A Novel Reverse Micellar System Composed of Bis(octylethylenediamine)zinc(II) Chloride in Aqueous Benzene and Chloroform Solutions

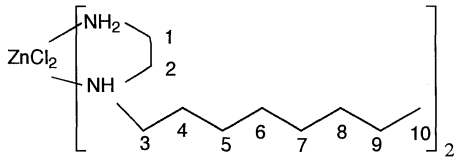
Masayasu Iida,* Akira Yonezawa, and Junko Tanaka
Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630

(Received March 21, 1997; CL-970202)

We prepared Zn(octylethylenediamine(= oct-en))$_2$Cl$_2$ and found that its solubilities to benzene and chloroform are appreciably enhanced with an addition of water. This solubilization can be attributed to the formation of reverse micelles. Vapor pressure osmometry(VPO) showed appreciable aggregations in benzene solutions, and ^{13}C and ^{2}H NMR relaxations for the zinc complex and water molecules, respectively, suggest their extensive motional restrictions in benzene and chloroform solutions by the aggregations.

Amphiphiles including metal complexes are expected to have highly organized functions in aggregated forms.[1] Recently, such kinds of amphiphiles have been prepared and used mainly in catalytic systems, while their physical properties have not been well characterized except for a few cases.[2,3] It is also noticed that most of amphiphilic metal complexes hitherto prepared are water-soluble and form normal micelles in aqueous solutions. On the other hand, reverse micelles are expected to provide a higher catalytic field than normal micelles. Many kinds of metallosoaps being oil-soluble are known and extensively used for industrial purposes.[4] However, they are almost non-electrolytes having strong metal-ligand ionic bonds and the behavior of their reverse micelles has not been well identified; furthermore, ionic surfactants soluble in nonpolar solvents are limited in number.

In the present study, we prepared zinc(II) octyl-ethylenediamine complexes and their aggregations in aqueous and non-aqueous solutions were studied using multinuclear NMR spectroscopy and VPO. We revealed that the solubility of the bis(oct-en) complex to benzene is greatly enhanced with an addition of water and that the aggregations occur extensively.



$ZnCl_2$(oct-en)$_2$ complex

The mono(oct-en) complex was prepared by mixing aqueous $ZnCl_2$(0.2 mol dm^{-3}) and oct-en(0.3 mol dm^{-3}) solutions at pH 6(controlled with hydrochloric acid) and then by stirring the mixture for one day. After an evaporation of the solvent, the mono complex was extracted into water from water/chloroform system. The crystal was obtained by recrystallization from ethanol. The bis complex was obtained using oct-en more than the three times the molar quantity of $ZnCl_2$ in ethanol-water 3 : 2 solvents. After an evaporation of the solvent, the bis complex was extracted into chloroform layer in water/chloroform system and then the crystal was obtained by recrystallization from ethanol.[5]

The water-soluble mono complex forms normal micelles whose CMC(= critical micelle concentration) determined by VPO and ^{35}Cl counterion relaxation rates[6] was 0.24 mol/kg at 27 °C.

We shall describe the solution behavior concerning the bis complex hereafter, unless otherwise noted. The solubility to benzene[7] is poor (around 40 mg/100 mL at 25 °C) while that to chloroform[7] is good (20 g /100 mL at 25 °C). It is characteristic that the solubilities to benzene and chloroform increase (especially for benzene) with an addition of small amounts of water. Thus, the solubilities were around 40 g/100 mL in aqueous(26 wt%) benzene and 50 g/100 mL in aqueous(1.5 wt%) chloroform; the content of water to form transparent solutions is appreciably different between the two solvents.

We confirmed the aggregation using a VPO and multinuclear NMR spectroscopies as follows. The vapor-pressure depression was measured in (aqueous and anhydrous) chloroform and aqueous benzene solutions with a Knauer VPO at 35 and 40 °C, respectively. In this method, the magnitude of the vapor-pressure depression is proportional to the difference in temperature (ΔT) between a solvent-wetted thermister and a solution-wetted one. The ΔT *vs.* m'(= solute concentration in g/kg) plot gave an apparent molecular weight. We therefore estimated the CMC value from the break point of the plot as 0.015 mol kg^{-1} and the degree of the aggregations as 1.3 from the slope of the plot[8] in chloroform at the concentrations below 0.04 mol kg^{-1}. If the water content increases, the VPO result was unchangeable in this concentration range. The aggregation number in aqueous benzene was also obtained from the slope of the same plot. The results are almost independent on the water/bis-complex molar ratios (= w_0) and the aggregation numbers obtained for w_0 = 5-15 are 20±4, which is appreciably larger than that in the chloroform solution.

As larger longitudinal relaxation rate means a larger motional

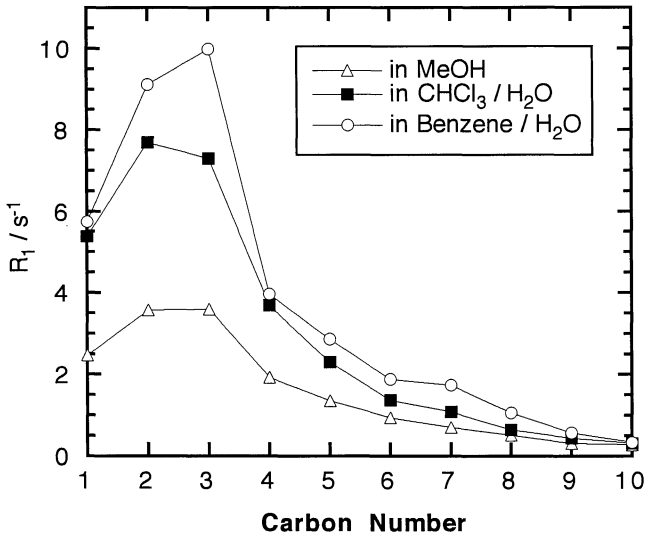


Figure 1. Dependence of the ^{13}C relaxation rates on the carbon positions for the three solvent systems. The concentration of the bis complex is 0.416 mol/dm^3 for the organic solvents.

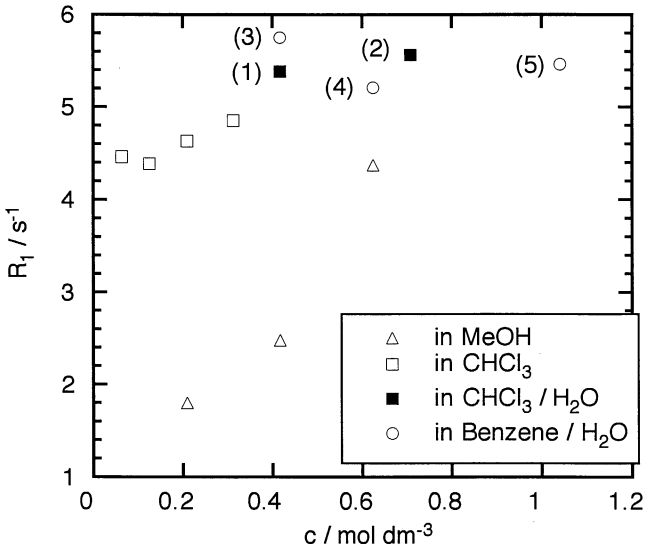


Figure 2. Concentration dependence of R_1 for the carbon 1 in the three solvent systems. The w_0 values are (1)1.2 (2)1.5 (3)13 (4) 18 (5) 11.

restriction of the probe nucleus of molecules in the (nearly or) extreme narrowing region, it is useful to compare the relaxation rates of the noted nuclei between the motionally weakly restricted system and the micellar systems. We compared the rates in the aqueous chloroform and benzene solutions with those in methanol where the aggregation may scarcely occur.

The ^{13}C relaxation rates gave information concerning the motional restriction of the carbon-chains of the octyl-ethylenediamine ligands. The rates largely depended on the carbon position of the ligands, as shown in Figure 1. The motions of the methyl group as carbon 10 are very similar between the three systems, while the carbon atoms in the headgroup are differently restricted in their motions.

In order to see the extent of the aggregations furthermore, we focused on the carbon 1 in various concentrations of the bis complex. Figure 2 clearly shows that the methylene moiety in the headgroup is motionally restricted in chloroform and benzene solutions. Although the aggregation number is appreciably larger in benzene solutions than in chloroform solutions, the extent of the motional restriction is very similar. This may be due to the larger size of the water pool in the former system(or larger w_0 values); this view is also supported by the ^2H_2O relaxations, which are significantly smaller in the former system as will be shown below. It is noticeable that even in methanol the aggregation will occur at higher concentrations.

If reverse micelles are formed, water molecules in the water pool should be motionally restricted to a great extent. We thus measured ^2H_2O relaxations in aqueous benzene and chloroform solutions of the bis complex and then compared their results with those in methanol solutions. Table 1 shows that the relaxation rates increase in the presence of the bis complex. The decrease of the ^2H_2O motion in methanol by the interaction with the bis complex suggests that the motion of the water molecule is

Table 1. ^2H_2O relaxation rates (R_1) in various solvents in the presence and absence of $Zn(oct\text{-}en)_2Cl_2$ at 32 °C

Complex, mol dm^{-3}	Solvent	w_0	R_1/ s^{-1}
0	neat ^2H_2O	——	1.92
0.208	MeOH	1.32	5.68
0.208	MeOH	10.6	5.99
0.208	benzene	10.6	65.4
0.624	benzene	6.98	87.8
0.624	benzene	14.1	48.3
0.208	chloroform	1.32	100.4

governed by that of the bis complex through the hydration to the hydrophilic headgroup. It is important that an increase in the w_0 value only slightly affects the result in methanol. On the other hand, the rate remarkably increases in benzene and chloroform solutions in the presence of significant amounts of the complex. The relaxation rate in benzene solutions significantly decreases with an increase in the w_0 value; this result means that the slower motions should be governed by the hydration to the aggregates having appreciably slower motions. The larger restriction of the ^2H_2O motion in the chloroform solution than in the benzene solution will be due to the smaller w_0 values, that is, the larger ratio of the water of hydration to the free water.

References and Notes

1 T. Sierra, in "Metallomesogens," ed by J. L. Serrano, Chapter 2, VCH, Weinheim (1996).
2 M. Iida, T. Sakai, N. Koine, and S. Kaizaki, *J. Chem. Soc. Faraday Trans*, **89**, 1773 (1993).
3 M. Iida, M. Yamamoto, and N. Fujita, *Bull. Chem. Soc. Jpn.*, **69**, 3217 (1996).
4 K. Ide, in "Kinzoku-sekken No Seishitsu To Ohyo," ed by T. Yoshida, S. Shindo, T. Ogaki, and K. Ide, Saiwai-shobo, Tokyo (1988).
5 Anal. Found: C, 39.02; H, 7.89; N, 9.12%. Calcd for $Zn(oct\text{-}en)Cl_2$: C, 38.92; H, 7.84; N, 9.08%. Anal. Found: C, 49.90; H, 10.03; N, 11.56%. Calcd for $Zn(oct\text{-}en)_2Cl_2$: C, 49.95; H, 10.06; N, 11.65%.
6 In the normal micelles, the chloride counterions are partially bound to the micellar surfaces. In such systems, the ^{35}Cl NMR relaxation is very useful to detect the extent of the aggregations and to determine the CMC values(Ref. 3).
7 In these solvents, the water content(determined by a Karl-Fischer titration) were 0.013 and 0.0070 wt% for the chloroform and benzene solvents, respectively.
8 In benzene solutions, the ^{35}Cl spectra of counterions of the bis complex are somewhat complicated and extraordinarily broad(close to 10 kHz) compared to those of the mono complex (around 10-30 Hz) in aqueous solutions. This result shows that most of the chloride counterions are bound to the headgroup of the reverse micelles. Thus we can assume that the chloride ions are not dissociated in the aqueous benzene and chloroform solutions; in this case, we can estimate the aggregation numbers from the slope of this plot.(Ref. 9)
9 K. Konno and A. Kitahara, *Kogyo Kagaku Zasshi*, **68**, 56 (1965).