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Effects of metal–counterion interactions on the percolation in microemulsions composed of bis(*N*-octylethylenediamine)metal(II) complexes in water/benzene and water/chloroform systems

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Abstract

Self-diffusions and electric conductivities of microemulsions composed of surfactant metal complexes, dianionobis(*N*-octylethylenediamine)zinc(II) (anion = chloro or nitrate), dichlorobis(*N*-octylethylenediamine)cadmium(II), and bis(*N*-octylethylenediamine) palladium(II) chloride (= $\text{ZnCl}_2(\text{oct-en})_2$, $\text{Zn}(\text{NO}_3)_2(\text{oct-en})_2$, $\text{CdCl}_2(\text{oct-en})_2$, and $[\text{Pd}(\text{oct-en})_2]\text{Cl}_2$, respectively) were studied in water/benzene or water/chloroform mixed solvent system. The electric conductivities of the solutions increase in the order, $\text{CdCl}_2(\text{oct-en})_2 < \text{ZnCl}_2(\text{oct-en})_2 < \text{Zn}(\text{NO}_3)_2(\text{oct-en})_2 \ll [\text{Pd}(\text{oct-en})_2]\text{Cl}_2$ systems. The profiles of the plots of the diffusion coefficients and of the electric conductivities versus water content depend on the ionicity of the metal-anion bond, i.e. in the $[\text{Pd}(\text{oct-en})_2]\text{Cl}_2$ and $\text{Zn}(\text{NO}_3)_2(\text{oct-en})_2$ systems both the diffusion coefficients and the electric conductivities are positively dependent while for the other two systems the slopes of the plots are negative. Among them, it is characteristic that the electric conductivity versus water content plot for the palladium complex system shows a sharp peak at W_0 (= $[\text{water}]/[\text{Pd complex}]$) = 43. These properties were explained on the basis of the pre-percolation phenomenon.

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Keywords: Metal complex surfactant; Microemulsion; Reverse micelle; Self-diffusion; Percolation

1. Introduction

Reverse micelles and W/O microemulsion systems containing heavy-metal ions are expected to

have highly organized functions [1]. Physical properties of double-chained surfactants having metal complex ions in the head group are also interesting, since they have delicate balance of the hydrophobic and hydrophilic moieties and provide various kinds of morphologies of aggregates [2–7]. We have investigated the structural characteriza-

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tion of reverse micelles and W/O microemulsions composed of double-chained surfactant metal complex, dichlorobis(*N*-octylethylenediamine)zinc(II), ($= \text{ZnCl}_2(\text{oct-en})_2$) in water/benzene mixed solvent system using transmission electron microscopy (TEM) and atomic force microscopy (AFM) [7]. One (M.I.) of the present authors with his co-workers has, on the other hand, performed X-ray crystallographic analyses of the $\text{ZnCl}_2(\text{oct-en})_2$, dinitratobis(*N*-octylethylenediamine)zinc(II) ($= (\text{NO}_3)_2(\text{oct-en})_2$), and bis(*N*-octylethylenediamine)palladium(II) chloride ($= [\text{Pd}(\text{oct-en})_2]\text{Cl}_2$), and revealed that, in the zinc(II) complex crystal, two anions coordinate to the zinc(II) center in the *trans* geometry while, in the palladium(II) complex crystal, two chloride ions are present only as the counterions [5,6]. Our group has furthermore prepared silver and palladium nanoparticles from bis(*N*-hexadecylethylenediamine)silver(I) complex in heptane/water system and from bis(*N*-octylethylenediamine)palladium(II) complex in chloroform/water system, respectively [8,9]. This shows the capability for the formation of diamine-protected metal nanoparticles from a series of bis(*N*-alkylethylenediamine)metal complexes. These results indicate that the reverse micelles and W/O microemulsion systems composed of double-chained metal complex surfactants have a large potential of providing unique aspects of the aggregation systems in solution, unobtainable in purely organic surfactant systems.

In the present paper, we report the detailed results on the aggregation behavior of the zinc, cadmium, and palladium complexes, which are good emulsifiers in water/organic solvents. We here focus on the relationship between the ionic interactions of the metal-counterions and the dynamic behavior of aggregation solutions. For this purpose, physical properties such as ^1H NMR self-diffusions and electric conductivities were mainly measured here. The aggregation behavior was studied in comparison between the ligating anions (chloro and nitrate) concerning their specific interactions with the zinc(II) center and then in comparison among the zinc(II), cadmium(II), and palladium(II) complex systems: the palladium(II) complex is regarded as a strong electrolyte while the other complexes are as weak electrolytes

or non-electrolytes according to the X-ray crystallographic analysis [5,6]. Some of the present results were compared with those for the typical W/O microemulsion system of aerosol OT (AOT).

2. Experimental section

The preparations of the metal complexes were followed the reported procedure [4–7]. We have reported X-ray crystallographic analyses for $\text{ZnCl}_2(\text{oct-en})_2$, $\text{Zn}(\text{NO}_3)_2(\text{oct-en})_2$, and $[\text{Pd}(\text{oct-en})_2]\text{Cl}_2$ [5,6]. The purifications of the solvents have also been previously reported [4–6]. When comparing the physical properties among the $\text{MX}_2(\text{oct-en})_2$ complex/water/organic solvent systems, we fixed the $\text{MCl}_2(\text{oct-en})_2$ concentration as $1.04 \pm 0.01 \text{ mol kg}^{-1}$ for the organic solvents (benzene or chloroform) unless otherwise stated. The physical properties of the solutions were studied mainly by changing the water content defined as W_0 ($= [\text{water}]/[\text{metal complex surfactant}]$) in the range of the homogeneous and transparent region.

The measurements of the self-diffusion coefficients were performed according to the previous procedure [5–7,10]. Temperature was controlled $30 \pm 0.5^\circ\text{C}$ with a JEOL GVT2 temperature control unit. The accuracy of the measured diffusion coefficient is estimated to be better than $\pm 5\%$.

The electric conductivity of the solution was measured using an admittance linear bridge (FUSO 362A) operated at 1 kHz. The conductivities of solvents used for the preparations of the solutions were below $5 \times 10^{-7} \text{ S cm}^{-1}$. All the solutions were bubbled with nitrogen gas before the conductivity measurements. The kinematic viscosity (ν) of each aqueous solution was measured with a Cannon–Fenske or Ubbelohde capillary viscometer. The shear viscosity (η) was obtained from the relationship of ν with the density (ρ) being measured by an Ostwald-type picnometer. These measurements were performed at $30 \pm 0.05^\circ\text{C}$.

The 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 have been previously described [11].

3. Results and discussion

3.1. Solubilities of $MX_2(oct-en)_2$ in water/organic solvents of low dielectric constants (the ternary phase diagrams for the formation of the homogeneous and transparent phase)

The solubilities of $MX_2(oct-en)_2$ in water/organic solvents of low dielectric constants are described by ternary phase diagrams for the formation of homogeneous and transparent (single phase) region. The results for the chloro or chloride of the zinc(II), cadmium(II), and palladium(II) complexes have been reported in the previous preliminary papers [6,7]. Some of them are redrawn in Fig. 1(a), (b), and (d). The hydrophobicity of the complexes judged from the solubilities in benzene and chloroform was in the order, $CdCl_2(oct-en)_2 > ZnCl_2(oct-en)_2 \gg [Pd(oct-en)_2]Cl_2$, which is consistent with that of the covalency/ionicity ratio of the metal–chloride bond.

For the dinitrato-zinc(II) complex, the single-phase region was much smaller than that for the dichloro-zinc(II) complex in the water/benzene (= Bz) system at 30 °C. Fig. 1(c) shows the result in comparing with the other chloro complex systems. The much smaller tendency of incorporating water in the nitrate system is due to the fact that the chloride ion has larger hydration energy than the nitrate ion has when they are free and then the hydration at the head group of the dichloro complex may be more favorable even when the chloride ion is ligating to zinc. The dichloro complex thus hydrates to a larger extent than the dinitrato complex does to form the single-phase region extensively in benzene.

3.2. Self-diffusion studies for $ZnX_2(oct-en)_2/H_2O$ /benzene, $CdCl_2(oct-en)_2/H_2O$ /benzene, and $[Pd(oct-en)_2]Cl_2/H_2O$ /chloroform systems

The self-diffusion coefficients of each component are utilized to monitor the structures of the

microemulsions and the extent of the aggregations under various conditions [12]. Fig. 2 shows the self-diffusion coefficients for water and the metal(II) complexes as functions of the water content. In comparing between the dichloro- (Fig. 2(a)) and dinitrato- (Fig. 2(c)) zinc(II) complex systems, we can see a contrast trend that the diffusion coefficients decrease with increasing water content in the former system while they increase in the latter system where the concentration range of the single-phase region is very narrow [13].

The decrease in the diffusion coefficients with increasing water content (W_0) was observed for the dichloro-zinc(II) and cadmium(II) complexes as well as those for water in the same systems (Fig. 2(a) and (b)). These diffusion coefficients are reflected by the increase in the sizes and structures of the water domains having 10–100 nm order sizes, since the diffusion coefficients by the present methodology were determined by following the root-mean-square displacements within the order of 0.1–10 μm [14].

In the palladium(II) single-phase region, on the other hand, the diffusion coefficients slightly increase with increasing water content (Fig. 2(d)) as seen in the dinitrato-zinc(II) complex. As the absolute values in the palladium complex system were comparable to those in the dichloro-zinc(II) and cadmium(II) complex systems, the extent of the aggregation will also be in a similar manner to the other systems. The increase in the diffusion coefficients with increasing water content for the dinitrato-zinc(II) and palladium(II) chloride complexes seems to be inconsistent with the increase in the size of the water domains in view of the above explanation for the dichloro-zinc(II) and cadmium(II) complex systems. This apparent inconsistency can be explained as an onset of the percolation phenomenon (we designate it as a “pre-percolation”) in the dinitrato-zinc(II) and palladium(II) systems as will be discussed below.

3.3. Viscosities of the microemulsions

We measured the viscosities as a function of the water content in the typical cases. Fig. 3 is the result for the dichloro-zinc(II) and cadmium(II), and palladium(II) chloride complex systems at

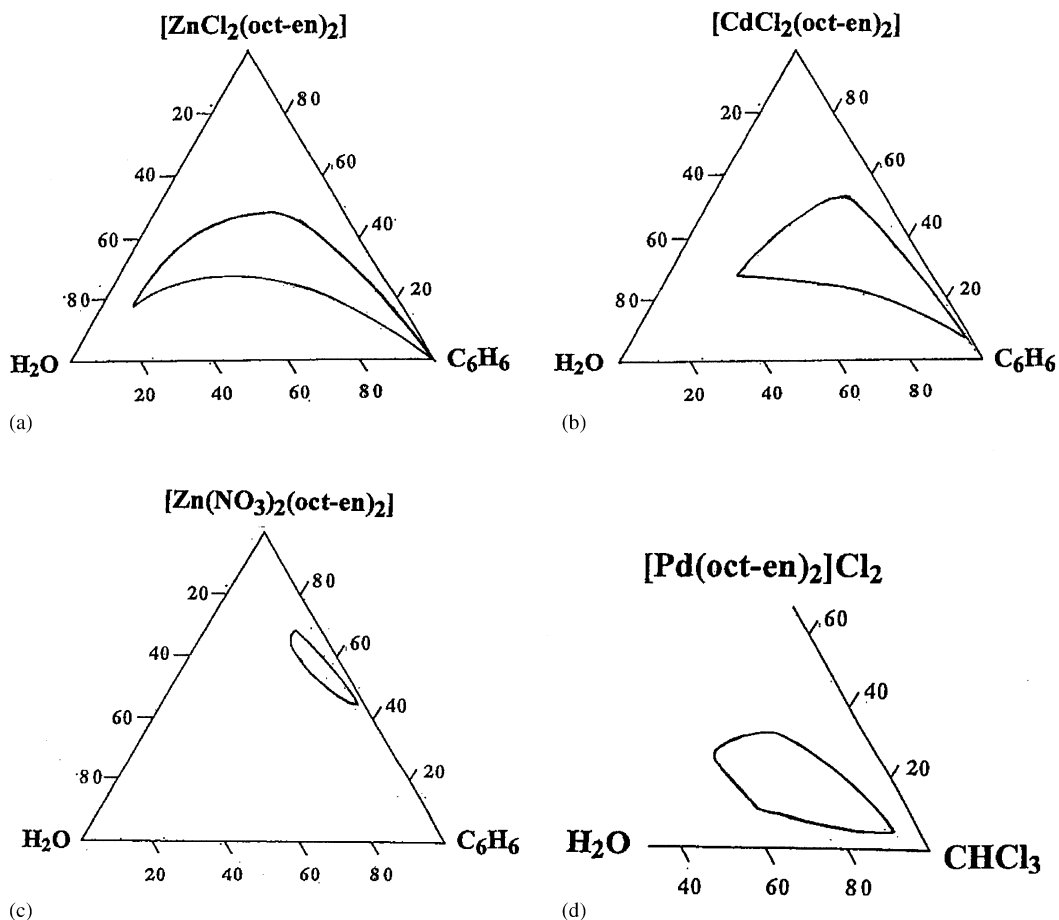


Fig. 1. Mass (wt.%) ternary phase diagrams for the homogeneous and transparent phases in $\text{MX}_2(\text{oct-en})_2/\text{water}/\text{benzene}$ ($=\text{C}_6\text{H}_6$) ((a)–(c)) and in $\text{PdCl}_2(\text{oct-en})_2/\text{water}/\text{chloroform}$ ($=\text{CHCl}_3$) ((d)) systems.

1.04 mol kg^{-1} and 30°C , which are the same conditions as measured for the self-diffusions and electric conductivities. In all the cases, the viscosities tend to decrease with increasing water content at lower W_0 ; however, they slightly increase in the zinc(II) and cadmium(II) systems at higher water content, and for the palladium(II) system they keep the decrease or are constricted to be constant. It is remarkable that the minimum in Fig. 3(a) corresponds to the transition region from the sponge phase to the W/O microemulsion according to [7].

The dependence of the diffusions on the water content seen in Fig. 2(a) and (b) is regarded as the sum of the two trends in the viscosities (Fig. 3(a)):

the one is observed at the smaller W_0 values and the other is at the larger W_0 values. The latter effect overcomes the former in the diffusions over the W_0 range. The slight differences in the viscosities between the zinc and cadmium systems are not clearly explainable. The relationship between the viscosity and the diffusion coefficients for water and the metal complexes will be discussed below.

3.4. TEM photographs

TEM photographs for the $\text{ZnCl}_2(\text{oct-en})_2$ system have been previously reported [7]. Fig. 4(a)–(c) are those for the $[\text{Pd}(\text{oct-en})_2]\text{Cl}_2/\text{water}/\text{chloroform}$

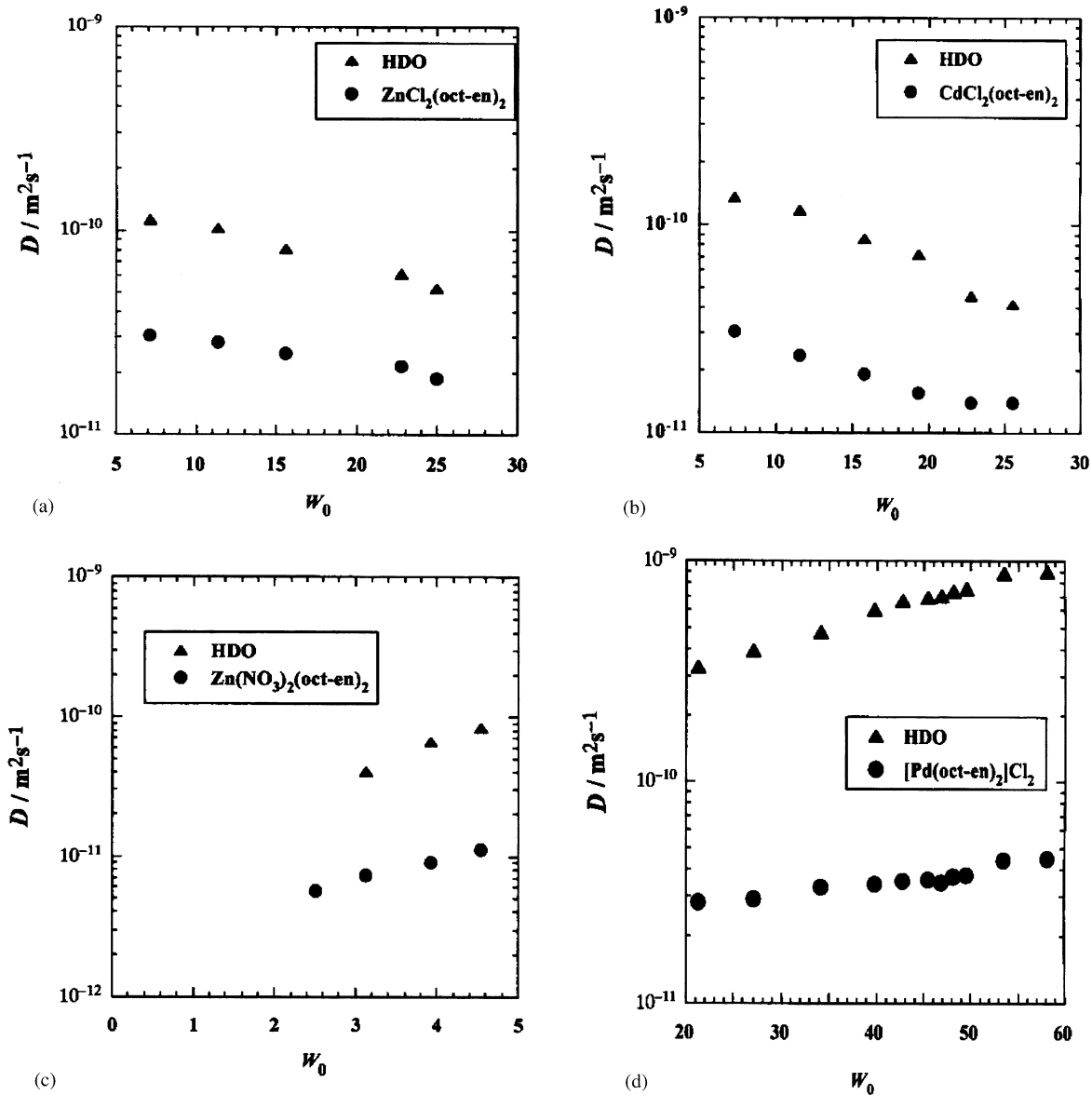


Fig. 2. Self-diffusion coefficients for water and the complexes depending on the water content. (a) $\text{ZnCl}_2(\text{oct-en})_2$ /water/benzene system, (b) $\text{CdCl}_2(\text{oct-en})_2$ /water/benzene system, $[\text{MCl}_2(\text{oct-en})_2]$ in benzene = 1.04 mol kg^{-1} . (c) $\text{Zn}(\text{NO}_3)_2(\text{oct-en})_2$ /water/benzene system. $[\text{Zn}(\text{NO}_3)_2(\text{oct-en})_2]$ in benzene = 2.02 mol kg^{-1} . (d) $\text{PdCl}_2(\text{oct-en})_2$ /water/chloroform system. $[[\text{Pd}(\text{oct-en})_2]\text{Cl}_2]$ in chloroform = 1.04 mol kg^{-1} .

form system depending on the water content. We can see that at $W_0 = 22$ the smaller W/O microemulsion domains (the radii are around 20–25 nm) are collected to form larger domains of around 500 nm size. This kind of structure has been reported

for the aqueous cetyltrimethylammoniumbromide solution containing *N*-methylidiphenylamine or 9-anthrylmethanol [15]. This structure seems to be an onset of the larger aggregate domains and is convenient for hydrated ions to hop from one

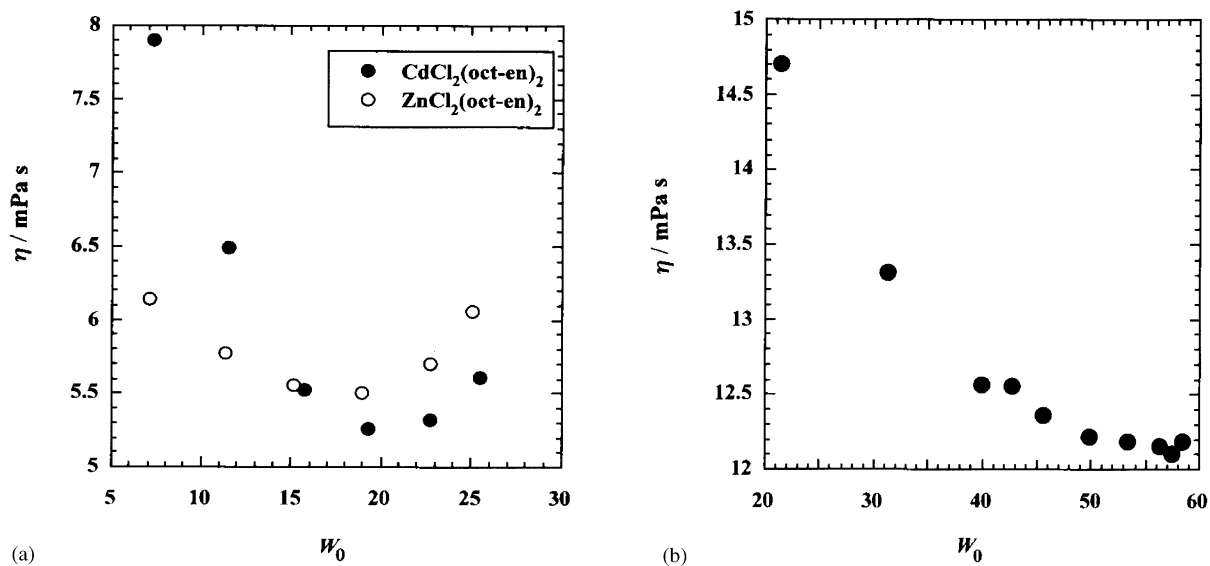


Fig. 3. Viscosities of the (a) $\text{ZnCl}_2(\text{oct-en})_2$ and $\text{CdCl}_2(\text{oct-en})_2$ in water/benzene solutions and (b) $[\text{Pd}(\text{oct-en})_2]\text{Cl}_2$ in water/chloroform solutions depending on the water content. All the complex concentrations in benzene (a) and chloroform (b) are 1.04 mol kg^{-1} .

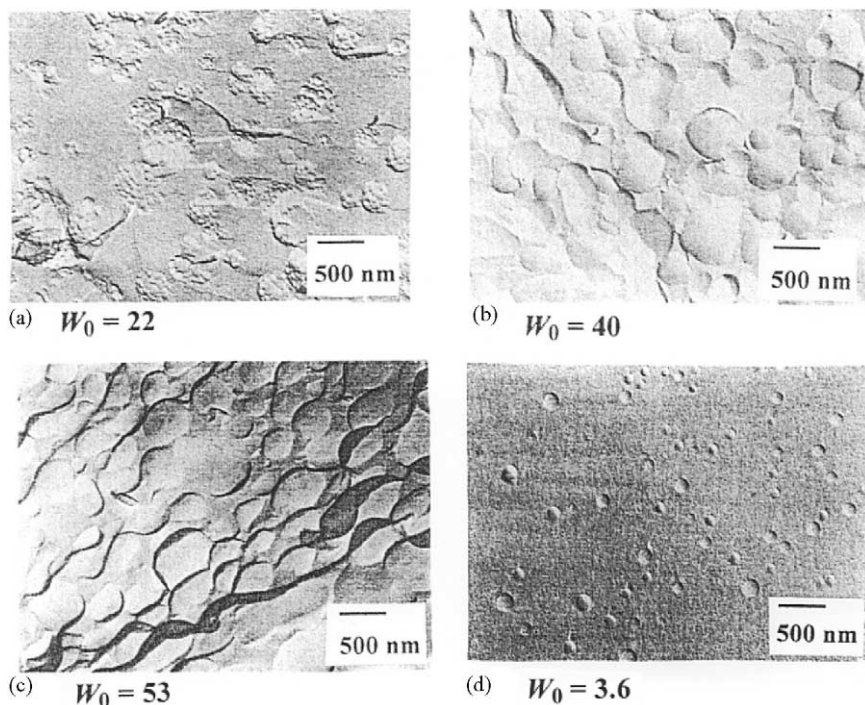


Fig. 4. (a)–(c) TEM photographs of the $[\text{Pd}(\text{oct-en})_2]\text{Cl}_2/\text{water}/\text{chloroform}$ system depending on water content (W_0). $[[\text{Pd}(\text{oct-en})_2]\text{Cl}_2]$ in chloroform = 1.0 mol kg^{-1} . (d) TEM photograph of $\text{Zn}(\text{NO}_3)_2(\text{oct-en})_2/\text{water}/\text{benzene}$. $[\text{Zn}(\text{NO}_3)_2(\text{oct-en})_2]$ in benzene = 2.0 mol kg^{-1} .

water-droplet to the neighboring one in the assembly. This is different from those in the $\text{ZnCl}_2(\text{oct-en})_2$ [7] or $\text{Zn}(\text{NO}_3)_2(\text{oct-en})_2/\text{water}/\text{benzene}$ systems at smaller water content ($W_0 = 3.6$) (Fig. 4(d)) where the uniform-sized small water clusters are homogeneously dispersed.

Fig. 4(b) and (c) show that the sizes of the water domains in the microemulsion structures are larger than those at $W_0 = 22$ and that the structure is close to the bicontinuous one. Under these conditions, the assemblies of the smaller water domains (W/O microemulsion) are disappeared. The structure of the microemulsion is not so drastically changed in the experimentally observed W_0 range as observed for the zinc complex system at $[\text{ZnCl}_2(\text{oct-en})_2] = 2.02 \text{ mol kg}^{-1}$ [7] while the size of water domains increases. Fig. 4(d) shows that the water domains in the $\text{Zn}(\text{NO}_3)_2(\text{oct-en})_2$ system have droplet shapes; in this system, the homogeneous solution can be formed under the condition only where the W_0 value is very small.

We now estimate the Stokes radii (R_0 in nm unit) for the spherical aggregates of the metal complex surfactants from the following Stokes–Einstein equation:

$$R_0 = \frac{22.0}{\eta_0 D} \quad (1)$$

where η_0 is the viscosity of the neat solvent (in mPas unit) and D the self-diffusion coefficients (in $10^{-11} \text{ m}^2 \text{ s}^{-1}$ unit) for the metal complex surfactants.

When we neglect the aggregate interactions and the obstruction effects, the largest R_0 value should be estimated. The R_0 values thus obtained were 11–14 nm for the palladium(II) chloride system and 13–20 nm for the zinc(II) complex system using $\eta_0 = 0.512 \text{ mPas}$ and 0.564 mPas for chloroform and benzene, respectively, at 30°C [16]. These estimated sizes are comparable to those for the smallest spherical domains depicted in Fig. 4(a) and (d). If the obstruction effects on the viscosities and on the self-diffusions are significant, the effective sizes of the water pools are smaller than those estimated above. Thus it is probable that we can observe only the larger domains of water pools by the TEM photographs, whereas there are many

smaller water-pools having similar shapes as those described in Fig. 4.

3.5. Electric conductivities and percolation in the $\text{ZnX}_2(\text{oct-en})_2/\text{H}_2\text{O}/\text{benzene}$, $\text{CdCl}_2(\text{oct-en})_2/\text{H}_2\text{O}/\text{benzene}$, and $[\text{Pd}(\text{oct-en})_2]\text{Cl}_2/\text{H}_2\text{O}/\text{chloroform}$ systems

The percolation is one of the unique properties in microemulsion systems and the mechanism is still controversial [19b, 21–24]. The present systems are appropriate to compare the extent of the percolation phenomenon by focusing on the head-group–counterion interactions; the surfactants have similar empirical formula but their metal–counterion interactions are significantly different.

The electric conductivities of the microemulsion systems are expressed as functions of the water content as shown in Fig. 5.

We can see the following contrast features. The slopes are negative in the $\text{ZnCl}_2(\text{oct-en})_2$ and $\text{CdCl}_2(\text{oct-en})_2$ systems (Fig. 5(a)), while it is positive in the $\text{Zn}(\text{NO}_3)_2(\text{oct-en})_2$ system (Fig. 5(b)) and rough trend is also positive in the $[\text{Pd}(\text{oct-en})_2]\text{Cl}_2$ system (Fig. 5(c)). Furthermore, the absolute values of the electric conductivities in the $[\text{Pd}(\text{oct-en})_2]\text{Cl}_2$ system are 300–1000 times larger than those in the $\text{ZnCl}_2(\text{oct-en})_2$ and $\text{CdCl}_2(\text{oct-en})_2$ systems and those in the $\text{Zn}(\text{NO}_3)_2(\text{oct-en})_2$ system are 10–100 times larger in the similar W_0 ranges. The ionicity of the nitrate–zinc(II) bond is closer to that of the chloro–zinc(II) bond in comparison to the palladium(II)–chloride bond in the crystal state according to the X-ray crystallographic analysis [6] and the solvent of the two zinc(II) systems is the same (benzene). The single phase of the $\text{Zn}(\text{NO}_3)_2(\text{oct-en})_2$ system is formed only at smaller W_0 values and the shape of the water domains shown in Fig. 4(d) is unfavorable for the percolation. However, the electric conductivity in the $\text{Zn}(\text{NO}_3)_2(\text{oct-en})_2$ system is appreciably larger than that in the $\text{ZnCl}_2(\text{oct-en})_2$ system [25]. This “pre-percolation phenomenon” occurs probably through the hydrated nitrate ions because of its weaker ligating ability.

In the dichloro–zinc(II) system, even if the structure of the microemulsions is changed from

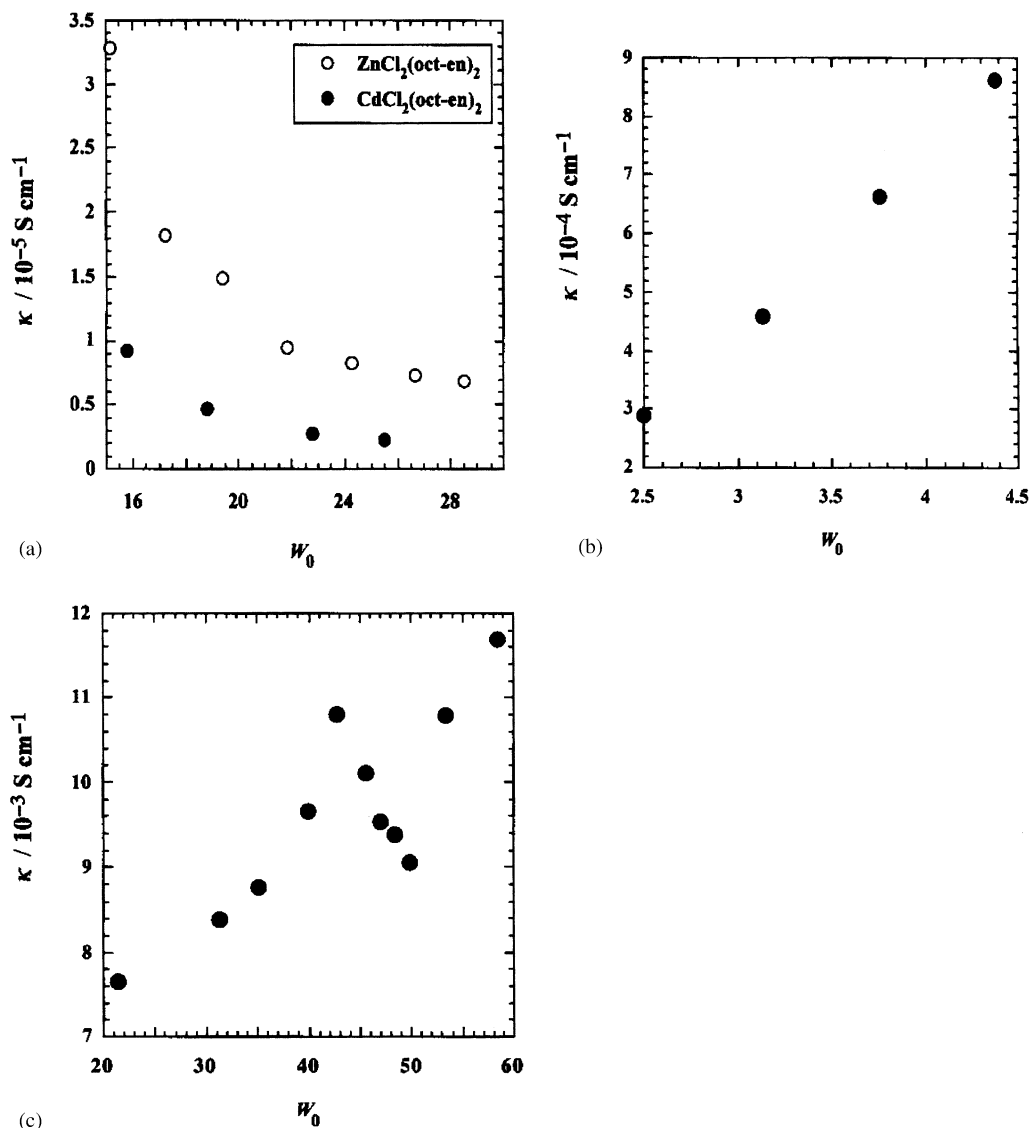


Fig. 5. Electric conductivities for the $\text{MX}_2(\text{oct-en})_2/\text{water}/\text{benzene}$ (or chloroform) systems depending on water content. (a) $\text{ZnCl}_2(\text{oct-en})_2$ and $\text{CdCl}_2(\text{oct-en})_2$ in water/benzene solutions, $[\text{MCl}_2(\text{oct-en})_2]$ in benzene = 1.04 mol kg^{-1} . (b) $\text{Zn}(\text{NO}_3)_2(\text{oct-en})_2/\text{water}/\text{benzene}$ system. $[\text{Zn}(\text{NO}_3)_2(\text{oct-en})_2]$ in benzene = 2.02 mol kg^{-1} . (c) $[\text{Pd}(\text{oct-en})_2]\text{Cl}_2/\text{water}/\text{chloroform}$ system. $[[\text{Pd}(\text{oct-en})_2]\text{Cl}_2]$ in chloroform = 1.04 mol kg^{-1} .

the W/O droplet to the bicontinuous phase in the component range studied here [7], the electric conductivities are very small and thus the percolation phenomenon hardly occurs. The decrease in the diffusions (Fig. 2(a) and (b)) and electric

conductivities in the $\text{ZnCl}_2(\text{oct-en})_2$ and $\text{CdCl}_2(\text{oct-en})_2$ systems with increasing water content can be explained by the growth of the water domains or of the metal–complex aggregates. For the electric conductivity, an increase in the ion-

binding of the counter ions accompanying with the growth of the aggregates and/or a dilution with an addition of water may be effective.

The increase in the electric conductivities with an increase in the water content for the chloride ions in the palladium(II) complex and for the nitrate ion in the zinc(II) complex can be attributed to the pre-percolation phenomenon. This effect would overcome both the dilution effect or the counterion-binding effect accompanying with the growth of the aggregates. The electric conductivities of the palladium system are appreciably larger than those of the other systems, and it is characteristic that there is a sharp peak at $W_0 = 43$, while the rough trend of the slope is positive (Fig. 5(c)). According to the TEM photographs (Fig. 4(a)–(c)), the morphologies of the palladium system gradually change from the W/O microemulsion structure to the bicontinuous one in the ranges of the electric conductivities studied here, and we can see that at $W_0 = 22$ the smaller W/O microemulsion clusters are collected to form larger clusters. This structure seems to be convenient for the pre-percolation. The higher electric conductivities can be attributed to the movement of the hydrated chloride ions in the W/O microemulsion [21]. The TEM photograph (Fig. 4) shows that the water pool expands above $W_0 = 40$ and an onset of the bicontinuous appears, and therefore, the pre-percolation would occur more likely at larger W_0 values. A dilution with an addition of water, however, tends to make the electric conductivities decrease, or a progress of the chloride-ion binding to the palladium complex aggregates by the formation of larger aggregates also makes the electric conductivities decrease [18–21]. These two opposite effects may produce a peak in the conductivity versus water content plot.

The profile in the conductivity versus water content plot in the palladium system is similar to that observed in the microemulsions of ionic surfactants so far reported, such as an AOT system [19–24]; however, in the systems hitherto reported the peak appears under the condition where the electric conductivities are much smaller (and thus the percolation slightly occurs) and the W_0 values are smaller than those in the present system. In the present system, the charge of the

$[\text{Pd}(\text{oct-en})_2]^{2+}$ ion is more favorable for attracting both the counter ions and water molecules than conventional univalent surfactant ions. The larger polarity of chloroform than that of hydrocarbons will also make the palladium–chloride bond more ionic compared with the AOT/hydrocarbon system. Therefore, the effects of the ionic interactions on the conductivities in the $[\text{Pd}(\text{oct-en})_2]\text{Cl}_2$ system will appear to a larger extent than that of the AOT system.

If the mobilities of the hydrated counter anions increase with an increase in the water content, it is more facilitated for the diffusion of water rather than for that of the metal complex. In order to compare the dependence of the diffusion coefficients on the water content between the metal complexes and water in each system, we estimated the slope of $\log D$ versus W_0 plot. The result is listed in Table 1. It is noticeable that the absolute values of the slopes are larger for water than those for the metal complex surfactants in all the systems. This trend is opposite to a general one, i.e. the dependence of the diffusion coefficients on the component concentration is larger for the solutes than for water in aggregation systems [26]. The present results for the dinitrato–zinc(II) and palladium(II) complex systems are consistent with the above explanation: the pre-percolation behavior due to the hydrated anions is more directly correlated with the diffusion of water rather than that of the metal complex surfactant. Similarly, the larger slope for water than that for the metal complex is seen in the dichloro–zinc(II) and cadmium(II) complex systems, although their slopes have an opposite sign to that of the dinitrato–zinc(II) and the palladium(II) complex systems. This trend in the slopes is due to the fact that an addition of water directly assists the growth of the water domains rather than that of the metal complex aggregates, as previously pointed out [7].

Although Eq. (1) is strictly applicable only to dilute solutions, the dependence of ηD values on the solution components is sometimes utilized to determine the extent of the aggregations: the dependence of the ηD values on the solute concentrations is significantly positive in highly aggregation systems while it is nearly constant in

Table 1
The slopes of $\log D$ vs. W_0 plot

System	ZnCl ₂ (oct-en) ₂	CdCl ₂ (oct-en) ₂	Zn(NO ₃) ₂ (oct-en) ₂	[Pd(oct-en) ₂]Cl ₂
Water	-0.017 ± 0.002	-0.030 ± 0.003	0.24 ± 0.03	0.013 ± 0.01
Metal complex	-0.009 ± 0.002	-0.020 ± 0.002	0.14 ± 0.01	0.005 ± 0.001

slightly aggregation systems [17,18]. That is, the dependence of the ηD values on the solute concentrations (corresponding to the reverse W_0) is generally governed by the viscosity rather than by the self-diffusion for the solvent and solute in highly aggregation systems [27]. From this viewpoint, we show the ηD versus W_0 plots for the three dichloro-complex systems in Fig. 6 where the self-diffusion coefficients (D) were used for HDO and for the metal complexes in each case.

It is remarkable that the slope is positive in the palladium system while it is negative in the zinc and cadmium systems. The result in the palladium system shows that the sign of the slope for ηD is the same as those of the self-diffusions for both HDO and the metal complexes and is opposite to those of their viscosities. This trend is also in

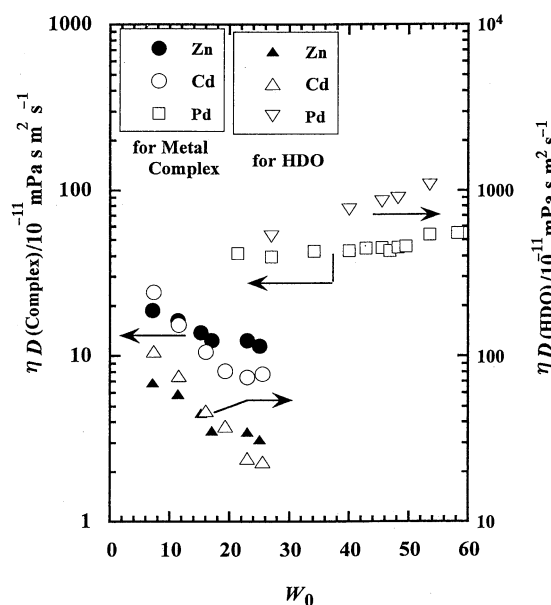


Fig. 6. The product of viscosity (η) and self-diffusion coefficient (D) for water or metal complex surfactants vs. water content (W_0) in the microemulsion systems of ZnCl₂(oct-en)₂, CdCl₂(oct-en)₂, and [Pd(oct-en)₂]Cl₂.

contrast with the general one and suggests that the change in the self-diffusions of the metal complex and of water with an addition of water are governed by the percolation phenomenon in the palladium system rather than by the growth of the metal complex aggregates or of the water domains.

When the pre-percolation effects on the electric conductivities and on the self-diffusions were not detected in the dichloro-zinc(II) and cadmium(II) complex systems, the dependence of the viscosities on the water content is slightly larger than that of the self-diffusions at higher W_0 (W/O microemulsion system) where the growth of the water domains and of the metal complex aggregates is reflected in both the self-diffusions and viscosities. On the other hand, at lower W_0 (sponge to bicontinuous phase), both the viscosities and the self-diffusions decrease with increasing W_0 . The decrease in the viscosities with increasing water content would be a result of a dilution effect, whereas the diffusions of water and the metal complexes depending on the water content reflect the growth of the water domains and of the metal-complex aggregates over the whole W_0 range.

4. Conclusions

The [Pd(oct-en)₂]Cl₂/water/chloroform system provides a unique type microemulsion having characteristic features due to the strong ionicities of the head group and its partial dissociation in the water pools. The pre-percolation behavior in the [Pd(oct-en)₂]Cl₂/water/chloroform and Zn(NO₃)₂(oct-en)₂/water/benzene systems significantly affects not only the electric conductivities but also the self-diffusions of water and of the metal complex surfactants.

The microemulsion systems composed of MCl₂(oct-en)₂ type surfactant showed a variety of the physical properties and the morphologies in

the aggregation systems and thus are appropriate to compare the aggregation behavior among the surfactants having similar empirical formula but different degrees of ionic dissociation.

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