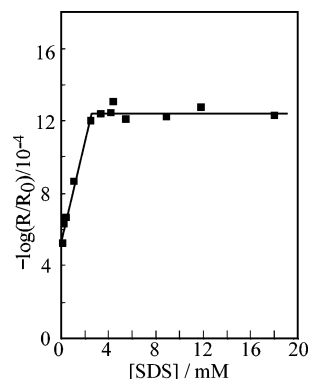


Figure 5. Intensity of the $\nu_a(\text{CH}_2)$ band in IER spectra of aqueous SDS as a function of the concentration.

In addition, this phenomenon was previously proved by the combination of the radiotracer method and the application of the Gibbs adsorption equation to the surface tension-concentration data of many surfactant systems, such as SDS, sodium tetradecyl sulfate, hexaoxyethylene-dodecyl ether, and *N*-dodecyl- β -alanine.^{25,27–29}

Furthermore, by comparing Figures 2 and 4, it is evident that the wavenumbers for the adsorbed SDS are lower than the corresponding values for the bulk solution at any concentration. This observation implies a higher conformational order for the alkyl chain of the adsorbed monolayer at the air–solution interface than monomer or micelle in the bulk solution.^{23,24}

Considering the molecular state of SDS at the air–solution interface and in bulk solution, adsorption and micellization behaviors can be classified into three concentration regions; below 3 mM, $3 \text{ mM} < [\text{SDS}] < 8 \text{ mM}$, and above 8 mM. In the region below 3 mM, the amount of adsorbed SDS increases constantly accompanying the improvement of the conformational order of the alkyl chain with increasing concentration, whereas in bulk solution only the monomer exists. In the $3 \text{ mM} < [\text{SDS}] < 8 \text{ mM}$ region, the increase in the SDS concentration results in an increase in the monomer concentration, while the adsorbed state of SDS at the interface remains constant, because saturated adsorption of SDS has already been attained. In the region above 8 mM, the adsorption amount and state of SDS and monomer concentration remain constant, but the micelle concentration increases with increasing SDS concentration. The conformational order of the alkyl chain is higher for adsorbed SDS than for the monomer and the micelle.

Adsorption Amounts of SDS at the Air–Solution Interface. IER intensity of $\nu_a(\text{CH}_2)$ bands against the concentration of SDS, obtained from the IER spectra in Figure 3, were plotted in Figure 5. The intensity was observed to rapidly increase up until 3 mM, and then remain constant above 3 mM. Since the intensity is thought to be proportional to the density of SDS adsorbed at the air–solution interface, the intensity profile in Figure 5 indicates that the adsorption amounts of SDS increase rapidly up until 3 mM and are saturated above 3 mM.

In an effort to evaluate the quantitative adsorption amounts of SDS from the data in Figure 5, a relation between the IER intensity and adsorption amounts is essential. An insoluble monolayer on the water surface is especially useful in examining this relationship, as the molecular density per unit of surface area can be easily controlled. Thus, the IER spectrum for a TDA spread monolayer with an identical alkyl chain length to SDS was examined. The reproducibility of the IER spectra was however, invariably poor, because the monolayer was unstable and collapsed easily. A polyion complex of TDA with PAA, which is a very stable spread monolayer, was then used in order to obtain an IER spectrum for TDA.

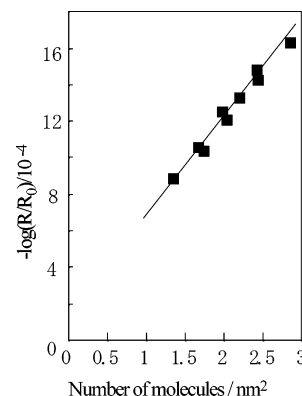


Figure 6. Intensity of the $\nu_a(\text{CH}_2)$ band in IER spectra of the insoluble monolayer of tridecanoic acid on water as a function of molecular density.

The IER spectra obtained, enabled the evaluation of the intensities of the $\nu_a(\text{CH}_2)$ band for various molecular areas. Figure 6 shows the intensity plotted against the reciprocal of the molecular area, the density of tridecanoic acid per unit area, D_{TDA} . The IER intensity was proportional to the density of tridecanoic acid.

The peak intensity also depends on the orientation of the dipole moment of the $\nu_a(\text{CH}_2)$ mode and the state of the alkyl chain. The peak position of the $\nu_a(\text{CH}_2)$ band was 2924 cm^{-1} at $D_{\text{TDA}} = 1.4 \text{ molecules/nm}^2$ and was shifted to 2923 cm^{-1} at higher density of $D_{\text{TDA}} = 2.8 \text{ molecules/nm}^2$. The peak position for TDA is almost the same as that for SDS at the air–solution interface at $[\text{SDS}] > 3 \text{ mM}$, indicating that TDA on water was in the liquid crystal state, i.e., fluid state, as well as SDS at the air–solution interface. Further, linear relationship between the IER intensity and D_{TDA} in Figure 6 suggests that the average orientation of the dipole moment of the $\nu_a(\text{CH}_2)$ mode of TDA does not change in the range of $D_{\text{TDA}} = 1.4\text{--}2.8 \text{ molecules/nm}^2$. From the above results, it is reasonable to conclude that the state of the alkyl chain and the average orientation of the dipole moment of the $\nu_a(\text{CH}_2)$ mode for SDS at the air–solution interface are almost constant, and are similar to those for TDA on water. Thus, in the present case, the IER intensity of the $\nu_a(\text{CH}_2)$ mode depends mainly on the density of surfactant.

We then used the calibration curve in Figure 6 to calculate the adsorption amount of SDS at $[\text{SDS}] > 3 \text{ mM}$. The resulting value was to be $3.4 \times 10^{-6} \text{ mol/m}^2$, 0.48 nm^2 per SDS molecule. This value was in good agreement with the reported value of 0.52 nm^2 , determined from the surface tension-concentration data.²⁵ Thus, the corrected IER spectra was successfully demonstrated to be a powerful technique to evaluate the amount of surfactant adsorbed at the air–solution interface.

The Effect of Temperature on Adsorbed State. To examine the effect of temperature on the state of the adsorbed monolayer, IER spectra of SDS at the air–solution interface and the corresponding transmission spectra of the bulk solution were measured at various temperatures. The plots of the absorption for the $\nu_s(\text{CH}_2)$ band for both the IER and transmission spectra against temperature are shown in Figure 7.

The absorption values of the infrared transmission spectra suddenly dropped from 2857 to 2850 cm^{-1} at about 10°C . This change was caused by a phase transition from the fluid state to the solid state of SDS, because the value below 10°C was the same as that of the crystalline state of SDS in a concentrated SDS–water system.²⁶ The observed phase transition temperature is consistent with the fact that the temperature of the Krafft point in aqueous SDS solutions is 9°C .³⁰ On the other hand, as can be seen in Figure 7, there is no significant change in the

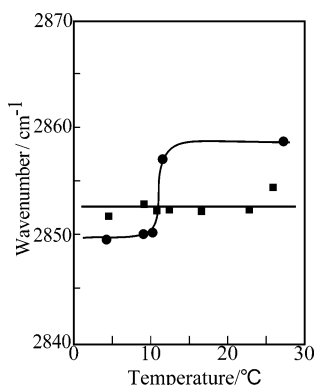


Figure 7. Temperature dependence of the wavenumber of the $\nu_s(\text{CH}_2)$ band in IER spectra (●) and infrared transmission spectra (○) of aqueous solution of 12 mM SDS.

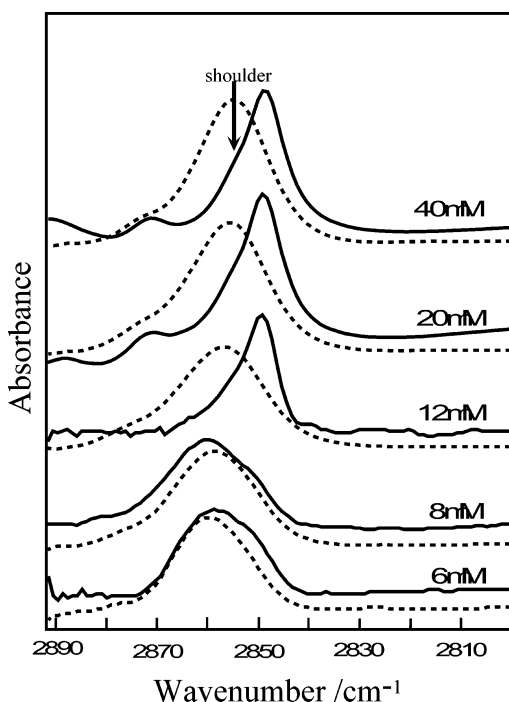


Figure 8. Infrared transmission spectra in the $\nu_s(\text{CH}_2)$ band region at various SDS concentrations at 5 °C (solid line) and 25 °C (dotted line).

IER spectra, indicating that the adsorbed SDS is maintained in the liquid crystal state, irrespective of temperature.³¹

The constant adsorbed state of SDS at the air–solution interface, regardless of the bulk state, seems to be inconsistent with the fact that SDS molecules adsorbed on water always exchange with the bulk species. The exchangeable species in the bulk phase are probably monomers, since micellar solutions do not exist at temperatures below the Krafft point and the bulk phase below this temperature is a molecular (monomer) solution.³²

In an effort to elucidate the temperature effect on the state of the monomer species in the bulk solution, the transmission spectra at various SDS concentrations at 5 and 25 °C was measured. As can be seen in Figure 8, at SDS concentrations below the CMC (8.1 mM), the spectra at 5 °C was almost identical to those at 25 °C, indicating that the monomer is in a fluid state at the temperature below the Krafft point. At SDS concentrations above the CMC, the spectra at 5 °C were significantly different from those at 25 °C. Interestingly, a shoulder at about 2860 cm^{-1} was observed in the spectra of higher concentrations at 5 °C. This observation suggests that

noncrystallized SDS molecules of monomer coexist with the crystalline hydrated SDS below the Krafft point temperature.

Conclusion

A comparison between the IER spectra of adsorbed SDS and the transmission spectra of bulk SDS solution was useful for elucidating the relationship between the adsorption behavior and micelle formation as a function of the SDS concentration. The conformational order of the SDS alkyl chain adsorbed at the air–solution interface was observed to improve gradually, until the ultimate saturation adsorption at $[\text{SDS}] = 3 \text{ mM}$. The conformational order of the adsorbed SDS was higher at any SDS concentration than that of the bulk species. Further examination of the temperature dependency of the IR spectra revealed that the adsorbed SDS state on water, is independent of the state of the bulk solution and of temperature.

Furthermore, the determination of the amount of SDS adsorbed at the air–solution interface was demonstrated to be successfully accomplished by evaluating the intensity of the IER spectra. This method may be advantageous in evaluating mixed surfactants or impurities in surfactant systems.

References and Notes

- (1) Yoneyama, M.; Fujii, A.; Maeda, S. *J. Am. Chem. Soc.* **1995**, *117*, 8188.
- (2) Holden, D. A.; Ringsdorf, H.; Deblauwe, V.; Smets, G. *J. Phys. Chem.* **1984**, *88*, 716.
- (3) Blair, H. S.; McArdle, C. B. *Polymer* **1984**, *25*, 999.
- (4) Seki, T.; Fukuda, R.; Yokoi, M.; Ichimura, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2375.
- (5) Kawai, T.; Hane, R.; Ishizaka, F.; Kon-No, K. *Chem. Lett.* **1999**, 375.
- (6) Huo, Q.; Dziri, L.; Desbat, B.; Russell, K. C.; Leblanc, R. M. *J. Phys. Chem. B* **1999**, *103*, 2929.
- (7) Koyano, H.; Bissel, P.; Yoshihara, K.; Ariga, K.; Kunitake, T. *Langmuir* **1997**, *13*, 5426.
- (8) Ahlers, M.; Ringsdorf, H.; Rosemeyer, H.; Seela, F. *Colloid Polym. Sci.* **1990**, *268*, 132.
- (9) Kjaer, K.; Als-Nielsen, J.; Helm, C. A.; Tippman-Krayer, P.; Mohwald, H. *J. Phys. Chem.* **1989**, *93*, 3200.
- (10) Kjaer, K. *Physica B* **1994**, *198*, 100.
- (11) Schwartz, D. K.; Braslau, A.; Ocko, B.; Pershan, P. S.; Als-Nielsen, J.; Huang, J. S. *Phys. Rev. A* **1988**, *38*, 5817.
- (12) Du, Q.; Freysz, E.; Shen, Y. R. *Phys. Rev. Lett.* **1994**, *72*, 238.
- (13) Bain, C. D.; Davies, P. B.; Ward, R. N. *Langmuir* **1994**, *10*, 2060.
- (14) Kawai, T.; Umemura, J.; Takenaka, T. *Chem. Phys. Lett.* **1989**, *162*, 243.
- (15) Dulhy, R. A.; Stephens, S. M.; Widayati, S.; Williams, A. D. *Spectrochim. Acta, Part A* **1995**, *1413* and references therein.
- (16) Sakai, H.; Umemura, J. *Langmuir* **1997**, *13*, 502.
- (17) Henon, S.; Meunier, J. *Rev. Sci. Instrum.* **1991**, *62*, 936.
- (18) Hönig, D.; Möbius, D. *J. Phys. Chem.* **1991**, *95*, 4590.
- (19) Kawai, T.; Kamio, H.; Kon-No, K. *Langmuir* **1998**, *14*, 4964.
- (20) Islam, Md. N.; Ren, Y.; Kato, T. *Langmuir* **2002**, *18*, 9422.
- (21) Fina, L. J.; Valentini, J. E.; Tung, Y. S. *ACS Smp. Ser.* **1994**, *581*, 44.
- (22) Ren, Y.; Shoichet, M. S.; McCarthy, T. J.; Stidham, H. D.; Hsu, S. L. *Macromolecules* **1995**, *28*, 358.
- (23) Umemura, J.; Mantsch, H. H.; Cameron, D. G. *J. Colloid Interface Sci.* **1981**, *83*, 558.
- (24) Kawai, T.; Umemura, J.; Takenaka, T. *Colloid Polym. Sci.* **1984**, *262*, 61.
- (25) Tajima, K.; Muramatsu, M.; Sasaki, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1991.
- (26) Kawai, T.; Umemura, J.; Takenaka, T. *Bull. Inst. Chem. Res., Kyoto Univ.* **1983**, *61*, 314.
- (27) Tajima, K.; Iwahashi, M.; Sasaki, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3251.
- (28) Okumura, T.; Nakamura, A.; Tajima, K.; Sasaki, T. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2986.
- (29) Koshinuma, M.; Sasaki, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2755.
- (30) Hato, M.; Shinoda, K. *J. Phys. Chem.* **1973**, *77*, 378.
- (31) The peak position in the IER spectra seems to be shifted to higher wavenumber at higher temperature. This is due to the increase in the chain flexibility with increasing temperature.
- (32) Laughlin, R. G. *The Aqueous Phase Behavior of Surfactants*; Academic Press: London, 1994; Chapter 9, p241.