Bull. Chem. Soc. Jpn., 57, 1149—1150 (1984)

Freezing of Water as Aggregated with Cationic Surfactants in Deuterochloroform

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(Received May 25, 1983)

Synopsis. Freezing of water solubilized with the cationic CTAX(hexadecyltrimethylammonium halides) and QDX (dihexadecyldimethylammonium halides) in deuterochloroform was observed by ^{1}H-NMR method. The freezing of water was largely affected by the characteristics of the water-surfactant aggregates by the *R*-value($=[H_2O]/[\text{surfactant}]$) and the structure of surfactant. In the 0.20 M ($1\,M=1\,mol\,dm^{-3}$) CTABr/0.16 M $H_2O/CDCl_3$ system, for example, the apparent freezing was observed at about −20 °C.

Various surfactants form aggregates with polar solutes, usually water molecules, in apolar media. People call the aggregates "reversed micelles" sometimes. "The aggregates" can provide specific and restricted reaction field for various chemical reactions[1] irrespectively of the concept of the cmc and aggregation number. In such a specific system equilibria, rates, and pathways of chemical reactions can be controlled by continuously and simultaneously changing the micropolarity and microviscosity of the reaction field and the activity of the cosolubilizates as a function of water content in the system.[2] Extending a series of our studies on the characterization of "the aggregates" or "reversed micelles", in this work, we would like to report an apparent freezing of water in the system. For this purpose, ^{1}H-NMR method for the water proton signal was utilized.[3,4]

Experimental

All the spectra were obtained using a JEOL 100 MHz NMR spectrometer at various probe temperatures with TMS as an internal standard. The probe temperature was calibrated carefully with methanol proton signals before and after measurements. Water content was determined on a Kyoto Electronics MFG Karl-Fischer Moisture Automatic Titrater, Model MK-AIII. Through all the runs deuterochloroform was employed as a bulk solvent to form the water-surfactant aggregates. Surfactants were the same as those used in a previous work.[3]

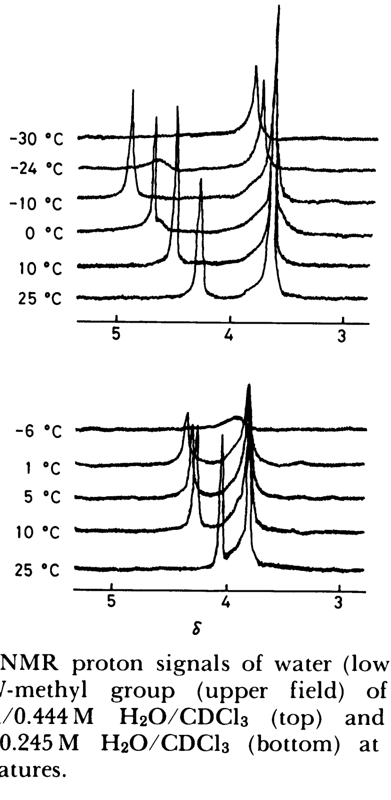

Fig. 1. NMR proton signals of water (lower field) and *N*-methyl group (upper field) of 0.20 M CTACl/0.444 M $H_2O/CDCl_3$ (top) and 0.10 M QDCl/0.245 M $H_2O/CDCl_3$ (bottom) at various temperatures.

Results and Discussion

Since the life time of both water protons, located in bulk phase and interacting with surfactant, is faster than the NMR time scale, only one signal of water proton was observed by NMR.[3]

First, lowering the probe temperature causes a downfield shift of the water proton signal with a concomitant line-broadening (Fig. 1). Further lowering the temperature shows a sudden and large line-broadening and a shift toward upper magnetic field of the signal. Hence, this point was defined tentatively as the apparent freezing point of water in this system. Second, the chemical shift of water proton siganl was due to both the *R*-value($=[H_2O]/[\text{surfactant}]$) and the structure of surfactant.[3,4]

Water in deuterochloroform containing no surfactants shows a signal at 1.96 ppm (25.0 °C). In the cationic surfactant–water aggregates, water molecules interact with the strongly electronegative cation-head of surfactants by means of coordination-type.[3] This means that the water proton signal in micellar system appears downfield far from the value in chloroform: In the present cationic aggregates, the water proton

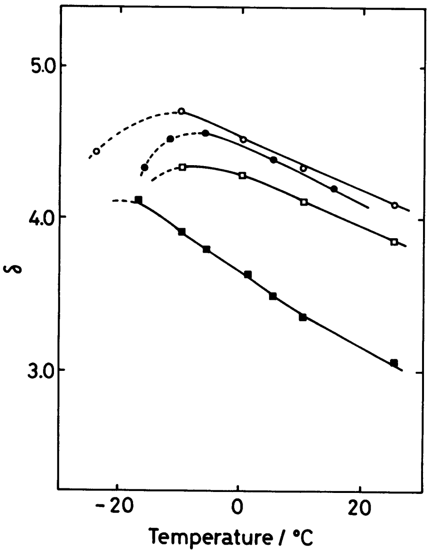

Fig. 2. Chemical shifts of water proton signal in the 0.20 M CTAX/$CDCl_3$ system as a function of the probe temperature: -○-, CTACl ($R=2.22$); -●-, CTABr ($R=2.24$); -□-, CTABr ($R=2.04$); -■-, CTABr ($R=0.80$), respectively. Drastic line-broadenings were observed over the broken line region.

signals were usually observed around 3—5 ppm (Figs. 1 and 2). Increasing the *R*-value produces hydrogen bonding between water molecules themselves and causes the paramagnetic shift of the proton signal as seen in Fig. 2. The chemical shift of the water proton under consideration seems to finally reach the value of pure bulk water (4.66 ppm). From the same reason, it is certain that upon lowering temperature the mobility of water molecules decreases and simultaneously both the hydrogen bonding between water molecules and the interaction between water and surfactants become stronger, resulting in further downfield shift of the signal (Fig. 2). Freezing and solubility decrease of water with lowering of temperature lead to a phase separation of the system. This was observed in a drastic change on the chemical shift and line width of the water proton signal. The apparent freezing point thus obtained was largely affected by the *R*-value, structure of surfactant, and bulk solvent. For example, in the case of CTABr aggregates in $CDCl_3$, the apparent freezing point was about −20 °C for R=0.80, −10 °C for 2.04, and −6 °C for 2.22, respectively. For QDBr micelles, it was about −1 °C for R=0.60 and 0 °C for 2.45. However, in the case of anionic AOT aggregates in $CDCl_3$, no decrease in the freezing temperature was observed even when the *R*-value was below unity.

In any event, the nature of water bound to surfactants in apolar media is rather different from that of bulk water. In addition, the present work suggests to us that one can conduct chemical reactions in an aqueous system even below 0 °C if an appropriate system was provided with the water-surfactant aggregates in apolar media.[5]

References

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