Ion Solvation and Association and Water Structure in an Aqueous Cerium(III) Chloride Solution in the Gigapascal Pressure Range

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1 **Abstract**

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3 X-ray diffraction measurements are performed on a 1 *m* (= mol kg⁻¹) CeCl₃ aqueous solution over a
4 temperature range of 300 K to 600 K and a pressure range of 0.1 MPa to 4 GPa. The experimental
5 interference functions are analyzed by an empirical potential structure refinement (EPSR) modeling.
6 The Ce³⁺ coordinates water molecules in a tricapped trigonal prism configuration under the ambient
7 condition. The number of water molecules around Ce³⁺ changes from 8.8 at 0.1 MPa/300 K to 11.5 at
8 4 GPa/600 K. The number of water molecules around Cl⁻ changes drastically from 10 under the
9 ambient condition to 17 at 4 GPa/600 K. The tetrahedral-like network structure of water under the
10 ambient condition is transformed toward a simple liquid-like packing in the GPa pressure range. The
11 corresponding coordination number is increased from 4.3 in the ambient condition to 9.7 at 4 GPa/600
12 K. The Ce³⁺-Cl⁻ association decreases with increasing pressure.

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1 Introduction

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3 Water and aqueous electrolyte solutions under high pressure have attracted much attention in both
4 fundamental and applied sciences. The nature of ion solvation is often discussed from the structure
5 making and breaking concept depending on the size and charge of ions.¹ High pressure will perturb
6 water structure and ion solvation, which gives us a hint for a deep understanding of ion solvation. Ion
7 solvation under high pressure plays a vital role in pressure-induced denaturation of proteins² and high-
8 pressure sterilization in food science,³ geological processes in the Earth,⁴ and salty ice formation in
9 planets.⁵ However, structural information on ion solvation and solvent water under high pressure and
10 high temperature at the molecular level is minimal because of experimental difficulties in handling
11 highly corrosive electrolyte solutions in extreme conditions. We have recently succeeded in
12 measurements of aqueous electrolyte solutions under high pressure and high temperature, particularly
13 in the gigapascal pressure range, using intense synchrotron radiation and pulsed neutrons combined
14 with high-pressure cells.^{6,7} Furthermore, by analyzing X-ray and neutron interference functions with
15 empirical potential structure refinement (EPSR) modeling,⁸ the detailed 3D structure of ion solvation
16 of monovalent Na^+ and Cl^- and divalent Ca^{2+} has been elucidated.^{6,7} It would be essential to investigate
17 the hydration of trivalent ions in the GPa pressure range to see how much the GPa pressure affects the
18 highly charged ion hydration.

19 In the present study, we focus on the solvation of Ce^{3+} as the light rare earth ions since an aqueous
20 CeCl_3 solution is an attractive catalyst for biomass⁹ and Ce^{3+} exerts diverse biological effects in vivo
21 substitution in biomolecule, mainly by their resemblance to Ca^{2+} ions.¹⁰ The solvation of Ce^{3+} in an
22 ambient condition has been widely investigated by large-angle X-ray diffraction,¹¹ EXAFS,^{12,13} Raman
23 spectroscopy,¹⁴ EXAFS combined with MD simulation,^{15,16} Hartree-Fock MO,¹⁷ INDO/S-CI MO,¹⁸ and
24 QM/MM-MD approach.^{19,20} From these studies, it has been established that Ce^{3+} has nine-fold
25 coordination in tri-capped trigonal prism with the Ce^{3+} - H_2O distance of 2.52~2.59 Å.
26 Raman spectral measurements¹⁴ showed that in aqueous CeCl_3 solutions in a concentration range from

0.270~2.167 mol/L the Ce^{3+} - Cl^- association occurs. An EXAFS study¹² has also concluded the inner-sphere Cl^- complexation with Ce^{3+} in an aqueous CeCl_3 solution with an excess of 14.0 M LiCl (Ce^{3+} - Cl^- distance = 2.89 Å, coordination number = 1.8). However, the above-referenced studies are limited to one-dimensional structure information of aqueous CeCl_3 solutions.

We perform synchrotron X-ray diffraction measurements on a 1 *m* CeCl_3 aqueous solution in a temperature range from 300 to 600 K and a pressure range from 0.1 MPa (hereafter described as 0 GPa for simplicity) to 4 GPa. The X-ray interference functions obtained are analyzed by EPSR modeling to extract the pair correlation functions, the coordination number distributions, the angle distributions, and the spatial density functions (3D structure) with temperature and pressure. The ion solvation and association and solvent water structures in a 1 *m* CeCl_3 solution the GPa pressure range are discussed and compared with those previously published in a 3 *m* NaCl solution⁷ and a 2 *m* CaCl_2 solution.⁶

Experimental

Sample preparation

Commercially available $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (special reagents 99.5%, Sigma-Aldrich) was used without further purification. A 1 *m* CeCl_3 aqueous solution was prepared by dissolving $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ powder into 0.1 M HCl, which had been degassed to avoid oxidation of Ce^{3+} to Ce^{4+} , to prevent the hydrolysis of Ce^{3+} to the required amount. The concentration of chloride ions was determined by precipitation titration using a standard AgNO_3 solution. The density of a sample solution was measured at 298 K with a vibrational densitometer (ANTON Paar K.G., DSA5000). The density under the ambient condition was extrapolated to high-temperature and high-pressure conditions measured on the basis of the literature data of water at the corresponding thermodynamic states as shown in Supporting Information (SI) (Fig. 1S).²¹ The concentration and the density of the sample solution are given in Table 1 in different thermodynamic states.

X-ray diffraction

High pressure X-ray diffraction experiments were carried out on BL14B1 at SPring-8.²² A sample solution was kept in a cylindrical diamond cell (1.5 mm in diameter and 1.2 mm in height) capped with a gold thin foil and sealed in a high-pressure assembly as shown in Fig.2S.²³ NaCl crystals were placed under the diamond cell as a pressure marker. In an ambient condition (0 GPa/300 K), a 2-mm ϕ glass capillary was used as a sample container. The pressure was estimated from the relationship of the shift of Bragg peaks of NaCl with pressure.²⁴ Heating of the cell was made by applying AC current to the graphite tube. The temperature was determined by the relation of temperature with the current applied that had been measured before the experiments.²⁵ X-ray diffraction data were collected in an energy-dispersive mode over an energy (E) region of 40~140 keV on an SSD in the scattering angle (2θ) range of 4 to 24° with an increment of 2 to 4°. The X-ray beam size was 300 μm in width and 50 μm in height. X-ray scattering from an empty cell was measured before and subtracted from the data of a sample. It should be noted that the $K\alpha$ and $K\beta$ lines of Ce appear at 34.2 keV and 39.1 keV, respectively, with the absorption edge of 40.6 keV. Thus, the scattering intensities measured up to 40 keV were used in the subsequent data analysis. The incoherent scattering was subtracted based on results of a theoretical calculation. The interference functions, $F(Q)$, was obtained by eq. (1).

$$F(Q) = \frac{(I^{\text{coh}}(Q) - \sum n_i f_i^2(Q))}{\sum n_i f_i^2(Q)} \quad (1)$$

Here, $I^{\text{coh}}(Q)$ is the experimental scattered intensities, and n_i and f_i denote the concentration and the atomic scattering factor of atom i , respectively. Q is the magnitude of the scattering vector expressed as $Q = (4\pi/hc)E \sin \theta$ (h is the Planck constant, and c is the velocity of light) from a set of diffraction patterns measured at the different scattering angles using an empirical method.^{23,26} Normalization of the experimental diffraction data to the absolute units was made by the method described in ref. 27. The radial distribution functions $G(r)$ were calculated by Fourier transformation of $F(Q)$ by eq. (2)

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$$G(r) = \int_{Q_{min}}^{Q_{max}} QF(Q) \sin(Qr) dQ. \quad (2)$$

EPSR modeling

EPSR modeling is a Monte Carlo (MC) calculation in a cubic box which contains 23 Ce^{3+} , 69 Cl^- , and 1000 water molecules to reproduce the measured density. A unique procedure of EPSR modeling is to compare the simulated interference factors $F(Q)$ with the experimental values and then modify the pair potentials described subsequently so that the simulated values reproduce the experimental ones. The details of EPSR modeling have been described in refs.8, 28, and 29. This procedure is repeated until a good agreement between the model and experiment is achieved. The pair potential was selected as SPC/E (extended simple point charge) for water,³⁰ and those of Ce^{3+} and Cl^- were taken from ref. 16. The potential parameters are summarized in [Table 1S](#). The EPSR calculations were made with EPSR25 program.³¹

Results and Discussion

Interference functions $F(Q)$ and total radial distribution functions $G(r)$

[Figure 1](#) compares the interference functions (top frame) and the corresponding radial distribution functions (bottom frame) from experiments with those from EPSR modeling of an aqueous 1 *m* CeCl_3 solution obtained in various thermodynamic states. A good agreement between experiments and modellings is obtained in all thermodynamic states. It should be noted that the experimental values are available up to $Q = 8 \text{ \AA}^{-1}$ as mentioned in the previous section and the simulated ones are plotted to $Q = 16 \text{ \AA}^{-1}$ to minimize the termination effect of Fourier transformation of eq. (2).

In the interference functions, we see a gradual change in the first peak feature from a double peak (a shoulder at $Q = \sim 2.1 \text{ \AA}^{-1}$ and a broad peak at $Q = 3.0 \text{ \AA}^{-1}$) at 0 GPa/300 K to a sharp single peak at $Q = 2.1 \text{ \AA}^{-1}$ at 4 GPa/600 K, These pressure dependent features suggest a substantial change in the structure of a 1 *m* CeCl_3 aqueous solution under compression to the GPa pressure range.

This structural change is observed in the corresponding radial distribution functions. At 0 GPa/300 K, the first peak is observed at 2.72 Å which should be ascribed to the sum of the contributions of both the Ce³⁺-H₂O bonds (2.52~2.57 Å¹¹⁻²⁹) due to the cation hydration and the 1st neighbor H₂O-H₂O bonds (2.79~2.82 Å^{6,7}). The Cl-H₂O bonds (3.16~3.18 Å^{6,7}) also contribute in part to the 2.72 Å peak. A broad peak seen at 4.5 Å corresponds to the second neighboring water molecules around Ce³⁺ and second neighbor H₂O-H₂O interactions of bulk water. The position of this peak shifts from ~4.4 Å at 0 GPa/300 K to ~5.4 Å under compression. The third peak is centered at 6.6 Å in the ambient condition and shifts to 8.0 Å at 4.0 GPa/600 K. The shift of the third peak is similar to that found for the third neighbor H₂O-H₂O interactions for liquid water under compression to GPa [1].

Cerium(III) ion solvation: Figure 2 shows the Ce-Ow pair correlation function (top) and the distribution of the coordination number (bottom) obtained by EPSR modeling. Ow denotes water oxygen atom. The coordination number of atom pair α - β is calculated from the corresponding pair correlation functions, $g_{\alpha\beta}(r)$, by eq. (3):

$$CN_{\alpha\beta} = 4\pi\rho_{\beta} \int_{r_{min}}^{r_{max}} g_{\alpha\beta}(r)r^2dr \quad (3)$$

where ρ_{β} is the number density of atom β , and r_{min} and r_{max} are the lower and upper limits of integration. The coordination number is sensitive to the value of r_{max} . In the present study, r_{max} was set at the first minimum distance and is given in Table 2. In all the pair correlation functions, the first sharp peak is observed at 2.61Å due to the Ce³⁺-H₂O bonds in the first coordination shell. On the other hand, the second peak ascribed to the Ce³⁺-H₂O interactions in the second coordination shell is composed of a shoulder at 4.7 Å and a broad peak at 5.1 Å in the ambient condition; with increasing pressure to the GPa range, the shoulder is gradually enhanced to a peak at 4 GPa/600 K. As can be seen in Fig. 4 (bottom), the distribution of the coordination number shifts to higher values with an increase in pressure. Accordingly, the mean coordination number of Ce³⁺ changes from 8.8 at 0 GPa/300 K to 11.5

at 4 GPa/600 K (Table 2). The ambient value is consistent with the nine-fold coordination previously confirmed by other methods.¹¹⁻²⁰ In the literature, nine water molecules are arranged in a tricapped trigonal prism configuration around Ce^{3+} (Fig. 3). To examine this configuration in the present solution in the GPa pressure range, the first peak was deconvoluted by a least-squares fitting procedure applied to the form of $rg(r)$ which gives a symmetrical shape. The Gauss-Lorentzian function was employed for peak shape with the Origin Pro.³⁴ Figure 3S shows an example of the peak analysis at 0 GPa/300 K. The optimized Ce^{3+} -prism oxygen distance, $r(\text{Ce}^{3+}\text{-Ow}_1)$, and the Ce^{3+} -equatorial oxygen one, $r(\text{Ce}^{3+}\text{-Ow}_2)$, are summarized in Table 2S. The crystallographic data^{32,33} are also included for comparison. Both Ce^{3+} -Ow distances in solution are longer than the corresponding values in the crystal.^{32,33}, which could be ascribed to the thermal fluctuation of the $\text{Ce}^{3+}\text{-H}_2\text{O}$ bonds in the solution. When the pressure is increased from 1 GPa to 4 GPa at 500 K, both prism oxygen and equatorial oxygen distances of Ce^{3+} are decreased by 0.005 Å and 0.002 Å, respectively. On the other hand, when the temperature is elevated from 300 K to 500 K at 1 GPa, $r(\text{Ce}^{3+}\text{-Ow}_1)$ and $r(\text{Ce}^{3+}\text{-Ow}_2)$ are lengthened by 0.013 Å and 0.010 Å, respectively. Thus, we can say that the Ce^{3+} hydration is more sensitive to temperature than to pressure.

The coordination numbers $CN(1)$ and $CN(2)$ were calculated on the basis of the areas of peaks I and II and the mean coordination number (Table 2S). Both $CN(1)$ and $CN(2)$ increase with increasing temperature and pressure. However, the ratio of $CN(1)$ to $CN(2)$ does not change significantly with temperature and pressure, suggesting that the tricapped trigonal prism configuration of Ce^{3+} is retained even in the GPa pressure range.

The coordination geometry of Ce^{3+} was further examined in terms of the angle distribution of Ow-Ce-Ow in Fig. 3. In the ambient condition, there appear the dominant peak at 60° and small peaks at 120° and 180°, and small broad peaks at 80° and 145°. According to the crystal structure (Fig.3),^{32,33} $\angle\text{O}_1\text{-Ce-O}_2 = 66^\circ$, $\angle\text{O}_1\text{-Ce-O}_{1A} = 76^\circ$, $\angle\text{O}_1\text{-Ce-O}_2 = 90^\circ$, $\angle\text{O}_2\text{-Ce-O}_{2A} = 120^\circ$, $\angle\text{O}_1\text{-Ce-O}_{2B} = 135^\circ$, and $\angle\text{O}_1\text{-Ce-O}_{1K} = 138^\circ$. Although the peak positions for a solution are not exactly consistent with the

values in the crystal, we can say that the tricapped trigonal prism configuration of Ce^{3+} is in the solution. This configuration is retained at 1 GPa/300 K, but at 1 GPa and higher temperature and high pressures, the broad peaks at 80° and 145° are diminished, and the peaks at 60° , 120° , and 180° are gradually enhanced. This finding suggests that the tricapped trigonal prism configuration is very distorted in the GPa pressure range.

Chloride ion solvation: Figure 4 shows the Cl-Ow pair correlation function (top) and the distribution of the coordination number (bottom) obtained by EPSR modeling. Table 2 summarizes the position of the first and the second solvation shells abbreviated as Cl-Ow(I) and Cl-Ow(II), respectively, and the mean coordination number of the first solvation shell of Cl^- . Here, I and II in parentheses denote the first and second coordination shells, respectively. Upon compression at a constant temperature, the Cl-Ow(I) distance shifts to the shorter distance by 0.06 Å from 3.24 Å at 0 GPa/300 K to 3.18 Å at 1 GPa/300 K and by 0.06 Å from 3.21 Å at 2 GPa/500 K to 3.15 Å at 4 GPa/500 K. On the contrary, when temperature is elevated at a constant pressure, the Cl-Ow(I) distance is slightly lengthened by 0.02 Å from 3.18 Å at 1 GPa/300 K to 3.20 Å at 1 GPa/500 K and by 0.03 Å from 3.15 Å at 4 GPa/500 K to 3.18 Å at 4 GPa/600 K. Thus, for Cl^- the pressure affects the hydration structure more significantly than the temperature, which is an opposite tendency to the Ce^{3+} hydration. Cl^- is a large monovalent anion and is well known as a structure breaking ion which disturbs the tetrahedral network structure of water and does not form the distinct solvation shells around the ion. Thus, water molecules are loosely packed around Cl^- , leading to the pressure sensitive hydration of Cl^- . There is no second solvation shell in the ambient condition. However, when the pressure is increased to the GPa pressure range, the second peak appears at 5.8 Å and shifts to a longer distance on heating and to a shorter distance on compression. At 4 GPa/600 K, the third solvation shell is observed at 7.8 Å. Thus, in the GPa pressure range, Cl^- behaves as a structure maker. A similar tendency has been observed in 3 *m* NaCl and 2 *m* CaCl_2 aqueous solutions.^{6,7} The change in the solvation shell of Cl^- is due to increasing free water molecules in aqueous solutions when temperature is elevated and pressure is increased to the GPa pressure range as shown in a subsequent section of solvent water structure.

1 The mean coordination number of Cl^- increases when temperature and pressure are elevated, e.g.
2 from 10.1 at 0 GPa/300 K to 17.4 at 4 GPa/600 K. When temperature and pressure are increased, the
3 hydrogen bonded network structure of solvent water is perturbed or partially broken to generate more
4 free water molecules. The free water molecules will surround Cl^- to form the extended solvation
5 shells of Cl^- .

6 **Figure 4S** shows the distribution of angle Ow-Cl-Ow. Characteristic peaks are observed at 48° , 80° ,
7 125° , and 160° under the ambient condition. The angle of 48° is less sensitive to pressure and
8 temperature, but the corresponding population substantially decreases when the thermodynamic state
9 is changed from 0 GPa/300 K to 1 GPa/400 K. The populations of the other three angles are rather
10 sensitive to pressure and temperature.

11 **Solvent water:** **Figure 5** shows the O-O pair correlation function (top) and the distribution of the
12 coordination number (bottom) obtained by EPSR modeling in different thermodynamic states. In the
13 pair correlation functions at 0.1 MPa, the first, second and third peaks are observed at about 2.70,
14 4.35, and 6.45 Å, characteristic for **tetrahedral-like network structure of water**^{6,7} in an aqueous 1 *m*
15 CeCl_3 solution. The positions of the first and the second peak are given in **Table 2**. **With increasing**
16 **pressure at a constant temperature, the peak position shifts to a shorter distance by 0.03 Å from 2.67**
17 **Å at 0 GPa/300 K to 2.64 Å at 1 GPa/300 K and by 0.10 Å from 2.76 Å at 1 GPa/500 K to 2.66 Å at 4**
18 **GPa/500 K. On the other hand, with increasing temperature at a constant pressure, the peak position**
19 **shifts to a longer distance by 0.12 Å from 2.64 Å at 1 GPa/300 K to 2.76 Å at 1 GPa/500 K and by**
20 **0.10 Å from 2.66 Å at 4 GPa/500 K to 2.76 Å at 4 GPa/600 K. The effect of temperature on the solvent**
21 **water structure is somewhat more significant than the pressure. This tendency is similar to that for Ce^{3+}**
22 **hydration. Thus, we can say that such structured solvation shells as Ce^{3+} and water is perturbed by**
23 **temperature rather than pressure. On the other hand, the loosened solvation shell of Cl^- is influenced**
24 **by pressure rather than temperature.**

25 **Figure 5S** shows the distribution of angle Ow-Ow-Ow in various thermodynamic states. Under

1 ambient condition, a predominant peak is observed in the range of 80°~120° due to the tetrahedral-like
2 network structure of water. When the pressure and temperature are elevated, the peak centered at 55°
3 is enhanced and shifts to a higher angle side. On the other hand, the predominant peak centered at 104°
4 is gradually decreased and shifts to a higher angle side. This characteristic feature suggests that the
5 tetrahedral-like network structure of water is distorted or partially collapsed to generate interstitial
6 water between the first and the second shells.

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8 In Table 2, the mean coordination number of Ow-Ow(I) pairs gradually increases from 4.3 at 0
9 GPa/300 K to 9.7 at 4 GPa/600 K. This result suggests that with increasing pressure and temperature
10 the hydrogen bonds among water molecules are bent or partially broken to generate interstitial water
11 molecules between the first and the second shells. With an increase in temperature and pressure, the
12 second neighbor peak at 4.35 Å at 0 GPa/300 K shifts to a longer distance side, whereas the third peak
13 shifts to a shorter distance side. It is noted that the second and third peaks at 1 GPa and 300 K are still
14 observed at distances similar to those at 0 GPa/300 K. This feature is characteristic to an aqueous
15 CeCl₃ solution since in a 1 GPa pressure range since the second and third peaks appear at 6.0 and 8.5
16 Å, respectively, in a 3 m aqueous NaCl solution⁷ and at 5.8 and 8.9 Å, respectively, in a 2 m aqueous
17 CaCl₂ solution⁶ ascribed to a closed packed arrangement seen in liquid Ar.³⁵ This differences in the
18 water structure between the CeCl₃ solution and the NaCl and CaCl₂ solutions could be due to a large
19 amount of water available in the 1 m CeCl₃ solution.

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21 Figure 6 shows the spatial density distributions of solvent water in the first shell (purple), the second
22 shell (green), and the third shell (blue, mesh) around a central water molecule. The range of the first,
23 the second, and the third solvation shells are summarized in Supplementary Information (SI) Table 3S.
24 At 0 GPa/300 K, a tetrahedral-like network structure is seen. When pressure is increased to 1 GPa, the
25 second and the third neighbor shells are broadened, demonstrating that the tetrahedral-like network
26 structure of water is very perturbed. When temperature is elevated from 300 to 500 K at 1 GPa, the

first shell is further broadened and the third shell becomes less. When pressure is increased from 1 to 4 GPa at 500 K, the second shell is developed due to compression. However, at 4 GPa/600 K, the second shell is again perturbed by thermal agitation.

Ion association Figure 7 shows the pair correlation function (top) and the distribution of coordination number (bottom) of $\text{Ce}^{3+}\text{-Cl}^-$ pairs. The first peak at 3.09 Å is ascribed to a direct contact ion association, whereas the second peak at 5.09 Å is due to a solvent separated ion association. As is seen in the top frame of Fig. 7, the first peak gradually decreases with increasing pressure and temperature. In Table 2, the mean coordination number of $\text{Ce}^{3+}\text{-Cl}^-$ pairs decreases from 0.88 ± 0.78 at 0 GPa/300 K to 0.31 ± 0.46 at 4 GPa/600 K. This change in the mean coordination number is probably due to the fact that more free water molecules generated by perturbation of the tetrahedral-like network structure of solvent water due to compression to the GPa pressure range surround Ce^{3+} and Cl^- as discussed in the previous sections. The mean coordination number of $\text{Na}^+\text{-Cl}^-$ in a 3 *m* NaCl aqueous solution is 0.5 ± 0.5 at 0 GPa/300 K and 0.8 ± 0.8 at 1.7 GPa/300 K, whereas the value of $\text{Ca}^{2+}\text{-Cl}^-$ in a 2 *m* CaCl_2 aqueous solution is 0.3 ± 0.9 at 0 GPa/300 K and 0.2 ± 0.5 at 1.0 GPa/298 K. The mean coordination number (0.88) of $\text{Ce}^{3+}\text{-Cl}^-$ at 0 GPa/300 K is somewhat larger than those for the aqueous NaCl and CaCl_2 solutions, which could be ascribed to the stronger electrostatic interactions of a highly charged Ce^{3+} and Cl^- . The pressure effect on the ion association in the GPa pressure range is reflected significantly on the solvent separated ion association. The corresponding interatomic $\text{Ce}^{3+}\text{-Cl(II)}$ distance is shortened by 0.05 Å from 5.09 Å at 0 GPa/300 K to 5.04 Å at 4 GPa/600 K. A similar pressure effect on the solvent separated ion association has been observed in the aqueous NaCl and CaCl_2 aqueous solutions in the GPa pressure range.^{6,7}

1 **Conclusions**

2 Synchrotron X-ray diffraction experiments combined with EPSR modeling have revealed the
3 microscopic structure of a 1 *m* CeCl₃ aqueous solution in the GPa pressure range as follows.

4 *Tricapped trigonal prism configuration of the Ce³⁺ solvation shell retains in the GPa pressure range,
5 but accompanied with an increase in coordination number by three and distortion of Ow-Ce-Ow angles.

6 *Cl⁻ solvation shell changes drastically with a change in mean coordination number from 10 at 0
7 GPa/300 K to 17 at 4 GPa/600 K

8 *The tetrahedral-like network structure of water at 0 GPa/300 K is transformed toward a simple liquid-
9 like packing like Ar in the GPa pressure range with an increasing coordination number from 4.3 at 0
10 GPa/300 K to 9.7 at 4 GPa/600 K. The hydrogen bonds between water molecules remain, but the
11 number of interstitial water molecules increases with increasing pressure to the GPa pressure range.

12 *The Ce³⁺-Cl⁻ association decreases with increasing pressure due probably to enhancement of the ion
13 solvation in the GPa pressure range caused by an increase in free water molecules generated by
14 compression to the GPa pressure range.

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1 Table 1. The concentration and the density of an aqueous CeCl_3 solution at different thermodynamic
2 states P and T .

P/GPa	T/K	Density/ g cm^{-3}	$[\text{CeCl}_3]/\text{mol dm}^{-3}$
1×10^{-4}	300	1.187	0.883
1.0	300	1.468	1.092
1.0	400	1.410	1.049
1.0	500	1.353	1.006
2.0	500	1.488	1.107
4.0	500	1.759	1.309
4.0	600	1.742	1.296

1 Table 2. The interatomic distances (r) and the mean coordination numbers (CN) of ion hydration and
2 association and water structure. The symbols (I and II) in parentheses represent the first- and second
3 coordination shells, respectively, of each atom-pair. $r_{\max}$ is the upper limit of integration of eq. (3).

		Ce-O _w (I)	Cl-O _w (I)	Cl-O _w (II)	O _w -O _w (I)	O _w -O _w (II)	Ce-Cl(I)	Ce-Cl(II)
0 GPa, 300 K	$r/\text{\AA}$	2.61	3.24	-	2.67	4.40	3.09	5.09
	CN	8.8±1.2	10.1±1.3		4.3±1.0		0.88±0.78	
	$r_{\max}/\text{\AA}$	3.00	4.00		3.40		3.60	
1 GPa, 300 K	$r/\text{\AA}$	2.61	3.18	5.79	2.64	4.35	3.15	5.07
	CN	9.4±0.8	13.4±1.0		5.9±1.1		0.31±0.46	
	$r_{\max}/\text{\AA}$	3.00	4.00		3.4		3.60	
1 GPa, 400 K	$r/\text{\AA}$	2.62	3.21	5.83	2.70	4.41	3.12	5.10
	CN	9.6±1.6	14.4±1.6		7.0±1.5		0.88±0.99	
	$r_{\max}/\text{\AA}$	3.15	4.56		3.60		3.90	
1 GPa, 500 K	$r/\text{\AA}$	2.61	3.20	5.88	2.76	4.41	3.12	5.08
	CN	9.8±1.5	11.3±1.3		5.8±1.3		0.38±0.86	
	$r_{\max}/\text{\AA}$	3.00	4.00		3.40		3.60	
2 GPa, 500 K	$r/\text{\AA}$	2.61	3.21	5.79	2.71	4.41	3.12	5.10
	CN	10.2±1.4	16.0±1.4		7.9±1.4		0.44±0.70	
	$r_{\max}/\text{\AA}$	3.18	4.56		3.66		3.49	
4 GPa, 500 K	$r/\text{\AA}$	2.61	3.15	5.68	2.66	4.48	3.12	5.04
	CN	11.0±1.0	17.4±1.4		9.4±1.3		0.25±0.43	
	$r_{\max}/\text{\AA}$	3.21	4.38		3.66		3.99	
4 GPa, 600 K	$r/\text{\AA}$	2.61	3.18	5.79	2.76	4.56	3.15	5.04
	CN	11.5±1.0	17.4±1.4		9.7±1.4		0.31±0.46	
	$r_{\max}/\text{\AA}$	3.24	4.47		3.63		4.20	

Figure Captions

Fig. 1. The interference functions (top) and the radial distribution functions (bottom) for a 1 *m* CeCl₃ aqueous solution at different thermodynamic states. Experiments (dots) and EPSR modeling (solid lines). The number next to the temperature is the shift value of y-axis.

Fig. 2. The pair correlation functions (top) and the distribution of the coordination number (bottom) of the Ce-Ow pairs obtained from EPSR modeling of a 1 *m* CeCl₃ aqueous solution at different thermodynamic states. Ow denotes water oxygen atom. The number next to the temperature is the shift value of y-axis.

Fig. 3. The distribution of angle Ow-Ce-Ow of the cerium hydration at various thermodynamic states. The top figure represents the hydrated Ce³⁺ in a tricapped trigonal prism configuration taken from Refs. 32 and 33.

Fig. 4. The pair correlation functions (top) and the distribution of the coordination number (bottom) of the Cl-Ow pairs obtained from EPSR modeling of a 1 *m* CeCl₃ aqueous solution at different thermodynamic states. The number next to the temperature is the shift value of y-axis.

Fig. 5. The pair correlation functions (top) and the distribution of the coordination number (bottom) of the Ow-Ow pairs obtained from EPSR modeling of a 1 *m* CeCl₃ aqueous solution at different thermodynamic states. The number next to the temperature is the shift value of y-axis.

Fig. 6. The spatial density functions of the neighboring water oxygen atoms around a central water molecule in various thermodynamic states. The red and white balls of the central water molecules

1 represent the oxygen and hydrogen atoms, respectively. The purple lobes correspond with the first-
2 neighbor water oxygen atoms, the green lobes the second-neighbor water oxygen atoms, and the blue
3 mesh the third-neighbor water oxygen atoms. The range of the second neighbor and the third neighbor
4 shells are given in Supplemental Information Table 1S.

5
6 Fig. 7. The pair correlation functions (top) and the distribution of the coordination number (bottom) of
7 the Ce-Cl pairs obtained from EPSR modeling of a 1 *m* CeCl₃ aqueous solution at different
8 thermodynamic states.

1 Fig. 1 T. Yamaguchi et al.

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1 Fig. 2 T. Yamaguchi et al.

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1 Fig. 3 T. Yamaguchi et al.

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Fig. 6 T. Yamaguchi et al.

0 GPa, 300 K

1 GPa, 300 K

1 GPa, 400 K

1 GPa, 500 K

2 GPa, 500 K

4 GPa, 500 K

4 GPa, 600 K

1 Fig. 7 T. Yamaguchi et al.

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Graphical Index