The Raman Scattering Spectra and Molecular Conformations of Cetyltrimethylammonium Bromide in Aqueous Solutions

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Laser Raman spectra of aqueous cetyltrimethylammonium bromide (CTAB) solutions were measured in the region of 1000—1150 cm^{-1}. The relative intensities (I_{1085}/I_{1128} and I_{1085}/I_{1067}) of skeletal optical modes are ploted against the concentration. Both relative intensities are found to decrease with increasing the concentration. This intensity change is marked around the second CMC. This observation shows that the all-trans chain segments of the CTAB molecules increase with the sphere-rod transition.

Introduction

Conformational changes of the hydrocarbon chains of surfactant molecules due to micellar formation have been conjectured in ^{13}C spin-lattice relaxation studies[1,2] and confirmed in Raman studies[3]. Lately, Kalyanasundaram et al. have reported an increase in rigidity of the micellar CTAB-hydrocarbon parts on addition of sodium bromide on the basis of Raman spectra[4].

In this paper, the concentration dependence of the Raman spectra of aqueous CTAB-solutions is investigated in order to obtain information about conformational changes in the surfactant hydrocarbon core accompanying the sphere-rod transition.

Experimental

Cetyltrimethylammonium bromide (CTAB) was purchased from Nakarai Chemicals LTD (Japan) and purified by recrystallisation from aceton-ethanol. The Raman spectra were taken at room temperature (22 ± 2 °C) with a JRS-400T Raman spectrometer.

The reported relative intensities are averages of 4—5 separate measurements. The increase of the background scatter with increasing surfactant concentration was taken into consideration.

Results and Discussion

In Raman spectra of hydrocarbon chains, a longitudinal acoustical mode resulting from an accordion-like motion of the whole chain is observed. The measurement of this vibrational mode gives direct evidence of conformational changes of the hydrocarbon chain, because the its frequency is inversely related to the number of all-trans bonds of the methylene chain.

By measuring the longitudinal acoustical mode Okabayashi et al. have shown that for potassium n-alkyl carboxylates the all-trans form of the hydrocarbon chain (carbon number: $n = 5, 6$) increases with the formation of micelles[3,5]. For aqueous solutions of surfactants having longer hydrocarbon chains it is difficult to discuss the

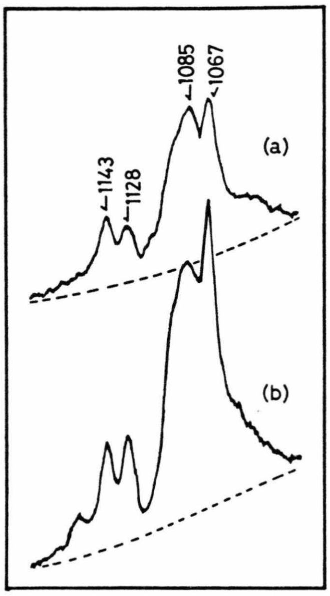

Fig. 1. Raman spectra of the aqueous CTAB solutions in the region of 1000—1150 cm^{-1} (the broken lines show the back-ground scattering); (a): 30 mg/cm^{3} and (b): 135 mg/cm^{3}.

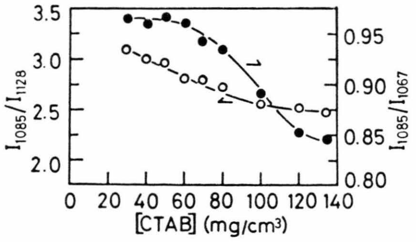

Fig. 2. Plots of relative intensities (I_{1085}/I_{1128} and I_{1085}/I_{1067}) as function of the CTAB-concentration.

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Reprint requests to Dr. H. Okabayashi, Dept. Industrial Chemistry, Nagoya Institute of Technology, *Gokiso, Showa-ku, Nagoya 466, Japan* conformational change in terms of the accordion-like mode because of the very weak intensities. However, the skeletal optical modes appearing in the region of 1000—1150 cm^{-1} are suitable for such investigations, because these modes are very sensitive to the conformational state of the hydrocarbon chain.

A hydrocarbon chain generally has its main Raman lines at 1065, 1080—1100 and 1130 cm^{-1}. The lines at 1065 and 1130 cm^{-1} have been ascribed to the all-trans forms of the chain segments, while the 1080—1100 cm^{-1} line corresponds to a chain structure having gauche rotamers [6, 7, 8]; the relative intensities of the 1065 and 1130 cm^{-1} lines to the 1080 cm^{-1} line have frequently been used as a measure of the conformational change[4, 9].

Figure 1 shows Raman spectra of aqueous CTAB solutions in the region of 1000—1150 cm^{-1}. The peak heights of the Raman lines at 1067 and 1128 cm^{-1} relative to that of the 1085 cm^{-1} line are plotted against the CTAB-concentration in Figure 2. In the concentration range around the second CMC, both I_{1085}/I_{1128} and I_{1085}/I_{1067} seem to decrease with an increase in the concentration. This observation shows that the variation of the micellar shape cause an intensity change of the Raman spectra and that this spectral change is associated with an increase in the population of the all-trans chain segment in the n-alkyl hydrocarbon chains. Thus, it is evident that an increase of rigidity in the hydrocarbon parts implies an increase of the all-trans form of the hydrocarbon part. This conclusion is consistent with the result which has been obtained by Kalyanasundaram et al.[4] in the case of the electrolyte-induced sphere-rod transition of the CTAB micellar system.

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