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STRUCTURE AND NATURE OF CATIONIC REVERSED MICELLES AS STUDIED BY NMR IN THE PRESENCE OF CUPRIC CHLORIDE

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Cupric chloride enhances solubilization of water into hexadecyltrimethylammonium chloride micelles in chloroform to a great extent. The NMR signals of water protons and *N*-methyl protons of the surfactant are extremely broad at low water concentrations in the presence of 31 mM cupric chloride. However, they become sharper with the increase in water concentration, indicating the decreased interaction of cupric ion with the surfactant and water in the micellar core.

Solubilization of water and other polar substances into an apolar medium is an interesting aspect of reversed micelles.[1,2] In addition to the mechanism of solubilization, the nature and state of a water pool formed in reversed micelles have been studied by means of various experimental techniques. However, the main focus was on the AOT (sodium 1,2-bis(2-ethylhexyloxycarbonyl)-1-ethanesulfonate) system that forms large and rather uniform micelles in hydrocarbon solvents,[3] while cationic surfactants that form smaller and more heterogeneous micelles attracted less attention. We would like to show in this communication that cupric chloride enhances solubilization of water into the cationic hexadecyltrimethylammonium chloride (CTACl) surfactant micelles and that the solubilized cupric ion plays a role as a good probe to study the nature of the polar core of micelles by means of NMR spectroscopy.

Approximately 1.1 M water is soluble in chloroform containing 0.20 M CTACl at 25.0 °C. Addition of 31 mM cupric chloride enhances solubilization of water up to about 5 M. Similar salt effects in the enhanced solubilization of water have been observed in related systems.[4,5] It should be noted that the increased solubility of water caused by cupric chloride is much greater than that expected from the hydration number for cupric chloride.[6] Thus, cupric chloride solubilizes water not only by a direct hydration to it but also by lowering the total free energy of the system.[2]

The cosolubilized cupric ion affects the NMR signals of surfactant and water in their linewidths, while its effect on the chemical shifts is insignificant. The linewidth ($\nu_{1/2}$) of respective proton signals in the presence of 31 mM cupric chloride changes with water concentration as shown in Fig. 1.[7] At low water concentrations, the cupric ion brings about a line broadening of *N*-methyl and water proton signals. At 1.1 M water concentration, for example, the *N*-methyl signal is about 6 times broader in the presence of the cupric ion than that in its absence (Table I). The water proton signal is even more broadened and, in fact, it is not observable up to the water concentration of 2.5 M. On the other hand, the linewidth of internal methylene proton signals remains unchanged over the entire water concentration range (4 Hz). The linewidths of *N*-methyl and water protons become sharper as the water concentration is increased, resulting in 9 and 64 Hz, respectively, at about 5 M water concentration. An NMR linewidth is dependent on paramagnetic relaxation as well as on the mobility of a molecule and the exchange rate of protons in question. It is obvious that the first mechanism is the most effective in the present system, since the linewidth change due to the latter mechanisms is usually much smaller (a few Hz) than that caused by the paramagnetic effect.[8] According to the previous study,[9] the copper complexes present in the cationic reversed micelles are mostly $CuCl_n(H_2O)_{4-n}$ and $Cu(H_2O)_6^{2+}$.[10] No wonder that water

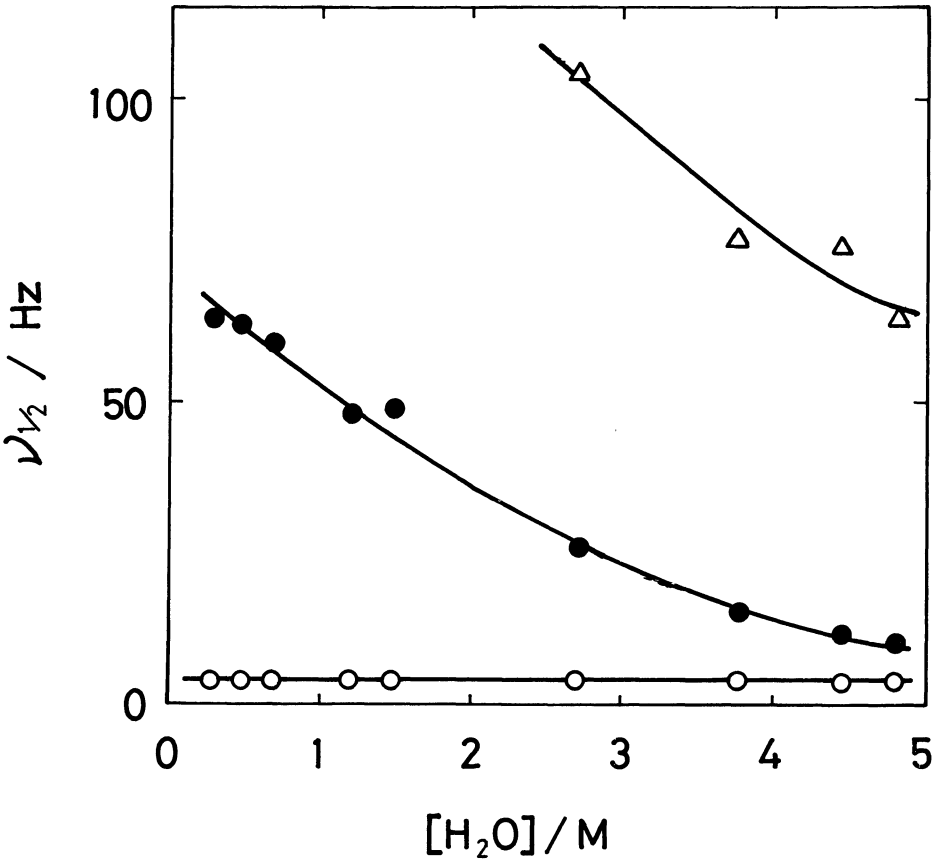

Fig. 1. ^{1}H-NMR linewidths of water proton (△) and of *N*-methyl (●) and methylene protons (○) of surfactant as a function of water concentration in the 0.20 M CTACl/chloroform micelles containing 31 mM cupric chloride.

Table I. ^{1}H-NMR Linewidths of Surfactant and Water Protons under Several CTACl Micellar Conditions$^{a)}$

			$\nu_{1/2}$, Hz		
Solvent	$[CuCl_2]$, mM	$[H_2O]$, M	*N*-CH_3	-(CH_2)-	H_2O(HOD)
$CHCl_3$	0	1.1	3	3	2
$CHCl_3$	31	1.1	50	4	unobserved
$CHCl_3$	31	5	9	4	64
$D_2O^{b)}$	0		2	6	1.5
$D_2O^{b)}$	31		3	7	9

a) [CTACl] = 0.20 M b) Normal aqueous micelles

proton signal is very broad under the present conditions, since a portion of water coordinates to the paramagnetic cupric ion. It is, however, interesting that *N*-methyl signal is also very broad especially at low water concentrations. This is good evidence to show that the cupric ion closely comes in contact with the cationic head of the surfactant and is confined in a water pool of reversed micelles. As the size of water pool expands the cupric ion separates from the micellar surface, and the linewidth of *N*-methyl protons at, for example, 5 M water approaches those in aqueous systems. In aqueous micelles, on the other hand, a 31 mM cupric ion hardly affects the linewidths of surfactant because of the electrostatic repulsion of cupric ion and the ammonium moiety of surfactant (Table I). In brief summary, as far as the present results are concerned, it is reasonable to draw a picture of cationic reversed micelles as an aggregate of surfactants with a water pool inside. The same conclusion has been drawn for the anionic AOT reversed micelles by a variety of experimental approaches.$^{11-13)}$ Recently, the nature of anionic reversed micelles composed of sodium octanoate, hexanol, and water has been investigated through ^{23}Na-NMR spectroscopy.$^{14)}$ It was found that the environment around sodium ion and its mobility in the micellar core were different from those in usual aqueous solutions, when the ratio of water to surfactant was small. However, as the ratio was increased these properties approach those found in aqueous solutions. This behavior of anionic reversed micelles is in line with our present findings on the cationic reversed micelles.

References and Notes

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