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The Aggregation of Dichlorobis(*N*-hexylethylenediamine)zinc(II) in Water and Water/Chloroform Mixed Solvents

Masayasu Iida,* Keiko Asayama, and Shiho Ohkawa

Department of Chemistry, Nara Women's University, Kitauoya-nishi-machi Nara 630-8506

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The aggregation of a surfactant metal complex, dichlorobis(*N*-hexylethylenediamine)zinc(II) (= $[ZnCl_2(\text{hex-en})_2]$), was studied in such solvents as water, methanol (or water–methanol mixed), and chloroform (or water-containing chloroform). This complex was readily dissolved in water to form aggregates extensively, and was also very soluble in water-containing chloroform to give reversed-type aggregates. In dilute aqueous solutions, the complex was hydrolyzed and precipitated, while the solution was stable at concentrations above 0.25 mol kg^{-1} where the complex aggregates considerably. Precipitation was prevented by the addition of NaCl; this effect can be attributed to chloride-ion binding. The aggregation behavior in solutions was investigated by measuring the self-diffusion coefficients for the complex and of the vapor pressure depressions. The degrees of aggregation of the aqueous and water-containing chloroform solutions were in a similar manner at higher concentrations, although the critical concentration for aggregation in the aqueous solution was considerably smaller than in the chloroform solution. The hydration mode of this surfactant complex is discussed in comparison to the D_2O longitudinal relaxations between the aqueous solutions and the water-containing chloroform solutions.

Surfactant metal complexes are anticipated to have widely interesting structural and reactive properties, since metal complexes can provide various kinds of head groups. One (M. I.) of the present authors with co-workers has found a unique aggregation behavior of single-chain surfactants[1] having a characteristic head group of metal complex ions, or a novel structure of lyotropic liquid crystals composed of a chiral dinuclear chromium(III) complex which does not have the usual amphiphilic structure.[2] Double-chain surfactants, on the other hand, can form more highly ordered aggregates and provide various morphologies compared to the single-chain ones from a view point of moderate hydrophile–lypophile balance (HLB).[3]

Previously, we reported on a preparation of dichloro (or dinitrato) bis(*N*-octylethylenediamine)zinc(II) (= $[ZnX_2(\text{oct-en})_2]$), and revealed that the geometry of the anions is *trans* and the octyl chains are *transoid* in the octahedral molecular structure based on an X-ray crystallographic analysis.[4] When a double-chain surfactant contains a metal complex as the head group, it tends to be easily crystallized, and is useful to study the physical properties in solution from a molecular structural viewpoint.[5,6] We can expect characteristic solvent effects on the aggregation behavior of double-chain surfactants of metal complexes, since such kinds of surfactants often have both strong hydrophilic and lypophilic moieties. Furthermore, surfactant metal complexes sometimes have specific effects of counterion interactions on the aggregation behavior.

In the present paper, we report on the preparation and aggregation behavior of dichlorobis(*N*-hexylethylenediamine)zinc(II) (= $[ZnCl_2(\text{hex-en})_2]$) in water, methanol, and chloroform systems. The physical properties of the solutions were studied using mainly NMR spectroscopies, such as the ^{1}H NMR pulsed field gradient spin-echo (PGSE) method for the complex and water and the deuterium longitudinal relaxations for the water of hydration. Although the present zinc(II) complex is significantly soluble in chloroform, it is appreciably hydrophilic compared to the corresponding octyl complex. This complex, however, is hydrolyzed to form precipitates in dilute aqueous solutions. There was a correlation between the hydrolysis rate and the magnitude of the interactions of the counterions. We focus here on the aggregation behavior of this unique type surfactant by comparing between the water and water-containing chloroform systems.

Experimental

Preparations of $[ZnCl_2(\text{hex-en})_2]$. *N*-hexylethylenediamine (= hex-en) was prepared according to a reported procedure.[7] The $ZnCl_2$ used was a guaranteed reagent from Wako Pure Chemical Industries. $[ZnCl_2(\text{hex-en})_2]$ was obtained using hex-en more than three-times the molar quantity of $ZnCl_2$ in ethanol–water 3:2 solvents. After evaporation of the solvent, the residual water of the crystal was removed by coevaporation with benzene 2–3 times. The excess hex-en ligand was removed by washing with diethyl ether. The crystal was obtained by crystallization 3 times from ethanol. Anal. Found: C, 45.32; H, 9.69; N, 13.17%. Calcd for $[ZnCl_2(\text{hex-en})_2]$: C, 45.24; H, 9.49; N, 13.19%. As previously reported,[4] we performed an X-ray crystallographic analysis for the corresponding *N*-octylethylenediamine complexes of the nitrate and chloride. From the results, we can assume the structure of the present complex in a crystal to be shown in Fig. 1.

Solvents and Reagents. Methanol was dried over a molecular sieve (3A) and then distilled. Chloroform was purified by extracting out a trace amount of impurity ethanol with the addition of water, dried on calcium chloride, and then distilled before use. The water contents in the neat methanol and chloroform used were

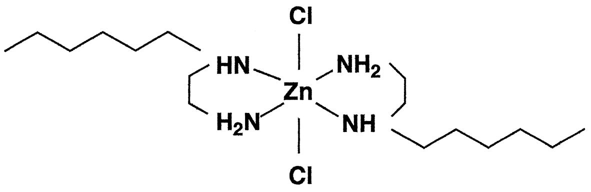

Fig. 1. A molecular structure of the [ZnCl$_2$(hex-en)$_2$] complex in crystal.

0.14 wt% and 0.0078 wt%, respectively, determined by Karl-Fischer titration. By dissolution of the anhydrous complex crystal into chloroform, the water was incorporated to be 0.033 wt% at 0.25 mol kg^{-1}. Although this gives a small w_0 value (0.07), the effect on the aggregation may be significant. The deuterated solvents (D$_2$O, CDCl$_3$, d_4-methanol (= MeOD), and d_6-ethanol (= EtOD)) were supplied by Merck Co. Water was distilled twice and ethanol once before use. The dodecyltrimethylammonium chloride (DodTMACl) was supplied by Tokyo Kasei Ltd.

Solubility Diagrams for [ZnCl$_2$(hex-en)$_2$]/H$_2$O/Organic Solvent Systems. For the ternary system of [ZnCl$_2$(hex-en)$_2$]/H$_2$O/(chloroform or methanol), we determined the components which form the single liquid-phase (usual solutions or normal micelle (aggregate)) solutions (L$_1$) in methanol/water, or reversed-type aggregate solutions (L$_2$) in water/chloroform by a visual observation at 30 ± 0.5 °C. The L$_2$ phase was identified from the relative self-diffusion coefficients of water to those of organic solvents.

In water/organic mixed-solvent systems, the concentrations were expressed in mol kg^{-1} unit, where the solvent weight was for water + methanol in the water/methanol system or for chloroform in the (small amounts) water/chloroform system. The composition of the water/methanol mixed solvent system was expressed by wt%.

Chloride-Ion Activities Using Ion-Selective Electrode. The degree of chloride-ion dissociation is necessary to estimate the extent of the self-aggregation of [ZnCl$_2$(hex-en)$_2$] from the vapor-pressure depression or the diffusion coefficients. The degree was determined from the chloride-ion activities measured by an ORION 701A ion meter equipped with the following appropriate electrodes at 25 ± 1 °C. An ORION Model 96-17B Combination Chloride Electrode was used for aqueous solutions, while for methanol solutions a Ag/AgCl electrode made from a Beckman silver electrode according to the Brown's method[8] was used referred to a calomel reference electrode, which was an ORION 90-02 with a KNO$_3$–agar salt bridge. The calibrations of aqueous and methanol solutions were made by sodium chloride and tetraethylammonium chloride (TEACl) solutions, respectively. The Nernst slopes were −57 mV and −47 mV for the aqueous NaCl and TEACl methanol solutions, respectively. In the methanol solution, we determined the amount of free chloride-ion from [ZnCl$_2$(hex-en)$_2$] by assuming that the TEACl was completely dissociated. Similar measuremets were performed for aqueous zinc(II) chloride and dodecyltrimethylammonium chloride (DodTMACl) solutions for a comparison.

Measurements. Vapor Pressure Depression. The vapor-pressure depressions for the aqueous, methanol, and chloroform solutions were measured with a Knauer Vapor Pressure Osmometer (VPO) at 37 °C (water) or 45 °C (methanol and chloroform). The magnitude of the depression is proportional to the difference in temperature (ΔT) between a solvent-wetted thermistor and a solution-wetted one. If the solute is a non-electrolyte, we can write

$$\Delta T = \kappa \frac{m'}{M_1}, \tag{1}$$

where κ is a constant depending on the solvent and the apparatus used, M_1 the apparent molecular weight of the solute, and m' the solute concentration in g kg^{-1} unit. We drew a ΔT vs m' plot using an aqueous sodium chloride solution and a benzil methanol solution as standards for the aqueous and methanol solutions, respectively. The degree of dissociation of chloride ions from the complex was estimated from the chloride-ion selective electrode, and the result was used for an analysis of the vapor-pressure depression data. The difference in the dissociation–association equilibrium between the two observation temperatures (27 and 37 or 45 °C) is assumed to be negligible. We determined the apparent molecular weights, or the aggregation numbers, by considering the degree of chloride-ion dissociations. For the methanol solution, at higher concentrations (above 0.8 mol kg^{-1}) the depression reading was unstable, or the scale was exceeded and therefore we could not perform the measurement. In the chloroform system, the VPO was measured under the condition where small amounts of water (the [water]/[complex] ratio is around unity) were contained. The small amounts of water may not have a direct influence on the measurements.[9]

Viscosities. The kinematic viscosity (ν) was measured with a Cannon–Fenske capillary viscometer at 27.00 ± 0.05 °C in water and methanol or at 30.00 ± 0.05 °C in chloroform. The shear viscosity (η) was obtained from the relationship $\nu = \eta/\rho$, where the density (ρ) was measured by an Ostwald-type picnometer.

NMR Measurements. The ^{2}H(D), ^{13}C, and ^{35}Cl NMR spectra were obtained on a JEOL GX-270 FT NMR spectrometer operating at 41.5, 67.9, and 26.5 MHz, respectively. The longitudinal relaxation time (T_1) for D$_2$O was obtained by the inversion-recovery method, using a pulse sequence of $(-180°$ pulse-t-$90°$ pulse-τ-$)_n$. For measurements of T_1, ten different pulse intervals (t) were used with a waiting time (τ) of more than $6T_1$. The D spectra were observed from 5% (aqueous or water/methanol solutions) or 20% (water/chloroform solutions) enriched D$_2$O. The T_1 measurements for D$_2$O were also performed at 13.7 MHz with a JEOL FX-90 FT NMR spectrometer to see the frequency dependence.

The longitudinal relaxation rate for D$_2$O (nuclear quantum number is 1) is expressed as

$$R_1(\omega_0) = \frac{3}{2}\pi^2\chi^2\left[\frac{0.2\tau_C}{1 + \omega_0{}^2\tau_C{}^2} + \frac{0.8\tau_C}{1 + 4\omega_0{}^2\tau_C{}^2}\right], \tag{2}$$

where χ is the quadrupole coupling constant of D$_2$O, τ_C the correlation time for the rotational motion of a water molecule, and ω_0 ($= 2\pi\nu_0$) the nuclear precession frequency. If the motions of water molecules are significantly restricted by the interactions with the zinc(II) complex aggregates, $1/\omega_0$ would be comparable to τ_C, and therefore R_1 would be dependent on the observation frequency (ν_0). The R_1 values at two observation frequencies will in principle give τ_C values using Eq. 2.

Self-diffusion coefficients were measured by the ^{1}H NMR FT-PGSE (Fourier Transform Pulsed Field Gradient Spin-Echo) technique. The measurements were performed on a JEOL FX-90 spectrometer operating at 90 MHz for protons. The spectrometer was equipped with an apparatus for producing a field gradient in the range of 0.3–1.0 T/m. The attenuation of the spin-echo amplitude after the Fourier transformation was sampled as a function of

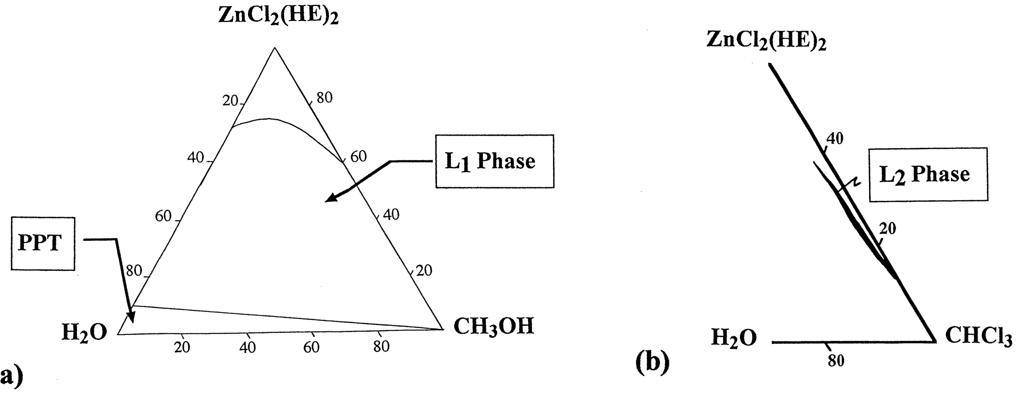

Fig. 2. Ternary solubility phase diagrams for the transparent and homogeneous solutions in the (a) water/methanol and (b) water/chloroform systems. The L_1 region stands for the non-aggregated or normal-type aggregate solutions. The PPT stands for the region where the precipitates are formed. The L_2 phase is reversed-type aggregate solutions.

the duration (δ) of the applied gradient pulses ($0.2 \le \delta \le 7.5$ ms). We followed the ^{1}H NMR signals for the HDO, methanol, and ethanol, and for the methylene protons of the zinc(II) complex. The chemical shifts of the methylene ($(CH_2)_4$) protons in the zinc(II) complex were -2.8 and -3.1 ppm from HDO in the chloroform and water/methanol systems, respectively. In order to obtain clear ^{1}H spin-echo signals, we used MeOD, EtOD, $CDCl_3$, and D_2O solvents, except for the measurements of organic solvents. The diffusion coefficients were reproducible within a 5% error. The temperatures were controlled within 0.5 degree using a JEOL GVT2 temperature control unit. The self-diffusions were measured at 27.00 ± 0.05 °C in water and methanol or 30.00 ± 0.05 °C in chloroform.

Results and Discussion

Solubilities and Decompositions of [$ZnCl_2$(hex-en)$_2$] in Water/Organic Solvent Systems. The [$ZnCl_2$(hex-en)$_2$] complex was easily dissolved in water, methanol, and ethanol, but it was then decomposed in dilute aqueous solutions, i.e., a precipitate was formed below 0.2 mol kg^{-1} at ambient temperature, while above 0.25 mol kg^{-1} the ^{13}C NMR spectrum showed that any change in the complex structure does not occur for at least 1 day. For a 0.05 mol kg^{-1} solution, the precipitation was almost completed within 30 s, and for a 0.1 mol kg^{-1} solution, there was an induction period of 300 s, and then precipitation followed with a half-life period of 80 s at 27 °C. These periods increased with increasing the complex concentration. The CHN elemental analysis for the precipitate[10] suggests that the ligands were significantly dissociated from the zinc(II) center by the hydrolysis. A dissolution of the complex into aqueous nitric acid solutions of pH 1–5 also resulted in precipitation. Precipitation due to hydrolysis is thus different from that for the simple zinc(II) chloride, whose hydrolysis is prevented by a slight acidification.[11] On the other hand, it is characteristic that sodium chloride effectively protects the complex from hydrolysis as follows. The presence of 0.5 mol kg^{-1} of NaCl in a 0.05 mol kg^{-1} [$ZnCl_2$(hex-en)$_2$] solution appreciably retards the hydrolysis; the induction period before precipitation is around half an hour. The presence of 0.2–0.3 mol kg^{-1} NaCl or 0.5 mol kg^{-1} $NaNO_3$ prevents a 0.1 mol kg^{-1} [$ZnCl_2$(hex-en)$_2$] solution from precipitation for more than 1 day. Sodium perchlorate, however, had no effect. These simple salts caused a coaguration at concentrations above 0.1 mol kg^{-1} [$ZnCl_2$(hex-en)$_2$]. The concentration range for stabilizing the aqueous solution was thus very narrow. There was a trend that the stronger ligating anions had larger effects on the protection of the zinc(II) complex solution from precipitation.

In methanol, ethanol, and chloroform, the complex was stable for more than 1 day, even if the solution contained significant amounts of water. We measured the changes in the ^{13}C and ^{1}H NMR spectra while varying the temperatures over 20–40 °C in water and -80 to 40 °C in methanol at 10 °C intervals, respectively; the spectra resulted in only line-broadenings by a slowing down of the motions of the zinc(II) complex ions with lowering the temperatures. The zinc(II) complex was thus stable in the aqueous and methanol solutions when precipitation did not occur. Figure 2 shows the concentration range where the transparent and homogeneous solution is stable for more than one day in the water/methanol and water/chloroform systems. The solubility behavior in the water/chloroform system is characteristic, i.e., the complex could be dissolved in neat chloroform up to 13 wt%, while the solubility was significantly increased with the addition of small amounts of water. This property suggests the formation of reversed-type aggregates in the water/chloroform system.

Degrees of Chloride Ion-Binding to the Zinc(II) Complex Measured by Chloride Ion Selective Electrode in Methanol and Water. We at first measured the chloride-ion activities (a_{Cl^-}) for aqueous $ZnCl_2$ solutions and confirmed that the result was consistent with the previous ones for Zn(II)-Cl$^-$ complexation, i.e., the chloride ions were almost free at concentrations below 0.2 mol dm^{-3}, while they extensively bound to the zinc(II) center at higher concentrations to form $ZnCl^+$, $ZnCl_3^-$, and $ZnCl_4^{2-}$.[12] Because zinc(II) has six coordination sites in solution, the chloride ions can bind to the zinc(II) center in [$ZnCl_2$(hex-en)$_2$], even if the four-coordination sites are occupied by two hex-en ligands. For aqueous DodTMACl and [$ZnCl_2$(hex-en)$_2$] solutions, we analyzed the results for a_{Cl^-} by considering the micelles or aggregate formation. On the basis of a pseudophase model for micellar formation, the aggregation of the complex ion is expressed based on the dissociation and association equilibria, as follows:

$$[ZnCl_2(\text{hex-en})_2] \rightleftarrows [ZnCl(\text{hex-en})_2]^+ + Cl^-, \tag{3}$$

$$n[\mathrm{ZnCl_2(hex\text{-}en)_2}] \rightleftarrows \{[\mathrm{ZnCl(hex\text{-}en)_2}]\}_n{}^{+n\alpha_\mathrm{m}} + n\alpha_\mathrm{m}\mathrm{Cl}^-. \quad (4)$$

In these equilibria, a_{Cl^-} can be appropriately expressed as

$$a_{\mathrm{Cl}^-} = \gamma_{\mathrm{Cl}^-} m = \gamma_-\{m_0 + \alpha_\mathrm{m}(m - m_0)\}, \quad (5)$$

where α_m is the degree of dissociation of chloride ion from the micelle, and m_0 the concentration of free surfactant above cmc. In Eq. 5, γ_{Cl^-} is defined as the apparent activity coefficient of the solution by assuming that [ZnCl$_2$(hex-en)$_2$] is a 1–1 electrolyte. Furthermore, γ_- is the activity coefficient for the chloride ion at a cmc below which the chloride ion is assumed to interact with the surfactant monomers by the Debye-Hückel interaction and, thus, m_0 in Eq. 5 corresponds to [ZnCl(hex-en)$_2{}^+$] in Eq. 3. Equation 5 can be reduced to

$$\gamma_{\mathrm{Cl}^-} = \gamma_-\{\alpha_\mathrm{m} + (1 - \alpha_\mathrm{m})\, m_0 / m\}. \quad (6)$$

The γ_{Cl^-} vs $1/m$ plot will give $\gamma_-\alpha_\mathrm{m}$ from the intercept. Equation 6 would be precisely applicable in dilute solutions. However, a curvature in Fig. 3(c) means that the aggregate formation at higher concentrations and, therefore, the following information, is obtained on the basis of Eq. 6. An inflection point (0.023 mol kg^{-1}) in the aqueous DodTMACl solution (Fig. 3(c)) nearly corresponds to the cmc (0.020 mol kg^{-1}) in the literature.[13] The smaller γ_{Cl^-} values in Fig. 3(a) show that the chloride ions are appreciably bound to the complex in the concentration range where precipitation does not occur. In the methanol solution (Fig. 3(b)), the γ_{Cl^-} values are also small, but the aggregation hardly occurs below 1.0 mol kg^{-1}, as discussed below. Although we showed a γ_{Cl^-} vs $1/m$ plot of Fig. 3(b) for a comparison, we cannot discuss the result in the methanol solution based on Eqs. 3–6. The curvature in Fig. 3(b) could therefore be mainly attributed to an increase in the chloride-ion binding to the zinc(II) complex with an increase in the concentration. In this case, it is reasonable to use the relationship $a_{\mathrm{Cl}^-} = \gamma_{\mathrm{Cl}^-} m = \gamma_-\alpha_{\mathrm{Cl}^-} m$, where a_{Cl^-} is the degree of chloride-ion dissociation from the free zinc(II) complex in methanol. The γ_{Cl^-} value is utilized in obtaining the degree of association from VPO below 1.0 mol kg^{-1}.

In the aqueous zinc(II) complex solution, the critical concentration (cc) for the aggregates could not be detected, but we here assume it to be 0.10 mol kg^{-1}, which was roughly estimated from the measured vapor pressure depression and the tentative depression line by assuming the contribution from the monomer, as described below. We estimated the γ_- values based on the Debye–Hückel equation in aqueous solutions.[14] From the intercepts of the plots in Figs. 3(a) and (c), we thus determined the α_m values and obtained the degrees of Cl$^-$ binding, $\beta_\mathrm{m} = 1 - \alpha_\mathrm{m}$, as follows: 0.85 for the Zn(II) complex (using 0.79 as γ_- at $\mu = 0.1$ mol kg^{-1}) in water and 0.60 for DodTMACl (using 0.88 as γ_- at $\mu = 0.02$ mol kg^{-1}) in water. The last value is close to the literature value (0.58).[16]

The more tight binding of the chloride ion in the zinc(II) complex system than in the DodTMACl system was remarkably observed in the ^{35}Cl NMR spectra. That is, the ^{35}Cl NMR spectra showed very wide and strained signals at any concentrations in both the aqueous and methanol solutions, while for DodTMACl the spectrum was always a simple and sharper one.

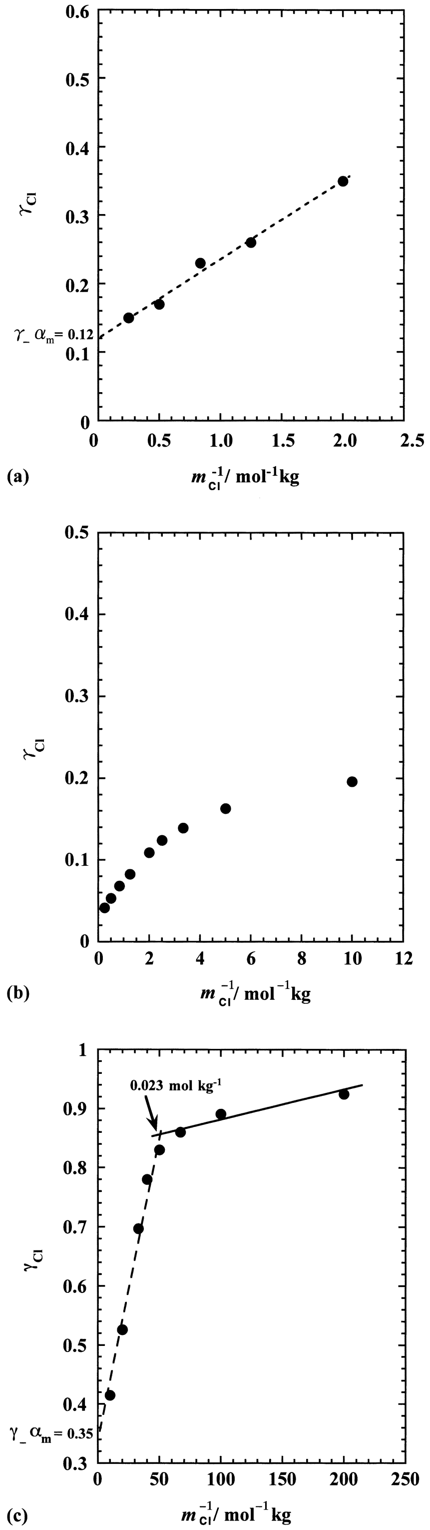

Fig. 3. The γ_{Cl^-} vs $1/m_{\mathrm{Cl}}$ plot for (a) aqueous [ZnCl$_2$(hex-en)$_2$] solution, (b) methanol [ZnCl$_2$(hex-en)$_2$] solution, and (c) aqueous DodTMACl solution. m_{Cl} is the total chloride concentrations.

Vapor-Pressure Depression of the Aqueous and Water/Methanol Solutions. In order to estimate the degree of sur-

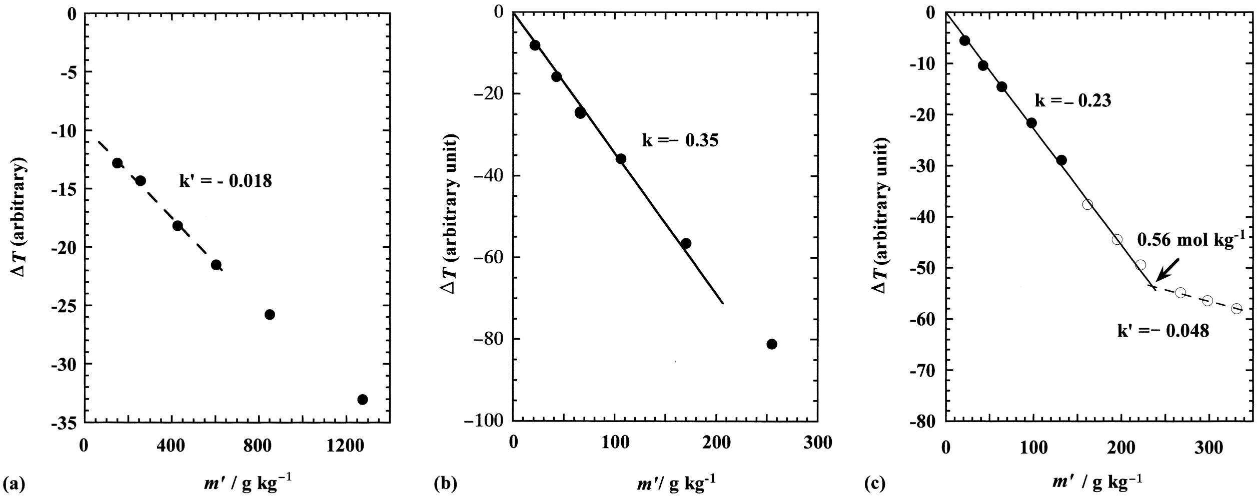

Fig. 4. The vapor pressure depressions of the (a) aqueous, (b) methanol, and (c) water/chloroform [ZnCl$_2$(hex-en)$_2$] solutions as functions of [ZnCl$_2$(hex-en)$_2$] concentrations. The closed circle is under the condition where no water was added and the open one is the result for the system containing small amounts of water. w_0 = [water]/[[ZnCl$_2$(hex-en)$_2$]] = 0.97–1.42. (in chloroform) The broken line in (a) at lower concentration is drawn by assuming $\kappa = -52$ (for aq soln), $M_1 = 425$, and a 1–1 electrolyte for [ZnCl$_2$(hex-en)$_2$] in Eq. 1.

factant aggregates, we measured the vapor-pressure depression; the results are shown in Fig. 4. Because the vapor pressure depression is a colligative property which is proportional to the [solute]/[solvent] molar ratio, as expressed by Eq. 1, the extent of self-associations of the complex ions is estimated by considering the degree of dissociation of chloride ion. In water, the solution is stable well above the cc and the complex extensively aggregated at the concentrations studied. Although the complex decomposed in water at lower concentrations, the monomers or the premicelles should be stable when the micelles coexist. In Fig. 4(a), we draw a calculated line of the vapor-pressure depression for the tentative monomer in the range of precipitation. The crossing point of the two extrapolated lines corresponds to the cc, which is around 0.1 mol kg^{-1}; this value is used above in the calculation of α_m.

Above cc, it is assumed that only equilibrium of Eq. 4 can contribute to the change in the vapor-pressure depression with a change in the concentrations. The slope of the plot in Fig. 4 corresponds to that for the aqueous and methanol solutions; the coefficients (κ) obtained from the standard reagents were −52 for water, −149 for methanol, and −139 for chloroform. By using the γ_{Cl^-} values obtained by the pocedure described above, we estimated the apparent molecular weight (M_1) or the aggregation numbers (n). In this case we used the mean γ_{Cl^-} values in Figs. 3a and b in the corresponding concentration range. The thus-obtained n values are 8.5 in the aqueous solution and 1.1 in the methanol solution. In the latter system, the value is determined at concentrations below 0.6 mol kg^{-1}, above where a precise VPO result was unobtainable due to the instrumental limit, as decribed in the experimental section. If the chloride ion is not completely dissociated in the TEACl methanol solutions used as the calibration reagent, the γ_{Cl^-} value is smaller than that in Fig. 3b, and the resultant n value is closer to 1.0. The degree of aggregation in the aqueous solutions would generally be governed by the alkyl-chain length; furthermore, this surfactant has a large head group for the alkyl-chain size. From these reasons, the aggregation numbers estimated in the present aqueous solutions are smaller than expected from the carbon numbers.[17]

Self-Diffusions and Viscosities in Water and in Methanol. We measured the self-diffusion coefficients for the solvents and surfactants to correlate them with the extent of aggregation; the result in the water/methanol system is shown in Fig. 5(a). An appreciable decrease in the diffusion coefficients of the zinc(II) complex with an increase in the water content means the formation of aggregates. The relationship of the diffusion coefficients (D_0) with the radius (R_0) of the spherical solute at infinite dilution can be expressed by the Stokes–Einstein equation as

$$D_0 = \frac{kT}{6\pi\eta_0 R_0}. \tag{7}$$

The D_0 value for the complex in MeOD, estimated from extrapolation of the linear parts of the D vs concentration plot in Fig. 5, is 9.3 × 10^{-10} m^2 s^{-1}. By using a viscosity of 0.565 mPa s for MeOD (η_0) and by assuming a present complex to be spherical,[18] we estimated the R_0 value to be 0.42 nm. Similarly, D_0 in EtOD was 5.0 × 10^{-10} m^2 s^{-1} (the detailed data are not shown here), and thus the R_0 value is 0.40 nm. These Stokes radii are somewhat larger than the radius (0.25–0.3 nm) of the head group of the complex estimated from an X-ray crystallographic analysis for [ZnCl$_2$(oct-en)$_2$],[4] but the hexyl chain length (it is 0.45 nm if fully extended) does not well contribute to the Stokes radii.

The diffusion coefficient for the free zinc(II) complex in water can be estimated from the experimental value in methanol (9.3 × 10^{-10} m^2 s^{-1}) using Eq. 7, and is around 5.4 × 10^{-10} m^2 s^{-1}, which is appreciably larger than the experimantal value of 1.65 × 10^{-10} m^2 s^{-1} at 0.25 mol kg^{-1} in water. This result also supports the significant aggregation of the zinc(II) complex in water at 0.25 mol kg^{-1}.

A break point in the D vs m^{-1} plot often corresponds to the

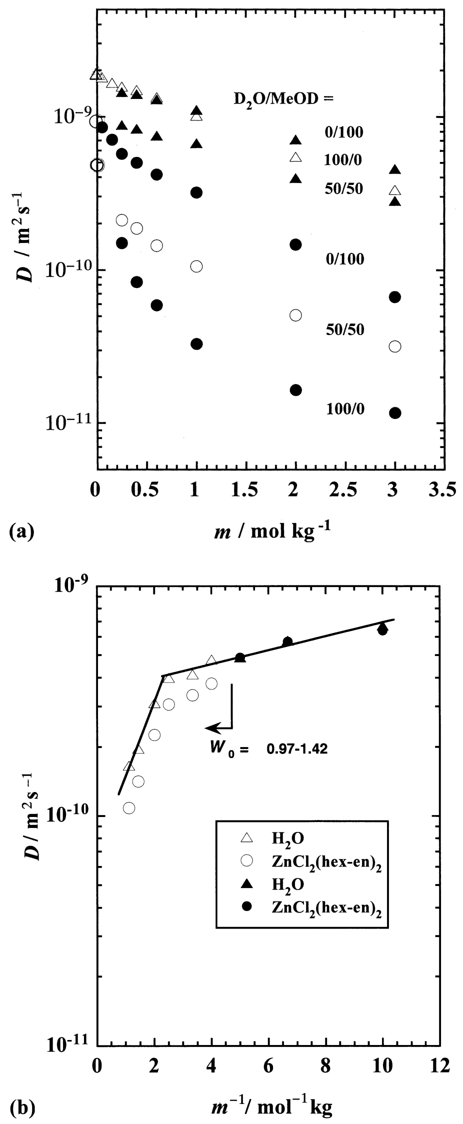

Fig. 5. (a) Self-diffusion coefficients for water (HDO, ▲ or △) and [$ZnCl_2$(hex-en)$_2$] (● or ○) as a function of the [$ZnCl_2$(hex-en)$_2$] concentrations depending on the water/methanol wt%. (b) Self-diffusion coefficients for the solvents and surfactants in the water/chloroform system as a function of the inverse [$ZnCl_2$(hex-en)$_2$] molality. (The closed mark is the result under the condition where no water was added and the open one is with small amounts of water).
The self-diffusions were measured in D_2O and the viscosities were in H_2O. The lines are drawn as an aid to the eye.

critical point for the micellar formation[21] (not shown here for the aqueous and methanol solutions). This kind of plot for the aqueous solution gave no clear break-point, since the concentration range studied was higher than the critical concentration. A similar plot for the methanol solution gave a slight break point at around 1 mol kg^{-1}. This result suggests that even in the methanol solution, the aggregation somewhat occurred at higher concentrations. However, a VPO measurement in methanol could not be performed in the high concentration range and, furthermore, the chloride-ion selective electrode did not detect the break point at around 1 mol kg^{-1} ($m_{Cl}{}^{-1}$ = 0.5 in Fig. 3(b)). The reason for the latter result would be due to the fact that the complex is close to a non-electrolyte in methanol, and that the dissociation of the chloride ion is not sensitive to aggregation.

The $\eta\cdot D$ value (Table 1) significantly increases at higher concentrations (1–2 mol kg^{-1}) in water. A similar trend has also been reported for cluster formation in concentrated $LiPF_6$ propylene carbonate solutions studied by one (M. I.) of us with coworkers.[22]

Aggregation in Water/Chloroform Mixed Solvent System. An enhancement of the solubility in chloroform with an addition of water suggests the formation of reversed-type aggregates. Figure 4(c) shows the vapor-pressure depression and the effect of water on it. This figure furthermore shows that an inflection point is observed at 0.56 mol kg^{-1}. Below this point, the slope of the vapor-pressure depression in Fig. 4(c) gives 1.5-times the molecular weight of the monomer without a break point. This result suggests the formation of smaller aggregates (or premicelles), even below the critical concentration, and that only small amounts of water (w_0 = 0.07 at 0.25 mol kg^{-1} where no water is added) assist in the aggregation of the zinc(II) complex. The incorporation of water for aggregation is due to the hydrophilicity of the head group; on the other hand, the hydrophobic double-hexyl chains would be favorable for dissolution in chloroform. The small [water]/[zinc(II) complex] molar ratios (w_0) suggest that most of the chloride ions are bound to the zinc(II) center.[23] This is supported by the fact that the dissociation of the chloride ion from the zinc(II) complex is slight in methanol, whose dielectric constant is about 7-times larger than that of chloroform. Thus, the zinc(II) complex is regarded as being a non-electrolyte in chloroform; the aggregation number is estimated to be 6.8 above the break point; this value is the average value in the range of w_0 = 0.97–1.42, since the aggregation number is significantly affected by the w_0 value.

The diffusion coefficients of the zinc(II) complex and of water in chloroform are significantly smaller than those in methanol. This result means the formation of larger aggregates in the chloroform system. Furthermore, the diffusion coefficients of solvent chloroform ($8–9 \times 10^{-10}$ m^2 s^{-1}) are much larger than those of water, which are close to those of the zinc(II) complex. This suggests the formation of reversed-type micelles. Figure 5(b) is a D vs m^{-1} plot for the zinc(II) complex and water in the chlororform system, and shows the critical point. That is, the addition of water promotes aggregation, and then the aggregates grow extensively from around 0.5 mol kg^{-1}, which is slightly smaller than the break point observed in the VPO data.

The Stokes radius (R_0), estimated by an extrapolation of the D vs m plot to infinite dilution (D_0 is 7.8×10^{-10} m^2 s^{-1}), is 0.52 nm. At concentrations below 0.5 mol kg^{-1}, the aggregation does not occur extensively. The $\eta\cdot D$ value (Table 1) also significantly increases at higher concentrations (1–2 mol kg^{-1}) in chlroform, as seen in water. The viscosity around the solutes should be significantly different from the shear viscosities because of the complicated interactions between the aggregates at higher concentrations.

An Increase in the Hydration to the Zinc(II) Complex by

Table 1. Viscosities (η) and Their Products ($\eta \cdot D$) with the Diffusion Coefficients of $ZnCl_2(hex\text{-}en)_2$ in Water, Methanol (MeOH), (27 °C) and Chloroform (ClF) (30 °C)

	in Water		in MeOH		in ClF		
m/mol kg^{-1}	η/mPa s	($\eta \cdot D/10^{-12}$ Pa m^2)	η/mPa s	($\eta \cdot D/10^{-12}$ Pa m^2)	m/mol kg^{-1}	η/mPa s	($\eta \cdot D/10^{-12}$ Pa m^2)
0	0.855		0.535		0	0.498	
0.25	1.31	(0.197)	0.667	(0.383)	0.23[a)]	0.805	(0.303)
0.40	2.09	(0.175)	0.751	(0.375)	0.38[b)]	1.17	(0.358)
0.60	3.52	(0.208)	0.974	(0.407)	0.63[c)]	2.14	(0.393)
1.0	10.2	(0.338)	1.29	(0.410)	0.94[d)]	4.73	(0.513)
2.0	27.1	(0.447)	2.99	(0.439)			

$[H_2O]$ = a) 0.03, b) 0.75, c) 1.35, d) 2.66 wt%.

Table 2. Correlation Times for D_2O in H_2O/MeOH Mixed Solvent Systems

H_2O/MeOH (wt%)	m/mol kg^{-1}	0	2.0	3.0
100/0	τ_f/ps	2.85		
	τ_{bs}/ns		2.0	2.2
50/50	τ_f/ps	4.84		
	τ_{bs}/ns		1.4	1.6
30/70	τ_f/ps	4.54		
	τ_{bs}/ns			1.3

Hydration number is assumed as 1 for τ_{bs}.

the Aggregation Studied by D_2O NMR Relaxations. The decrease in the self-diffusions of water at higher concentrations would be due to hydration of the $[ZnCl_2(hex\text{-}en)_2]$ complex by self-associations. This result is different from that in a long-chain surfactant sytem, such as dodecyl sodium sulfate (SDS), where the diffusion coefficient of water is nearly constant above cmc.[24] This difference in the diffusion coefficients of water between the present system and the SDS one is attributed to the larger hydrophilicity of the present complex.

D_2O NMR relaxations will provide more microscopic and detailed information on the hydration than the self-diffusions of water. Figures 6(a)–(c) show the D_2O NMR relaxation rates as a function of the zinc(II) complex concentrations in water and/or methanol measured at two observation frequencies. There is a clear trend that the motions of the water molecules are largely restricted by hydration of the zinc(II) complex, and that the difference in the relaxation rates between the two observation frequencies gradually increases with an increase in the complex concentrations.

The relaxation rates can be expressed as a linear combination of the two states:

$$R_1 = p_f R_{1f} + p_b R_{1b}, \tag{8}$$

$$p_f + p_b = 1, \tag{9}$$

where the subscript f denotes the free state and b the binding state.

The slope of the plot shows the contribution from the water bound to the zinc(II) complex, and that the [bound water]/[free water] molar ratio linearly increases with increasing the zinc(II) complex concentration. As aggregation occurs in aqueous solutions, even in the lower concentration range, the difference in the relaxation rates between the two observation frequencies is detected at a lower concentration. (Fig. 6(a)) However, at higher concentrations, the absolute values of the relaxion rates are larger in the methanol-rich solution (Figs. 6(b) and (c)) than in the aqueous solution (Fig. 6(a)), since the ratio of the hydration water to the bulk water should be appreciably larger.

We now estimate the rotational correlation times of water molecules from the results in Fig. 6. From Eq. 2, the relaxation rate for the motionallly faster water molecule (under extreme narrowing condition) can be expressed as[25]

$$R_{1f} = \frac{3}{2}\pi^2\chi^2\left(1 + \frac{\eta'^2}{3} - A^2\right)\tau_f, \tag{10}$$

where η' is the asymmetry parameter of the field-gradient tensor and A the parameter related to the order parameters. For simplicity, we here assume $\eta'^2, A^2 \ll 1$. The intercept in Fig. 6 was determined for each solvent and the estimated rotational correlation times (τ_f in Table 2) are nearly proportional to the viscosity.

When the extreme narrowing condition does not hold, the difference in the relaxation rates between the two observation frequencies is significant due to the motionally slower water bound to the zinc(II) complex aggregates. We can thus, in principle, estimate the correlation times of the hydration water from the R_1 values at the two observation frequencies. The difference for the aqueous solution can be written as

$$\begin{aligned} &R_1(13.7\,\text{MHz}) - R_1(41.5\,\text{MHz}) = \\ &729 \times \frac{n_h}{55.6} m \times \left\{\left[\frac{0.2\tau_{bs}}{1 + 0.00746\tau_{bs}^2} + \frac{0.8\tau_{bs}}{1 + 0.0298\tau_{bs}^2}\right] - \left[\frac{0.2\tau_{bs}}{1 + 0.0681\tau_{bs}^2} + \frac{0.8\tau_{bs}}{1 + 0.272\tau_{bs}^2}\right]\right\}, \end{aligned} \tag{11}$$

where n_h is the hydration number of the zinc(II) complex, χ is taken as 222 kHz,[26] and τ_{bs} is represented in units of ns.

Figures 6(a)–(c) show that the difference in the relaxation rates between the two observation frequencies appears above 1.0 mol kg^{-1}. In the water/methanol systems, it can be assumed that the water molecules selectively solvate to the head group, rather than the methanol ones, and therefore the 55.6 value in Eq. 11 is multiplied by x, being the weight fraction of water. We thus determined the τ_{bs} values at concentrations where the differences in the relaxation rates are significant; the results are listed in Table 2. In this table the hydration number is assumed to be unity; if n_h is larger than unity, the correlation times are reduced by a factor of $1/\sqrt{n_h}$. There is a trend that the correlation times significantly increase with an increase in

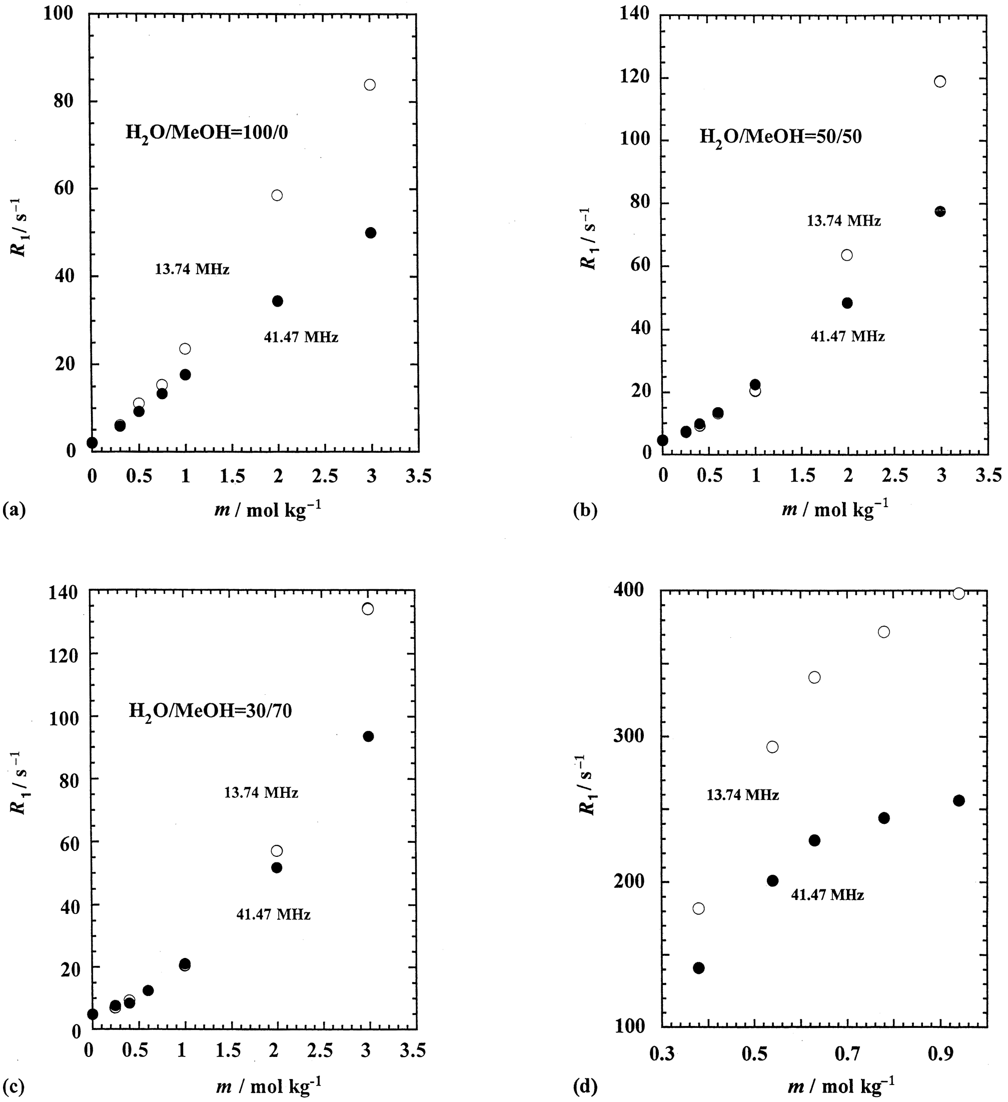

Fig. 6. D_2O NMR longitudinal relaxation rates measured at two observation frequencies as a function of $[ZnCl_2(hex\text{-}en)_2]$ concentrations for (a) aqueous solutions, (b) water/methanol = 50/50 wt% solutions, (c) water/methanol = 30/70 wt% solutions and (d) water-containing chloroform system.

the water content. This would arise from an increase in the extent of the aggregations of the zinc(II) complex.

The larger R_1 values in the water/chloroform system (Fig. 6(d)) compared to those in the water/methanol system show that the water molecules are motionally restricted to a larger extent in the chloroform system. In this system, all of the water molecules are assumed to bind to the zinc(II) complex with slower motions; their correlation times are designated as τ_{bs}. Therefore, the ratio of the relaxation rates measured at two observation frequencies can be written as

$$\frac{R_1(13.7\,\mathrm{MHz})}{R_1(41.5\,\mathrm{MHz})} = \frac{\left[\dfrac{0.2\tau_{bs}}{1 + 0.00746\tau_{bs}{}^2} + \dfrac{0.8\tau_{bs}}{1 + 0.0298\tau_{bs}{}^2}\right]}{\left[\dfrac{0.2\tau_{bs}}{1 + 0.0681\tau_{bs}{}^2} + \dfrac{0.8\tau_{bs}}{1 + 0.272\tau_{bs}{}^2}\right]}, \tag{12}$$

where τ_{bs} is represented in units of ns. The observed relaxation rate gives the τ_{bs} value at each concentration; the results are listed in Table 3 and 4.

Table 3. Correlation Times for D_2O in H_2O/ClF Mixed Solvent Systems (27 °C)

m/mol kg^{-1}	0.38	0.54	0.78	0.94
τ_{bs}/ns	12	16	17	19

The thus-obtained correlation times are significantly larger than the τ_{bs} values in the water/methanol systems in Table 2. The values in Table 2 are somewhat ambiguous due to the assumptions of the quadrupole coupling constant (χ) and the hydration number. However, hydration numbers larger than unity lead to smaller τ_{bs} values than those estimated here in the water/methanol system, i.e., the difference should be larger than those obtained here. It is therefore clear that the hydration water is more motionally restricted in the water/chloroform system than in aqueous solutions. This result is consistent with the diffusion data (Figs. 5(a) and (b)). The diffusions of the

Table 4. Correlation Times (τ_{bs}/ns) for D_2O in H_2O/ClF Mixed Solvent Systems Depending on Temperature

T/K	0.38 mol kg^{-1}	0.54 mol kg^{-1}	0.78 mol kg^{-1}	0.94 mol kg^{-1}
305	9	10	15	22
310	7	8	10	14
315	6	7	9	10

zinc(II) complex are, on the other hand, significantly slower in the aqueous solutions than in the water-containing chloroform solutions (Figs. 5(a) and (b)). It is thus characteristic that the motion of the hydration water is more restricted in the water-containing chloroform solutions both translationally and rotationally than in the aqueous solutions, whereas the zinc(II) complex is more motionally restricted in the latter system. This opposite trend can be attributed to the fact that in the chloroform system there is no bulk water that is exchangeable with the hydration water.

The relaxation times at 305–315 K were also measured in the water/chloroform systems; the correlation times obtained by the above method are listed in Table 4. From an Arrhenius plot of the correlation times at 300–315 K, we estimated the activation energies for the motions of water molecules; the results are 42 ± 8 kJ mol^{-1} in the range of 0.38–0.94 mol kg^{-1}. These values are appreciably larger than that (20 kJ mol^{-1}) of the neat water molecules.

In conclusion, a moderate balance of the hydrophilicity-lypophilicity of the surfactant metal complex causes an extensive aggregation in both water and water-containing chloroform. The aggregation behavior and the hydration mode were compared between the normal and reversed-type aggregates in the same concentration range.

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10 The CHN elemental analysis for the precipitates did not give reproducible results. For example, Anal. Found: C, 16.25; H, 3.54; N, 1.57%. Calcd for $[ZnCl_2(hex\text{-}en)_2]$: C, 45.24; H, 9.49; N, 13.19%.

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14 For the estimation of γ_-, we use the following Debye–Hückel equation for the $\gamma_\pm$ value

$$\log \gamma_\pm = -\frac{A\sqrt{\mu}}{1 + Ba\sqrt{\mu}},$$

where A and B are the Debye–Hückel parameters, a the closest distance of approach of ions, and μ the ionic strength.[15] In water, A and B are 0.5133 dm$^{3/2}$ mol$^{-1/2}$ and 0.3355 × 10^{10} m^{-1} dm$^{3/2}$ mol$^{-1/2}$, respectively, at 27 °C. In this system, we take 0.55 nm as an a parameter from the size of the zinc(II) complex. The ionic strength at cmc is somewhat ambiguous and we assume that $[ZnCl_2(hex\text{-}en)_2]$ behaves as 1:1 electrolyte at and below cmc. Although this assumption somewhat affects the result of α_m, the magnitudes are not large. For example, $\gamma_\pm = 0.749$ at $\mu = 0.2$ mol kg^{-1} and 0.790 at $\mu = 0.1$ mol kg^{-1} in water.

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18 The deuterated factors are 1.05 for MeOD and 1.19 for D_2O. The factor for MeOH is estimated from the results of the CH_3OD and C_6D_6 neat solvents.[19, 20]

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