Hydrophilic-Hydrophobic Balance of Bis(octylethylenediamine) Zn(II), Cd(II), and Pd(II) Chlorides in Methanol/Water and Chloroform/Water Systems

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Double-chained bis(*N*-octylethylenediamine (= OE)) complexes, such as $Zn(OE)_2Cl_2$, $Cd(OE)_2Cl_2$, and $Pd(OE)_2Cl_2$, were prepared and their selective solubilities in water/chloroform and water/methanol solutions were studied. Although all the complexes are poorly soluble in water, they showed clearly different solubilities in the water/organic mixed solvents depending on each amphiphilic character.

Double-chained surfactants of metal complexes have shown unique aggregation behavior in organic solvents or in water,[1-5] since they have both strong hydrophobic and strong hydrophilic moieties and sometimes show stereochemically characteristic features. One (M.I.) of the present authors has found unique solubility and aggregation behavior of $Zn(OE)_2X_2$ (X = Cl or NO_3).[2,3] It is noticeable that they showed extensive solubilities in water/benzene mixed solvent to form highly ordered aggregates (microemulsions). On the other hand, double-chained (bis(*N*-*n*-alkylethylenediamine)) surfactant Co(III) complexes have been shown to have a unique character that the *cisoid/transoid* diastereomer ratio in solution depends on the water/ethanol molar ratios due to the hydrophobic interactions between the alkyl chains of the ligands in water.[4]

In the present study, we have obtained single crystals of $M(OE)_2Cl_2$ (M = Zn, Cd, Pd) and performed an X-ray crystallographic analysis for the Zn and Pd complexes. The metal complexes were prepared almost according to the previously reported method.[2,3] These double-chained surfactants obtained are readily to be purified and to form single crystals in contrast to the popular emulsifiers such as AOT (aerosol OT) and dioctyldimethylammonium chloride. The ORTEP drawings of the zinc(II) and palladium(II) complexes are given in Figure 1. The structure of the zinc(II) chloride complex in crystal was revealed to be similar to that of the corresponding nitrato complex; the coordination geometry around a zinc(II) is octahedral, the chloro groups are *trans* (Zn-Cl bond length is 2.560(1) Å), and the octyl chains are *transoid* (Zn-N bond length is 2.086(4) or 2.196(4) Å).[6] On the other hand, for the palladium(II) complex, the geometry is square planar (Pd-N bond length is 2.039(4) or 2.047(3) Å) and the chloride ions are not coordinated to the metal (Pd···Cl distance is 4.159(1) or 4.250(1) Å).[7] Although we did not perform an X-ray crystallographic analysis for the cadmium(II) complex, its structure may be close to that of the zinc(II) complex since the Cd-Cl bond is stronger than the Zn-Cl bond and cadmium also tends to take octahedral geometry. It is characteristic that in spite of the appreciably larger stability constant for the Pd-Cl complex in aqueous solution compared to the other metals,[8] the large separation of Pd···Cl means its ionic character, which is ascribed to the preferential occupation of the four coordination sites by the two octylethylenediamines. We can thus consider that the palladium complex will be a strong electrolyte while the zinc and cadmium complexes may be weak electrolytes similarly to $ZnCl_2$ and $CdCl_2$.

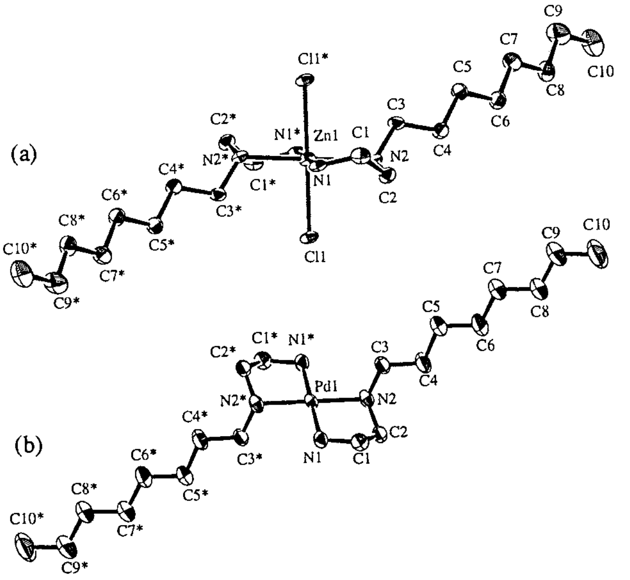

Figure 1. ORTEP diagrams of (a) *trans*-dichloro-*transoid*-bis(*N*-octylethylenediamine)zinc(II) complex and (b) *transoid*-bis(*N*-octylethylenediamine)palladium(II) complex cation.

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 zinc(II) and cadmium(II) complexes are significantly soluble in chloroform while the palladium complex is insoluble. The selective solubilities of the three complexes in water/chloroform solutions were visually determined and the partial ternary-phase diagrams are described in Figure 2. The solubility in chloroform was increased with an addition of water and this trend is remarkable for the palladium(II) complex. The solubility enhancement with an addition of water suggests a formation of reversed micelles in water/chloroform as previously reported.[2,3]

In order to see the hydrophilic-lyophilic balance, we furthermore described the solubility diagrams in methanol/water mixed solvents. Although the three complexes are poorly soluble in water, they are readily soluble in methanol. It is also characteristic that the zinc and cadmium complexes are hydrolyzed to be precipitated in the presence of significant amounts of water. This precipitation could not be protected even with an addition of acid. There is a distinct trend that the precipitation is retarded with an increase in the complex concentrations. In Figure 3 we describe transparent solution region (L_1) and the region (PPT) where the precipitation occurs within

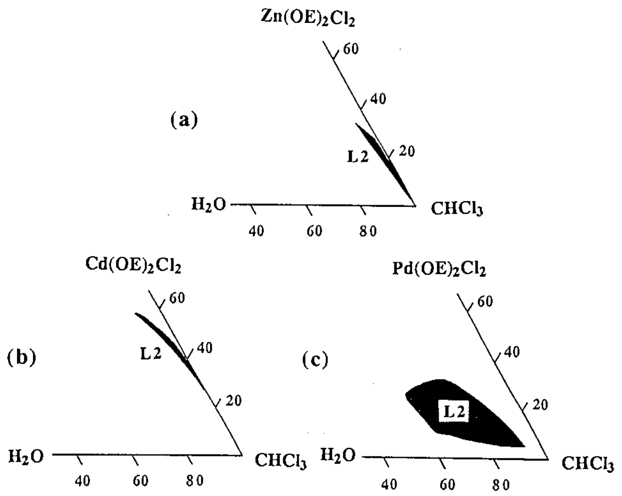

Figure 2. Partial mass(wt %) ternary phase diagram of $M(OE)_2Cl_2$/ water/ chloroform. M= (a) Zn, (b) Cd, (c) Pd. L_2 is water in oil phase.

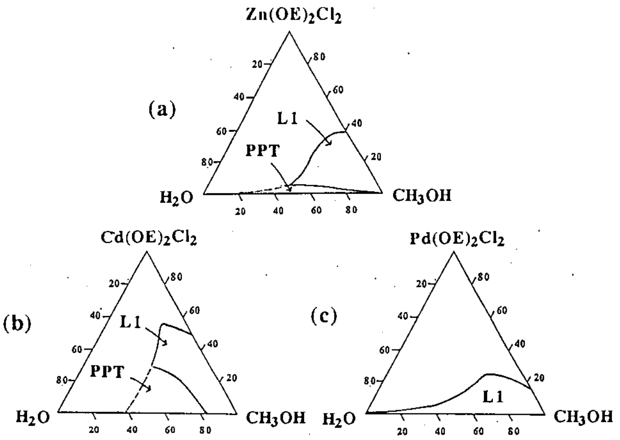

Figure 3. Mass(wt %) ternary phase diagram of $M(OE)_2Cl_2$/ water/ methanol. M= (a) Zn, (b) Cd, (c) Pd. L_1 is normal or micellar solution. PPT is the region where the precipitation occurs.

one day. The boundary between the insolubility region and the PPT one was ambiguous by the visual observation. However, we can certainly see that the cadmium complex has the largest feature to be dissolved in methanol in preference to water and the palladium complex has the largest affinity to water without hydrolysis.

In both chloroform and methanol systems, Figures 2 and 3 show that although the solubilities of zinc and cadmium complexes are appreciably higher in the neat organic solvents than in neat water, an adequate amount of water assists the solubilities. This feature can be ascribed to selective hydration to the hydrophilic moieties of metal complexes; its trend appears more clearly in the chloroform system than in the methanol system. As previously reported for the nitrato zinc(II) complex,[3] the incorporation of water into chloroform system would give rise to self-association of the complex to form reversed micelles while its high solubility in water/benzene mixed solvent suggests extensive formation of W/O microemulsions.[2,3] The palladium complex shows similar solubility profile (Figure 2(c)) where the complex is highly soluble in water/chloroform mixed solvent system. In this system extensive aggregates such as microemulsion would be formed and appreciable amounts of water are incorporated into the aggregates. The difference in the solubility between the zinc or cadmium complex and the palladium complex is remarkable. As the palladium complex should be a strong electrolyte, it will be more hydrophilic than the other complexes, whereas it can only be significantly dissolved in water in the coexistence of organic solvents. When comparing between the zinc and cadmium complexes, we can see that the cadmium complex has higher solubility in chloroform and methanol and therefore has higher hydrophobicity. This trend can be ascribed to the larger covalence of Cd-Cl bond than the Zn-Cl one.

We stress that the double-chained metal complexes are poorly soluble in water but they behave as amphiphiles in water/organic mixed solvent systems.

References and Notes

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5 X. Lu, Z. Zhang, and Y. Liang, *Langmuir*, **12**, 5501 (1996); *Langmuir*, **13**, 533 (1997).

6 Crystal data: $C_{20}H_{48}N_4ZnCl_2$, M = 480.91, triclinic, space group $P\bar{1}$ (No. 2), a = 6.601(4) Å, b = 17.939(9) Å, c = 5.754(2) Å, α = 95.11(3)°, β = 101.40(3)°, γ = 80.01(5)°, V = 656.6(5)Å^3, Z = 1, and D_{calcd} = 1.22 g cm^{-3}. A colorless prismatic crystal (0.43 x 0.30 x 0.08 mm) was fixed on the top of a glass fiber with Paraton N oil, and 2312 reflections ($4 < 2\theta < 52$ °) were measured on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation at -118 °C. An absorption correction by Ψ–scan method was applied (μ = 11.5 cm^{-1}). The structure was solved by direct methods using the program SIR92 and was refined with full-matrix least-squares techniques to R = 0.055 and R_w = 0.060 for 1653 independent reflections with $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms, located at ideal positions, were not refined. All calculations were performed on a Silicon Graphics O2 Station with teXsan program system.

7 Crystal data: $C_{20}H_{48}N_4Cl_2Pd$, M = 521.93, triclinic, space group $P\bar{1}$ (No. 2), a = 7.800(3) Å, b = 16.781(5) Å, c = 5.115(1) Å, α = 93.82(2)°, β = 98.66(2)°, γ = 92.12(3)°, V = 659.7(3)Å^3, Z = 1, and D_{calcd} = 1.31 g cm^{-3}. A colorless prismatic crystal (0.48 x 0.15 x 0.05 mm) was fixed on the top of a glass fiber, and 2318 reflections ($4 < 2\theta < 50$°) were measured on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation at 23 °C. An absorption correction by Ψ–scan method was applied (μ = 9.18 cm^{-1}). The structure was solved by direct methods with the program DIRDIF and was refined with full-matrix least-squares techniques to R = 0.037 and R_w = 0.044 for 2152 reflections with $I > 3\sigma(I)$. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms, located from difference Fourier maps, were refined isotropically.

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