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Microemulsions composed of metal complex surfactants, bis(octylethylenediamine (= OE)) Zn(II), Cd(II), and Pd(II) chlorides, in water/chloroform and water/benzene systems

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Bis(*N*-octylethylenediamine (= OE)) zinc(II), cadmium(II), and palladium(II) complexes ($Zn(OE)_2Cl_2$, $Cd(OE)_2Cl_2$, and $Pd(OE)_2Cl_2$) were prepared, and the characteristic structures of the aggregates were investigated in such mixed solvents as water/chloroform, water/benzene, and water/methanol using ^1H NMR pulsed-gradient spin echo (PGSE) and TEM (transmission electron microscopy) methods. These complexes form reverse micelles or w/o microemulsions in water/chloroform or water/benzene depending on the hydrophilicity of the headgroup.

1. INTRODUCTION

Double-chained surfactants of metal complexes have shown unique aggregation behavior in organic solvents or water,[1-6] since their HLB is intermediate and they sometimes display characteristic stereochemistry.[4] We have prepared such kinds of metal complex surfactants as $Zn(OE)_2Cl_2$, $Cd(OE)_2Cl_2$, and $Pd(OE)_2Cl_2$. They are readily to form single crystals and not hygroscopic. They are thus desirable for the X-ray crystallographic analysis as double-chained surfactants. We have previously clarified the structures of the Zn(II) and Pd(II) complexes in crystals as follows.[2,3] In the former complex, the geometry is octahedral, the aniono groups are *trans*, and the octyl chains are *transoid*; on the other hand, in the Pd(II) complex the geometry is square planar and the chloride ions are not coordinated. The molecular structure of *trans*-dichloro-*transoid*-bis(*N*-octylethylenediamine)zinc(II) complex is given in Fig. 1.

In the present paper, we report the solubilities and aggregation behavior of $M(OE)_2Cl_2$ (M= Zn, Cd, Pd) in water/methanol, water/chloroform and water/benzene systems in comparison of the metal-chloride interactions between the three metals.

2. EXPERIMENTAL

The $M(OE)_2Cl_2$ (M= Zn, Cd, and Pd) complexes were prepared according to the previous methods. [2,3] The purities were confirmed by elemental analysis and ^{13}C NMR spectra. The selective solubilities of the complexes in water/chloroform or water/benzene system were visually determined and the ternary phase diagrams were drawn. The aggregation behavior was studied by the measurements of diffusion coefficients of the complexes and water on a JEOL FX 90 NMR spectrometer. The diffusion coefficients were reproducible within a precision of 5% or better. TEM was observed on a Hitachi H-800 electron microscope at an accelerating voltage of 100 kV. Freeze-fracture replicas were prepared by using a Balzers cryofract (BAF-400). Details of the procedure were described elsewhere. [3, 6]

3. RESULTS AND DISCUSSION

All the complexes are poorly soluble in water (around 1% for the palladium complex and below 0.1% for the zinc and cadmium complexes). The Zn(II) and Cd(II) complexes are significantly soluble in chloroform while the Pd(II) complex is poorly soluble. The solubilities in chloroform increased with the addition of water; for the palladium complex, the magnitude was especially large in spite of the low solubility in neat water. Partial ternary phase diagrams for the three complexes in water/chloroform mixed solvents are given in Fig. 2. It is remarkable that the palladium complex has a large L_2 region, which reflects its higher hydrophilicity (or polarity) of the headgroup caused by the ionic character of the palladium-chloride bond. In the Zn(II) and Cd(II) complexes, on the other hand, the chloride ion coordinates to the metal center in crystal. The strength of the metal-chloride bond in the complexes would be in the order, $Cd(OE)_2Cl_2 > Zn(OE)_2Cl_2 >> Pd(OE)_2Cl_2$, whereas in the simple chloride salts the covalency of the metal-chloride ion bond is in the order, $PdCl_2 > CdCl_2 > ZnCl_2$.

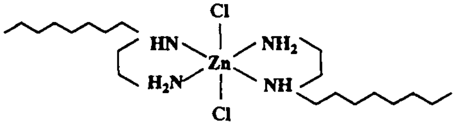

Fig. 1. A molecular structure of $Zn(OE)_2Cl_2$.

(In Figures, $M(OE)_2Cl_2$ is abbreviated as $M(OE)_2$.)

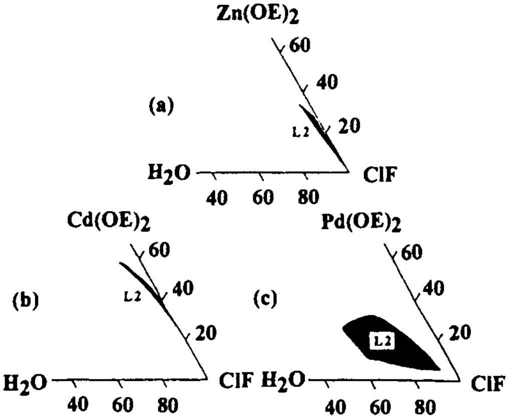

Fig. 2. Partial mass (wt %) ternary phase diagram for the three complexes in water/chloroform (ClF) mixed solvents. L_2 is water in oil phase.

Figure 3 shows the diffusion coefficients for water and the Zn(II) complex in the chloroform and methanol systems as functions of the complex concentrations. Appreciable decrease in the water diffusion coefficients compared to that for the neat water (2.32x10^{-9} m^2s^{-1}) means the motional restriction of water molecules by the Zn(II) complex. We furthermore found that the addition of water slightly (20-30%) retards the diffusion of the Zn(II) complex in the concentration ranges of 0.5-1.0 mol kg^{-1} in the chloroform system. This result suggests the formation of aggregates incorporating water. The trend for the diffusion coefficients in the Cd(II) complex system was similar to that in the Zn(II) complex system, as seen for the solubility behavior. (Fig. 2)

The difference in the diffusion coefficients between the Zn(II) complex and water is significantly smaller in the chloroform system (Fig. 3) compared to the methanol (Fig. 3) and benzene (Fig. 4) systems. The diffusion coefficients and phase diagrams suggest that the reverse micelles are formed for the Zn(II) and Cd(II) complexes in water/chloroform medium, while the microemulsions are formed for the Zn(II) and Cd(II) complexes in water/benzene and for the Pd(II) complex in water/chloroform. (Fig. 5)

It is characteristic that the diffusion coefficients of water molecules and metal complexes increase with an increase in water content in the Pd(II) microemulsion system (Fig. 5) while they decrease in the Zn(II) (Fig. 4) and Cd(II) systems. In the Pd(II) complex system, the degree of the dissociation of the chloride ion would be larger compared to the other two metal systems since the Pd-Cl bond is more ionic; therefore, water molecules may more easily move from one water pool to the other ones together with the chloride ions.

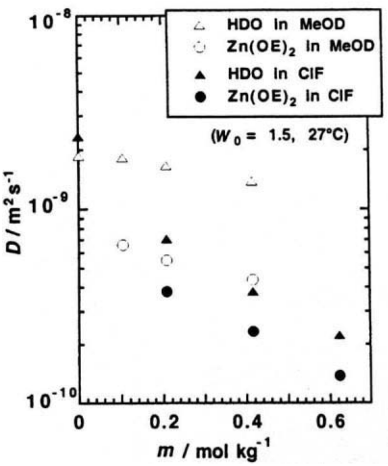

Fig. 3. Diffusion coefficients for the Zn(II) complex and water in chloroform and methanol systems depending on the complex concentrations.

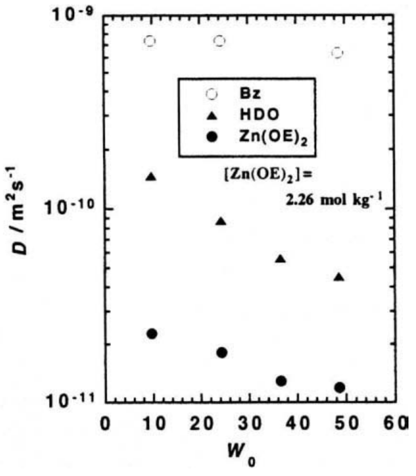

Fig. 4. Diffusion coefficients for the Zn(II) complex and water in the water/benzene systems depending on the water content. (W_0 = $[H_2O]/[Zn(II)$ complex])

The structures of the microemulsions were directly observed by TEM. Figure 6 shows typical cases of TEM photographs for the $Zn(OE)_2Cl_2/H_2O$/benzene system where the weight ratio of the $Zn(OE)_2Cl_2$: benzene is 1:1. In this figure, at 15 wt % water content (1), spherical particles with diameters of 25-30 nm were uniformly dispersed. Those particles must be water-in-oil (w/o) microemulsions having water pools in the cores. The TEM texture changed at 20 wt % water content (2) to sponge phase with water channels. For a solution with 40 wt % water content (3), the TEM photograph displayed typical texture of bicontinuous phase which has benzene and water domains. A solution with 30 wt % water content shows a mixture of sponge and bicontinuous phases. Bicontinuous phase was observed even for a 1.5 : 1 solution of the $Zn(OE)_2Cl_2$: benzene ratio with 50 wt % water content.

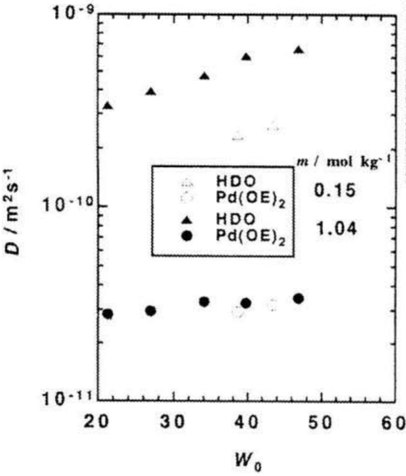

Fig. 5. Diffusion coefficients for the Pd(II) complex and water in water/chloroform system depending on the water content (W_0).

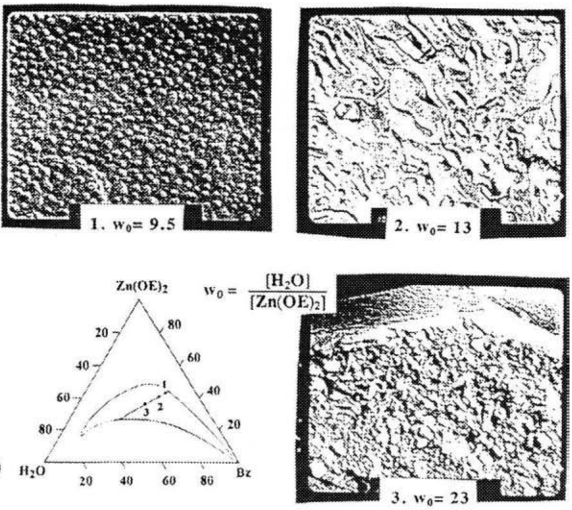

Fig. 6. Ternary solubility diagram for the Zn(II) complex/water/ benzene system and the TEM photographs at the respective (1-3) compositions on the phase diagram.

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