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# Inflection Points in the Coordination Number around $Ce^{3+}$ and $CeF^{2+}$ in a Mixed System of Methanol and Water

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The stability constants ($\beta_{1(F)}$) of the monofluoro complex of Ce(III) and those ($\beta_{1(Cl)}$) of the monochloride solvent-shared ion-pair of Ce(III) have been determined in mixed solvents of methanol and water at 0.10 and 1.00 mol dm$^{-3}$ ionic strengths, respectively. The variation in the $Ce^{3+}$–$Cl^-$ distance, which was calculated using the Born-type equation and the Gibbs' free energy derived from $\beta_{1(Cl)}$, indicated a change in the coordination number (*CN*) of $Ce^{3+}$ from $CN = 9$ to a mixture of $CN = 9$ and 8 in the vicinity of the mole fraction of methanol ($X_s$) = 0.23. The variation in $\ln \beta_{1(F)}$ with an increase in $X_s$ in the mixed-solvent system showed an acute-angled convex inflection point at $X_s$ = about 0.22 and an acute-angled concave inflection point in the vicinity of $X_s = 0.28$. It was concluded that the convex inflection point denoted the same change in the *CN* of $Ce^{3+}$ from $CN = 9$ to a mixture of $CN = 9$ and 8, and that the concave point was a change in the *CN* of Ce(III) in $CeF^{2+}$ from $CN = 9$ to a mixture of $CN = 9$ and 8.

Knowledge about the properties of solvated ions is of fundamental importance in order to understand the chemical behavior of ions in solutions. Kanno and Hiraishi[1] have determined the hydration number in the primary hydration sphere of tripositive lanthanoid ions ($Ln^{3+}$) using Raman spectroscopic analysis. They showed that the hydration number of $Ce^{3+}$ was 9. Fourest et al.[2] showed $La^{3+}$ and $Pr^{3+}$ at the position of hydration number 9 on an S-shaped variation curve of the primary hydration number for some $Ln^{3+}$ and tripositive actinoid ions ($An^{3+}$) against their crystallographic radii, but did not show the position of $Ce^{3+}$. The radius of $Ce^{3+}$ (119.6 pm) of coordination number (*CN*) 9 is intermediate between those of $La^{3+}$ (121.6 pm) and $Pr^{3+}$ (117.9 pm) of $CN = 9$;[3] therefore, it is probable that the position of $Ce^{3+}$ on the S-shaped curve is between $La^{3+}$ and $Pr^{3+}$.

Methanol is bulkier than water. Hence, it is expected that the solvation number of the primary solvation sphere of $Ce^{3+}$ decreases from $CN = 9$ to a lower *CN* when the mole fraction of $CH_3OH$ ($X_s$) in the mixed $CH_3OH+H_2O$ solution increases. Suganuma et al. examined the variation in the solvation number of the primary solvation sphere of $Eu^{3+}$ in a mixed $CH_3OH+H_2O$ solution.[4] The variation was determined on the basis of the variation in the stability constant of $EuF^{2+}$, forming a contact ion-pair with increasing $X_s$. The $X_s$ value ($\fallingdotseq 0.03$) of the inflection point for the variation from a mixture of $CN = 9$ and 8 to $CN = 8$ on the solvation number around $Eu^{3+}$ was determined by the variation in the sum of (1) the cation solvation effect ($-\Delta g/RT$) employed by us[5] and (2) the electrostatic attraction between $Eu^{3+}$ and $F^-$ in $H_2O$ and mixed $CH_3OH+H_2O$ solvent solutions ($\Delta g_v/RT$). Suganuma et al. also examined the variation in the solvation number of the primary solvation sphere of $Eu^{3+}$ in a mixed $CH_3OH+H_2O$ solution based on another concept.[6] This was on the basis of the variation in the $Eu^{3+}$–$Cl^-$ distance ($d_{Eu-Cl}$). The $d_{Eu-Cl}$ in a mixed solvent system was estimated using the Born-type equation[7—11] and the Gibbs' free energy derived from the stability constant of $EuCl^{2+}$, forming a solvent-shared ion-pair. The inflection point for the variation in $d_{Eu-Cl}$ was $X_s \fallingdotseq 0.014$. The $X_s$ value ($\fallingdotseq 0.03$) of the inflection point obtained from the contact ion-pair in a solution of 0.10 M (1 M = 1 mol dm$^{-3}$) ionic strength was in fairly good agreement with that ($\fallingdotseq 0.014$) from the solvent-shared ion-pair in a solution of 1.00 M ionic strength.

From the presumed position for $Ce^{3+}$ on the S-shaped variation curve[2] of the primary hydration number, it is expected that the variation in the solvation number around $Ce^{3+}$ from 9 to a mixture of 9 and 8 may occur at a higher $X_s$ than the $X_s$, which was shown in the variation in the solvation number around $Nd^{3+}$ in the same variation manner.[12] This implies that the inflection point in the solvation number around $Ce^{3+}$ from $CN = 9$ to a mixture of $CN = 9$ and 8 may be proved from the variations in the stability constant of $CeF^{2+}$ ($\beta_{1(F)}$) and the stability constant of $CeCl^{2+}$ ($\beta_{1(Cl)}$) with increasing $X_s$ in the region $0 < X_s < 0.35$, where solvent-extraction techniques can be applied.[13] In addition, because the fluoride ion is smaller than water and methanol, and has a negative charge, one might observe that the $X_s$ value at the inflection point in the *CN* of $Ce^{3+}$ is different from that of Ce(III) in $CeF^{2+}$ in a mixed-solvent system.

The first objective of the present study was to examine the existence of an inflection point for the variation in $d_{Ce-Cl}$ in $CeCl^{2+}$, being a solvent-shared ion-pair in a mixed $CH_3OH+H_2O$ solution with 1.00 M ionic strength and of the inflection point for the variation in ($-\Delta g/RT+\Delta g_v/RT$) of $CeF^{2+}$ formation in a mixed $CH_3OH+H_2O$ solution with 0.10 M ionic strength. The second was to inspect whether the $X_s$ value at the inflection point in the *CN* of $Ce^{3+}$ can be distinguished from that of Ce(III) in $CeF^{2+}$.

## Experimental

The stability constant of $CeF^{2+}$, $\beta_{1(F)}$ ( = $[CeF^{2+}]/\{[Ce^{3+}][F^-]\}$), in trace concentrations of Ce(III) in 0.10 M (H,Na)(F,$ClO_4$) solutions of mixed $CH_3OH+H_2O$ solvents, and the stability constant of $CeCl^{2+}$, $\beta_{1(Cl)}$ ( = $[CeCl^{2+}]/\{[Ce^{3+}][Cl^-]\}$), in trace concentrations of Ce(III) in 1.00 M (H,Na)(Cl,$ClO_4$) solutions of mixed $CH_3OH+H_2O$ solvents were obtained by a back-extraction technique with $^{141}Ce$ (from the Japan Atomic Research Institute). Other reagents and extraction procedures using bis(2-ethylhexyl) hydrogenphosphate (HDEHP)–toluene at 298.2 K were previously described.[5,12,13] Preliminary extraction experiments varying $[(HDEHP)_2]_{org}$ in mixed $CH_3OH+H_2O$ solutions at 0.10 and 1.00 ionic strengths showed that the distribution ratio of $^{141}Ce$ ($D$) had an approximate third-power dependence on $[(HDEHP)_2]_{org}$ (3.0±0.07 at $X_s$ = 0.00, 0.10, 0.23, and 0.35, respectively). Determinations of the hydrogen- and fluoride-ion concentrations and calculations of $\beta_{1(F)}$ and $\beta_{1(Cl)}$ were performed as described for a system of $NdF^{2+}$ and $NdCl^{2+}$ in a mixed $CH_3OH+H_2O$ solution.[12,13] NaCl was also assumed to be completely ionized under the experimental conditions.

## Results and Discussion

**Variation in $d_{Ce\text{–}Cl}$ against $X_s$.** The values of $\beta_{1(Cl)}$ of $CeCl^{2+}$, a solvent-shared ion-pair,[12,14,15] in mixed $CH_3OH+H_2O$ solutions are summarized in Table 1. The exchange rate of the solvated solvent molecules in the primary solvation sphere around $Ce^{3+}$ is thought to be very high;[16] therefore, the shape of the primary solvation sphere of $Ce^{3+}$ on the coordination of $Cl^-$ can be regarded as being a sphere on the average. Münze[7—10] and Choppin and Unrein[11] have used a Born-type equation to calculate the stability constants of Ln(III) and An(III) in aqueous solutions. Suganuma et al. have also used the equation to calculate the distance of $Ln^{3+}$–$Cl^-$ ($d_{Ln\text{–}Cl}$) (Ln = Nd, Sm, Eu, and Tm) in mixed $CH_3OH+H_2O$ solutions.[6,12,17] The $Ce^{3+}$–$Cl^-$ distances ($d_{Ce\text{–}Cl}$) in the mixed $CH_3OH+H_2O$ solutions were also calculated using the following Born-type equation:[11]

$$RT\ln\beta_{1(Cl)}=\frac{N_A\times e^2\times Z_{Ce^{3+}}\times Z_{Cl^-}}{\varepsilon\times d_{Ce\text{–}Cl}}+RT\nu\ln M_s-RT\sum\ln f,\quad(1)$$

Table 1. Stability Constants of $CeCl^{2+}$ and the Estimated Values of $Ce^{3+}$–$Cl^-$ Distance ($d_{Ce\text{–}Cl}$) at 298.2 K

| Mole fraction of $CH_3OH$ in the bulk solution ($X_s$) | $\beta_{1(Cl)}$ | $d_{Ce\text{–}Cl}$ $10^2$ pm |
|---|---|---|
| 0.000 | 0.92±0.08 | 4.65±0.10 |
| 0.014 | 0.96±0.06 | 4.66±0.06 |
| 0.037 | 1.01±0.15 | 4.71±0.17 |
| 0.073 | 1.02±0.07 | 4.85±0.07 |
| 0.100 | 1.16±0.07 | 4.84±0.07 |
| 0.129 | 1.17±0.08 | 4.94±0.07 |
| 0.180 | 1.36±0.17 | 4.99±0.13 |
| 0.229 | 1.41±0.09 | 5.15±0.07 |
| 0.267 | 2.71±0.19 | 4.71±0.06 |
| 0.308 | 4.76±0.26 | 4.43±0.04 |
| 0.353 | 1.27±0.18 | 5.74±0.18 |

where $N_A$ is Avogadro's constant, $e$ is the elementary charge, $Z_{Ce^{3+}}$ and $Z_{Cl^-}$ are the ionic charges of $Ce^{3+}$ and $Cl^-$, $\varepsilon$ is the dielectric constant in the secondary solvation sphere of $Ce^{3+}$, $d_{Ce\text{–}Cl}$ is the distance between $Ce^{3+}$ and $Cl^-$, $\nu$ is $-1$, $M_s$ is the total molarity of mixed solvent containing no electrolyte, and $\Sigma\ln f$ is expressed as the following equation:

$$\sum\ln f=\frac{-\Delta Z^2\times A\times I^{1/2}}{1+B\times a^\circ\times I^{1/2}}-C\times I^{1/2}-D\times I,\qquad(2)$$

where $\Delta Z^2 = -6$, $A = (\varepsilon T)^{-3/2}\times1.826\times10^6$, $B = 50.29\times(\varepsilon T)^{-1/2}\times10^8$, $C=0.75$, $D=-0.15$, $a^\circ=4.3\times10^{-8}$ cm, and $I$ is the ionic strength. It was assumed that the values of $\Delta Z^2$, $C$, $D$, and $a^\circ$, which had been utilized for the complexations of $LnF^{2+}$ and $AnF^{2+}$ in an aqueous medium of 1.0 M ionic strength by Choppin and Unrein,[11] are effective in the present system.

The estimated value of $d_{Ce\text{–}Cl}$ is affected by the values of $C$ and $D$ in Eq. 2. It is not to take into account any other influence (for example, the short-range interactions between ions and solvents, the variation in the viscosity with an increase in $X_s$, the formation of solvent-separated ion-pair between $Ce^{3+}$ and $ClO_4$, and so on), except for the dielectric constant of the solution in Eq. 1. Thus, the estimated $d_{Ce\text{–}Cl}$ will be somewhat uncertain.

Because it is difficult to observe the dielectric constant in the secondary solvation sphere of $Ce^{3+}$, and it is thought that the dielectric constant in the secondary solvation sphere is close to that in the bulk solution,[18] the dielectric constant of the mixed solvent[19] was adopted in the distance calculation. The values of $d_{Ce\text{–}Cl}$ in the mixed $CH_3OH+H_2O$ solutions are summarized in Table 1. They are also plotted in Fig. 1 against $X_s$. The distance in the aqueous solution was determined to be $(4.6_5\pm0.1_0)\times10^2$ pm. The value of $d_{Ce\text{–}Cl}$ is intermediate between (1) the sum of ionic radii[3] of $Ce^{3+}$ and $Cl^-$ (about $3.0\times10^2$ pm) and (2) the above value (about $3.0\times10^2$ pm) plus the diameter of a water molecule (about $2.8\times10^2$ pm), being regarded as a sphere (about $5.8\times10^2$ pm). Therefore, the calculated values of $d_{Ce\text{–}Cl}$ in the aqueous and mixed

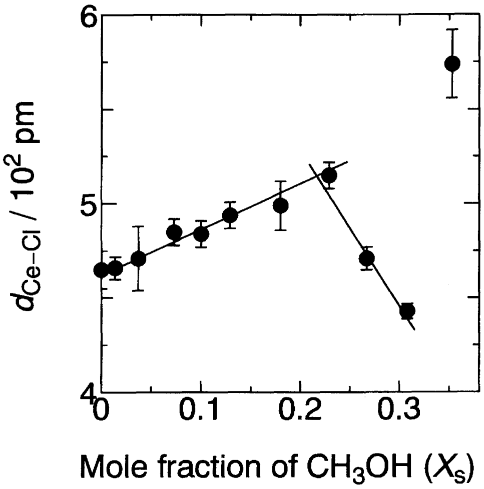

Fig. 1. The variation in the estimated values of $Ce^{3+}$–$Cl^-$ distance ($d_{Ce\text{–}Cl}$) at 298.2 K with $X_s$.

solutions do not indicate the state of "a contact ion-pai", but do indicate in the state of "a solvent-shared ion-pair". The calculated distance may show a somewhat smaller value than the real one, because the employed dielectric constant values are somewhat larger than those in the secondary solvation sphere.

The $d_{\text{Ce–Cl}}$ increases linearly along with an increase in $X_s$ in the region $0.00 \leqq X_s < 0.23$, and decreases linearly with $X_s$ in $0.23 \leqq X_s < 0.31$. It is thought that the point of $Ce^{3+}$ on the S-shaped variation shown by Fourest et al.[2] lies between the points of $La^{3+}$ and $Pr^{3+}$ of hydration number 9; therefore, the *CN* of $Ce^{3+}$ will not change immediately from 9 to 8 by coordination with a slight methanol molecule. If the *CN* of $Ce^{3+}$ remains 9, even with increasing $X_s$, the coordination of a bulky methanol acts as (I) an elongating factor of $d_{\text{Ce–Cl}}$ along with an increase in the mean volume of the primary solvation sphere of $Ce^{3+}$. On the other hand, a decrease in *CN* acts as (II) a lowering factor of $d_{\text{Ce–Cl}}$, being attributable to a decrease in the mean volume of the primary solvation sphere of $Ce^{3+}$ and to a decrease in the mean ionic radius of $Ce^{3+}$. Thus, it is determined that the *CN* of $Ce^{3+}$ varies from $CN = 9$ to a mixture $CN = 9$ and 8 in the vicinity of $X_s = 0.23$.

In large-angle X-ray diffraction measurements of 3 M $Ln(ClO_4)_3$ (Ln = Y, Er, Tb, Sm, and La) aqueous solutions, Johansson and Wakita[15] showed a number of peaks due to $ClO_4^-$ at a distance of more than 500 pm from $Ln^{3+}$ (secondary hydration sphere). Johansson and Yokoyama[14] also showed the presence of $ClO_4^-$ in the secondary hydration sphere of $Er^{3+}$ in a 1 M $Er(ClO_4)_3$ solution. If the value of $X_s$ becomes still larger, the total solvent concentration in a mixed $CH_3OH+H_2O$ solution of 1.00 M (H,Na)(Cl,$ClO_4$) will be considerably smaller than that of a $H_2O$ solution. There is a strong presumption that $ClO_4^-$ is able to invade the secondary solvation of $Ce^{3+}$ at high $X_s$. In such cases, the obtained $\beta_{1(\text{Cl})}$ does not have a significant value. It is probable that a large value of $d_{\text{Ce–Cl}}$ at $X_s = 0.35$ is caused by an invasion of $ClO_4^-$ into the secondary solvation of $Ce^{3+}$.

**Value of $\ln\beta_{1(\text{F})}$.** The values of $\ln\beta_{1(\text{F})}$ for $CeF^{2+}$ summarized in Table 2 are plotted in Fig. 2 as a function of $X_s$. The thermodynamic treatments for the formation of $CeF^{2+}$ in $H_2O$ and mixed $CH_3OH+H_2O$ solutions are expressed as followes:

$$\beta_{1(\text{F})}(H_2O) = [CeF(H_2O)_n^{2+}]/\{[Ce(H_2O)_l^{3+}][F(H_2O)_m^-]\}, \quad (3)$$

$$\beta_{1(\text{F})}(\text{mix}) = [CeF(H_2O)_s(CH_3OH)_t^{2+}]/\\ \{[Ce(H_2O)_o(CH_3OH)_p^{3+}][F(H_2O)_q(CH_3OH)_r^-]\}. \quad (4)$$

The relationship between $\ln\beta_{1(\text{F})}(\text{mix})$ and $\ln\beta_{1(\text{F})}(H_2O)$ can be expressed by the following equation:[4,20]

$$\ln\beta_{1(\text{F})}(\text{mix}) = \ln\beta_{1(\text{F})}(H_2O) + \Delta G_{\text{tr}}(F^-)/RT - \Delta g/RT + \Delta g_v/RT, \quad (5)$$

where $\Delta G_{\text{tr}}(F^-) = [\Delta G_{\text{F,solv}}(\text{mix}) - \Delta G_{\text{F,solv}}(H_2O)]$, $-\Delta g = \{[\Delta G_{\text{Ce,solv}}(\text{mix}) - \Delta G_{\text{CeF,solv}}(\text{mix})] - [\Delta G_{\text{Ce,solv}}(H_2O) - \Delta G_{\text{CeF,solv}}(H_2O)]\}$, and $\Delta g_v = [-\Delta G_{\text{CeF}}(\text{vac,mix}) + \Delta G_{\text{CeF}}(\text{vac},H_2O)]$. The terms of $\Delta G_{\text{F,solv}}(\text{mix})$, $\Delta G_{\text{Ce,solv}}(\text{mix})$, $\Delta G_{\text{CeF,solv}}(\text{mix})$, $\Delta G_{\text{F,solv}}(H_2O)$, $\Delta G_{\text{Ce,solv}}(H_2O)$, and $\Delta G_{\text{CeF,solv}}(H_2O)$ are the solvation energies of $F^-$, $Ce^{3+}$, and $CeF^{2+}$ in the mixed $CH_3OH+H_2O$ and $H_2O$ solutions, respectively. Both values of $\Delta G_{\text{CeF}}(\text{vac,mix})$ and $\Delta G_{\text{CeF}}(\text{vac}, H_2O)$ are the Gibbs' free energies of formation in a vacuum at the interionic distances in $H_2O$ and the mixed $CH_3OH+H_2O$ solutions, respectively. The value of $(-\Delta g/RT + \Delta g_v/RT)$ in Fig. 2 has a smaller effect on the variation in $\ln\beta_1(\text{mix})$ than the effect based on $\Delta G_{\text{tr}}(F^-)/RT$, similar to the Eu(III) system.[4]

Table 2. Stability Constants and Thermodynamic Parameters of $CeF^{2+}$ at 298.2 K

| Mole fraction of $CH_3OH$ in the bulk solution ($X_s$) | $\ln\beta_{1(\text{F})}$ | $\Delta G_{\text{tr}}(F^-)/RT^{21)}$ kJ mol$^{-1}$ | $\Delta G/RT$ kJ mol$^{-1}$ |
|---|---|---|---|
| 0.000 | 7.35±0.05 | 0.00 | 0.00 |
| 0.014 | 7.53±0.05 | 0.10 | 0.08 |
| 0.037 | 7.70±0.04 | 0.27 | 0.08 |
| 0.073 | 7.92±0.02 | 0.53 | 0.04 |
| 0.101 | 8.18±0.03 | 0.73 | 0.10 |
| 0.130 | 8.18±0.03 | 0.94 | −0.11 |
| 0.181 | 8.47±0.03 | 1.31 | −0.19 |
| 0.230 | 8.63±0.03 | 1.66 | −0.38 |
| 0.268 | 8.43±0.04 | 1.94 | −0.86 |
| 0.309 | 8.74±0.02 | 2.24 | −0.85 |
| 0.353 | 9.28±0.01 | 2.56 | −0.63 |

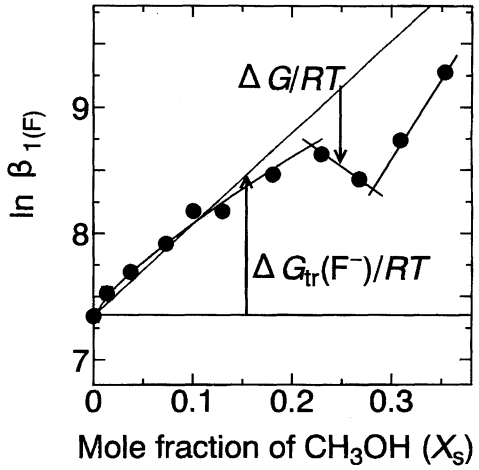

Fig. 2. The variations in $\ln\beta_{1(\text{F})}$ (●) of $CeF^{2+}$ and $(\ln\beta_{1(\text{F})}(H_2O) + \Delta G_{\text{tr}}(F^-)/RT^{21})$ at 298.2 K with $X_s$. The value of $\Delta G/RT\,(= -\Delta g/RT + \Delta g_v/RT)$ is $(-\ln\beta_{1(\text{F})}(H_2O) + \ln\beta_{1(\text{F})}(\text{mix}) - \Delta G_{\text{tr}}(F^-)/RT^{21})$.

**Variation in $(-\Delta g/RT + \Delta g_v/RT)$ with $X_s$.** It is difficult to experimentally obtain the Gibbs' free energies of solvation for $Ce^{3+}$ and $CeF^{2+}$ in all solutions. Equation 5 shows that a difference in the $\ln\beta_{1(\text{F})}$ value between $H_2O$ and the mixed $CH_3OH+H_2O$ solutions is governed by three factors: $\Delta G_{\text{tr}}(F^-)/RT$, $-\Delta g/RT$, and $\Delta g_v/RT$. Because the value of $\Delta G_{\text{tr}}(F^-)$ has been experimentally obtained by Hefter and McLay,[21] the sum of $-\Delta g/RT$ and $\Delta g_v/RT$ ( $= \Delta G/RT$), expressed by

$$\Delta G/RT = [\Delta G_{\text{Ce,solv}}(\text{mix}) - \Delta G_{\text{Ce,solv}}(H_2O)]$$

$$-[\Delta G_{\mathrm{CeF,solv}}(\mathrm{mix}) - \Delta G_{\mathrm{CeF,solv}}(\mathrm{H_2O})]$$
$$-[\Delta G_{\mathrm{CeF}}(\mathrm{es,mix}) - \Delta G_{\mathrm{CeF}}(\mathrm{es,H_2O})], \qquad (6)$$

can be calculated using Eq. 5 by adopting the values of $\ln\beta_1(\mathrm{mix})$ and $\ln\beta_1(\mathrm{H_2O})$. These values are listed in Table 2, and are shown in Fig. 2.

The variation in $\Delta G/RT$ in Fig. 2 shows a smooth curve for $0 \leqq X_s < 0.22$, a steep lowering for $0.22 < X_s \leqq 0.28$, and an increase for $0.28 < X_s < 0.36$ with increasing $X_s$. This has two inflection points in the neighborhood of $X_s = 0.22$ and 0.28. The value of the dielectric saturation ($\varepsilon_{\mathrm{sat}}$) around $Ce^{3+}$ in a mixed $CH_3OH+H_2O$ solution is estimated to be $\varepsilon_{\mathrm{sat}} = 1.77$ by the square of the refractive index,[22] because the refractive indices of water, methanol, and their mixture are nearly the same value ($\fallingdotseq 1.33$).[23] The magnitude of this electrostatic interaction between $Ce^{3+}$ and $F^-$ should not vary with $X_s$ when the ionic potential of Ce(III) for the $CeF^{2+}$ complex is kept constant. Thus, the smooth curve for $0 \leqq X_s < 0.22$ is dependent on the variation in $(\Delta G_{\mathrm{Ce,solv}}(\mathrm{mix}) - \Delta G_{\mathrm{CeF,solv}}(\mathrm{mix}))$, because the variation in $\Delta G_{\mathrm{tr}}(F^-)/RT$ is approximately linear.[21]

The changing coordination numbers around Ce(III) of the solvated $Ce^{3+}$ and the $CeF^{2+}$ complex with increasing $X_s$ should be accompanied by a change in the radius of Ce(III). The electrostatic solvation energy of $Ce^{3+}$ ($\Delta G_{\mathrm{es,solv}}$) for $CN = 9$ and 8 in aqueous and methanol solutions was calculated using the equations of Latimer et al.[24] and of Tanaka and Ogata,[25] and is shown in Table 3. It can be seen from the results in Table 3 that a decrease in *CN* for $Ce^{3+}$ increases the absolute value of $\Delta G_{\mathrm{Ce,solv}}(\mathrm{mix})$.

Under these circumstances, the *CN* of Ce(III) for the $CeF^{2+}$ complex remains 9 when the solvation number in the primary solvation sphere of $Ce^{3+}$ starts to change from $CN = 9$ to a mixture of $CN = 9$ and 8 with increasing $X_s$; an increase in $|\Delta G_{\mathrm{Ce,solv}}(\mathrm{mix})|$ for $CN = 8$, in comparison with that for $CN = 9$, acts as a large negative factor in the variation in $\ln\beta_1(\mathrm{mix})$. It is reasonable that a steep lowering of $\Delta G/RT$ for $0.22 < X_s \leqq 0.28$ corresponds to the above-mentioned matter. The obtained maximum point in the neighborhood of $X_s = 0.22$ for the solvation number of $Ce^{3+}$ from $CN = 9$ to a mixture of $CN = 9$ and 8 is in fair agreement with that based on the value of $d_{\mathrm{Ce-Cl}}$ shown in Fig. 1.

It is difficult to obtain the values of $\Delta G_{\mathrm{CeF,solv}}(\mathrm{H_2O})$ and $\Delta G_{\mathrm{CeF,solv}}(\mathrm{mix})$. We thus assume that those can be expressed by $8/9 \times \Delta G_{\mathrm{es,solv}}(\mathrm{H_2O}) \times (1-\zeta)$ and $8/9 \times \Delta G_{\mathrm{es,solv}}(\mathrm{mix}) \times (1-\zeta')$ for $CN = 9$ of Ce(III) and $7/8 \times \Delta G_{\mathrm{es,solv}}(\mathrm{mix}) \times (1-\zeta'')$ for $CN = 8$. The terms of $(1-\zeta)$, $(1-\zeta')$, and $(1-\zeta'')$ are lowering factors for the solvation energies of $CeF^{2+}$ due to a repulsion effect between the $F^-$ and the oxygen atoms of the solvated molecules in the primary solvation sphere of $CeF^{2+}$ in the aqueous and the mixed solutions of $CN = 9$ and 8 of Ce(III), respectively. The repulsion effect will increase with an increase in the solvated molecules around $CeF^{2+}$. It is thus reasonable that the values of $\zeta$ and $\zeta'$ are larger than the $\zeta''$, and $\zeta \fallingdotseq \zeta'$. When the *CN* of Ce(III) for the $CeF^{2+}$ complex moves from 9 to 8, it is thought that the value of $-[7/8 \times \Delta G_{\mathrm{es,solv}}(\mathrm{mix}) \times (1-\zeta'') - 8/9 \times \Delta G_{\mathrm{es,solv}}(\mathrm{H_2O}) \times (1-\zeta)]$ in the region of $X_s < 0.4$ is positive, because the $Ln^{3+}$ is preferentially solvated by water in a $CH_3OH+H_2O$ solution.[26] This indicates that the effect based on the variation in $\Delta G_{\mathrm{CeF,solv}}(\mathrm{mix})$ acts as a positive factor in the variation of $\ln\beta_1(\mathrm{mix})$. Furthermore, the ionic radius of $Ce^{3+}$ will decrease when the *CN* of Ce(III) moves from 9 to 8. The distance between $Ce^{3+}$ and $F^-$ should become shorter. Thus, the term $-[\Delta G_{\mathrm{CeF}}(\mathrm{es,mix}) - \Delta G_{\mathrm{CeF}}(\mathrm{es,H_2O})]$ in Eq. 6 also acts as a large positive factor in the variation of $\ln\beta_1(\mathrm{mix})$. It is reasonable that the inflection point in the vicinity of $X_s = 0.28$ corresponds to the variation in the *CN* for Ce(III) in the $CeF^{2+}$ complex.

Table 3. The Calculated Electrostatic Solvation Energy of $Ce^{3+}$ ($\Delta G_{\mathrm{es,solv}}$) Based on the Equation of Latimer et al.[24]

| Coordination number | $\Delta G_{\mathrm{es,solv}}(\mathrm{water})$ kJ mol$^{-1}$ | $\Delta G_{\mathrm{es,solv}}(\mathrm{methanol})$ kJ mol$^{-1}$ |
|---|---|---|
| *CN*=8 | $-3.30 \times 10^3$ | $-3.26 \times 10^3$ |
| *CN*=9 | $-3.21 \times 10^3$ | $-3.17 \times 10^3$ |

**Conclusion.** The variation in the coordination number (*CN*) of $Ce^{3+}$ from 9 to a mixture of 9 and 8 occurs at lower $X_s$ than that of Ce(III) of the $CeF^{2+}$ complex in the mixed $CH_3OH+H_2O$ solution. Those values are $X_s$ = about 0.23 and about 0.27, respectively.

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