X-ray Diffraction Study on Aqueous Scandium(III) Perchlorate and Chloride Solutions over the Temperature Range −45 to 95 °C

Pavel Smirnov, Hisanobu Wakita, and Toshio Yamaguchi*

Department of Chemistry, Faculty of Science, Fukuoka University, Nanakuma, Jonan-ku, Fukuoka 814-80, Japan

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X-ray scattering measurements have been performed on aqueous 1.6 and 2.8 M $ScCl_3$ and 4.7 M NH_4Cl solutions at room temperature and on aqueous 1 and 3 M $Sc(ClO_4)_3$ solutions over a temperature range of −45 to 95 °C. It has been shown that in the perchlorate solutions at room temperature Sc^{3+} forms the first coordination shell consisting of about seven water molecules at a distance of 215 pm and the second coordination shell at a distance of 410 pm. The number of water molecules bound to Sc^{3+} slightly increases with decreasing temperature. Contact ion pairs are formed with an $Sc^{3+}-Cl^-$ distance of 264 pm in the $ScCl_3$ solutions, whereas solvent-separated ion pairs are preferable in the $Sc(ClO_4)_3$ solutions over the temperature range investigated. The perchlorate ion has its hydration shell at a distance of 360 pm. At subzero temperatures, the hydrogen bonds are gradually reinforced with lowering temperature to partially evolve the intrinsic water structure.

Introduction

The structures of many hydrated ions have so far been investigated at ambient temperature by X-ray and neutron diffraction and X-ray absorption spectroscopy.[1] Despite these efforts the hydration structure of Sc^{3+} remains ambiguous. This is partly because Sc^{3+} has an intermediate ionic radius (75 pm) between those of Al^{3+} (54 pm) with the hydration number 6[1] and Y^{3+} (90 pm) with the hydration number 8[1] in group 3 elements. Very recently we have performed X-ray diffraction and X-ray absorption fine structure measurements on concentrated aqueous $Sc(ClO_4)_3$ and $Sc(CF_3SO_3)_3$ solutions at room temperature and found that about seven water molecules are coordinated to Sc^{3+} with an $Sc^{3+}-OH_2$ distance of 218 pm;[2] this result is consistent with the expectation from Raman spectra of glassy aqueous $ScCl_3$ and $Sc(ClO_4)_3$ solutions.[3] In the crystal structure of $[Sc(H_2O)_9](CF_3SO_3)_3$, however, the Sc^{3+} is surrounded by nine water molecules with six short $Sc^{3+}-OH_2$ bonds (217.1 pm) and three long ones (247 pm) in a tricapped trigonal fashion.[4] The structural difference in hydrated Sc^{3+} in solid and in solution has motivated us to further investigate its hydration structure under nonambient conditions.

In the past decade we have performed structural investigations of various aqueous solutions of (1−1) and (2−1) electrolytes over a wide range of temperatures and revealed that the hydration structure of ions is perturbed very much by temperature.[5,6] As an extension of such studies, it would be interesting to see how the neighboring solution structure is affected by trivalent Sc^{3+} under nonambient conditions. The perchlorate and chloride ions were selected as counteranions since the former is the least complex-forming ion and the latter is a complex-forming ion.

The hydration of the perchlorate ion has been investigated in aqueous solutions of various electrolytes as $HClO_4$, $MClO_4$ (M = Li, Na, and Mg), and $Ln(ClO_4)_3$ (Ln = lanthanide ions) with different salt concentrations by X-ray and neutron diffraction.[7−13] It has been found that the perchlorate ion forms a weak hydration shell at 370−380 pm with a concentration-dependent hydration number from 4 to 8.

The hydration of chloride ions has been established over a wide range of temperatures and pressures from X-ray and neutron diffraction measurements of various aqueous solutions.[1] At subzero and room temperatures six water molecules are coordinated to Cl^- at 315 pm,[14] but near the critical temperature (375 °C) there are only about four water molecules around Cl^-.[15]

In the present study, we have measured X-ray scattering from aqueous 1 and 3 M $Sc(ClO_4)_3$ solutions over a temperature range of −45 to 95 °C to investigate the hydration of Sc^{3+} and the anion, hydrogen bonding, and ion association. Aqueous 1.6 and 2.8 M $ScCl_3$ and 4.7 M NH_4Cl solutions were also measured at room temperature for a comparison, in particular, to investigate the degree of ion pairing. The present findings are discussed with previous results on aqueous electrolyte solutions under nonambient conditions.

Experimental Section

Preparation of Sample Solutions. Aqueous $ScCl_3$ and $Sc(ClO_4)_3$ solutions were prepared by dissolving Sc_2O_3 (99.9%, Wako Chemicals) in either concentrated HCl or $HClO_4$ aqueous solutions with heating and acidified slightly with hydrochloric and perchloric acids, respectively, to prevent hydrolysis. An aqueous NH_4Cl solution was prepared by dissolving commercially available NH_4Cl (98.5%, Wako Chemicals) into distilled water to a required amount. The concentration of Sc^{3+} was determined by standard complexion titration. The concentration of the perchlorate ion was determined by acid−base titration of a standard potassium hydroxide solution against the effluent after the sample solution was passed through cation exchange resins (DOW-50W). The concentrations of Cl^- were determined by gravimetric analysis as AgCl. The densities of the sample solutions at room temperature were measured with

* Author to whom correspondence should be addressed (telephone +81-92-871-6631, ext 6224; fax +81-92-865-6030; e-mail yamaguch@sunsp1.sc.fukuoka-u.ac.jp).

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TABLE 1: Compositions of the Sample Solutions (mol dm^{-3}), Density ρ (g cm^{-3}) at Room Temperature, and Water/Salt Molar Ratios

	$Sc(ClO_4)_3$		$ScCl_3$		NH_4Cl
	3 M	1 M	2.8 M	1.6 M	4.7 M
Sc^{3+}	3.00	1.06	2.82	1.59	
NH_4^+					4.71
ClO_4^-	9.01	3.19			
Cl^-			8.66	4.76	4.71
H_2O	36.3	48.9	49.4	52.3	45.0
ρ	1.68	1.25	1.33	1.18	1.06
$[H_2O]/[salt]$	12.1	46.1	17.5	33.0	9.60

picnometers. The densities of the $Sc(ClO_4)_3$ solution in a temperature range of 0−40 °C were measured at every degree with a densimeter DMA 35 (Anton Paar K.G.), whereas those at subzero temperatures were estimated by extrapolation. The compositions of the sample solutions are given in Table 1.

X-ray Diffraction Measurements. X-ray diffraction measurements of the sample solutions were made with a Rigaku $\theta-\theta$ type diffractometer. Temperatures measured were 25 °C for the aqueous 1.6 and 2.8 M $ScCl_3$ and 4.7 M NH_4Cl solutions, 95, 50, and 25 °C for the aqueous 1 M $Sc(ClO_4)_3$ solution, and 95, 50, 25, −15, −30, and −45 °C for the aqueous 3 M $Sc(ClO_4)_3$ solution. Low-temperature measurements of the 1 M $Sc(ClO_4)_3$ solution at temperatures below 0 °C and of the 3 M $Sc(ClO_4)_3$ solution at temperatures below −45 °C were not made because the solutions crystallized on further cooling. Mo Kα radiation (λ = 71.07 pm) was used. X-rays scattered from the free surface of a sample solution were monochromatized with an LiF (200) bent crystal. Cooling of the solutions was made on a special cryostat described before.[16] The temperature of the sample solution was measured with a copper−constantan thermocouple and controlled to within ±0.2 °C by use of a temperature control system. For high-temperature experiments an aluminum metal foil (7 μm) was further used on a Mylar window (100 μm) of the cell to prevent evaporation. The accumulated counts were 160 000 at each discrete point. The experimentally obtained X-ray intensities were corrected for background, absorption, polarization, multiple scattering, and Compton scattering as previously described.[17] The structure function, $i(s)$, is given by

$$i(s) = I^{\mathrm{coh}}(s) - \sum_i x_i f_i^2(s) \qquad (1)$$

where $f_i(s)$ represents the atomic scattering factor of atom i corrected for the anomalous dispersion.

The radial distribution functions $D(r)$ were calculated by means of the Fourier transform as

$$D(r) = 4\pi r^2 \rho_0 + 2r\pi^{-1}\int_0^{s_{\max}} si(s)M(s)\sin(rs)\,\mathrm{d}s \qquad (2)$$

Here, ρ_0 (=$[\Sigma x_i f_i(0)]^2/V$) stands for the average scattering density of a sample solution and $s_{\max}$ is the maximum s value attained in the measurements ($s_{\max}$ = 0.166 pm^{-1}). A modification function $M(s)$ of the form $[\Sigma x_i f_i^2(0)/x_i f_i^2(s)]\exp(-100s^2)$ was used for the sample solution.

A comparison between the experimental structure function and the theoretical one based on a model was made by a least-squares refinement procedure of minimizing an error square sum:

$$U = \sum_{s_{\min}}^{s_{\max}} s^2\{i(s)_{\mathrm{exptl}} - i(s)_{\mathrm{calcd}}\}^2 \qquad (3)$$

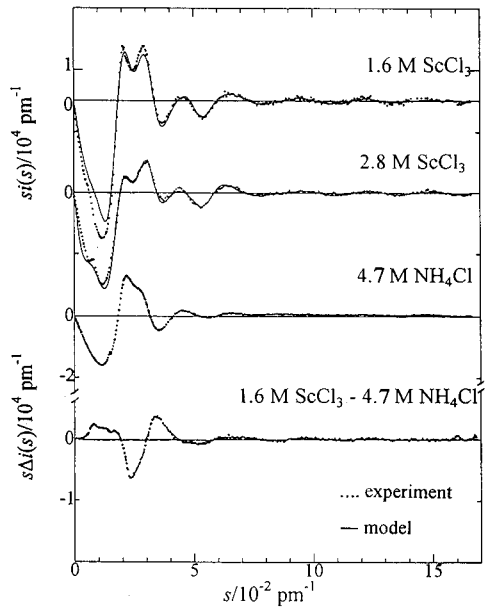

Figure 1. Structure functions $i(s)$ multiplied by s for the 1.6 and 2.8 M $ScCl_3$ and 4.7 M NH_4Cl aqueous solutions with their difference function at room temperature. The experimental values are given by dots and those calculated with the parameter values in Table 2 by solid lines.

The theoretical intensities $i(s)_{\mathrm{calcd}}$ were obtained by

$$i(s)_{\mathrm{calcd}} = \sum_i\sum_{\substack{g\\ i\neq g}} x_i n_{ij} f_i(s) f_j(s)\sin(r_{ij}s)(r_{ij}s)^{-1}\exp(-b_{ij}s^2) - \sum_i\sum_{\substack{g\\ i\neq g}} x_i x_j f_i(s) f_j(s)\, 4\pi R_j^3 V^{-1}\{\sin(R_j s) - R_j s\cos(R_j s)\}\times (R_j s)^{-3}\exp(-B_j s^2) \qquad (4)$$

The first term of the right-hand side of eq 4 is related to the short-range interactions characterized by the interatomic distance r_{ij}, the temperature factor b_{ij}, and the number of interactions n_{ij} for atom pair $i-j$. The second term arises from the interaction between a spherical hole and the continuum electron distribution beyond this discrete distance. R_i is the radius of a spherical hole around the ith atom and B_i the softness parameter for emergence of the continuum electron distribution.

All treatments of the X-ray diffraction data were carried out with the program KURVLR.[18]

Results and Discussion

Radial Distribution Functions (RDFs). The experimental structure functions for the aqueous 1.6 and 2.8 M $ScCl_3$ and 4.7 M NH_4Cl solutions are shown in Figure 1. The corresponding RDFs, $D(r) - 4\pi r^2\rho_0$, are depicted in Figure 2.

In Figure 2, the first peak at ∼220 pm is ascribed to $Sc^{3+}-H_2O$ bonds due to the cation hydration according to previous works[2,4] and the sum of the radii of Sc^{3+} and H_2O.[19] The predominant peak is observed at 310 pm for the 1.6 M $ScCl_3$ solution and is shifted to 315 pm for the 2.8 M solution. This peak corresponds to the Cl^--H_2O interactions within the anion hydration as previously found in other aqueous chloride solutions.[1,14,15] The enhancement of the peak around 300 pm for the 1.6 M solution, compared with that for the 2.8 M solution, is caused by an increase in the first-neighbor water−water interactions at 285 pm, which has usually been observed

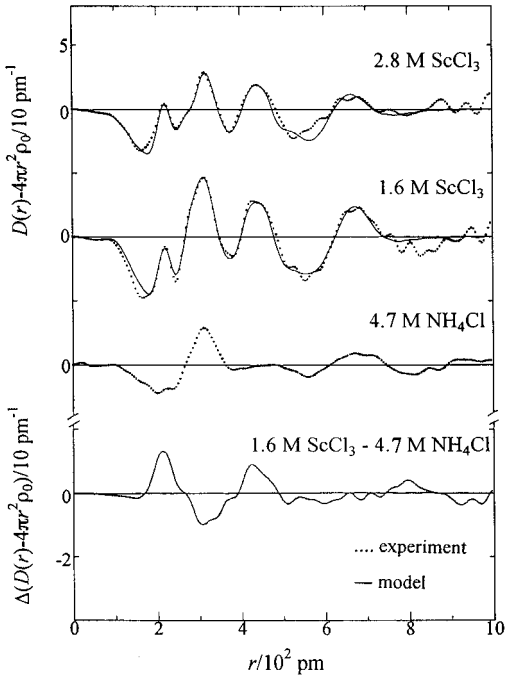

Figure 2. Radial distribution functions in the form of $D(r) - 4\pi r^2\rho_0$ for the 1.6 and 2.8 M $ScCl_3$ and 4.7 M NH_4Cl aqueous solutions with their difference function at room temperature. Shown are experimental (dots) and calculated (solid lines) values, which are obtained by Fourier transform of the values in Figure 1.

for liquid water[20] and aqueous solutions.[7−13] The corresponding peak in the 2.8 M $ScCl_3$ solution appears as a shoulder around 290 pm. The broad peak in the range 420−450 pm arises mainly from two kinds of interactions: one is the second-neighbor water−water interactions,[20] and the other is the interactions related to the second coordination shell of Sc^{3+}.[2] The large peak centered at 650−660 pm includes several interactions and is thus difficult to analyze quantitatively. However, a similar broad peak has generally been observed around 650 pm in aqueous solutions,[14] thus ascribed probably to water-related interactions.

Since Cl^- is a complex-forming ion, the possibility of the contact $Sc^{3+}-Cl^-$ ion association was examined. On the basis of the ionic radii of Sc^{3+} (75−87 pm) and Cl^- (181 pm), the $Sc^{3+}-Cl^-$ interactions were expected to appear around 256−268 pm, which would be superimposed on the tails of the peaks at 220 and 300 pm. To extract the Sc^{3+}-related interactions in the RDF of the 1.6 M $ScCl_3$ aqueous solution, the structure function of the 4.7 M NH_4Cl aqueous solution was subtracted from that of the 1.6 M $ScCl_3$ solution after the stoichiometric volumes were normalized to contain the same amount of H_2O or $H_2O + NH_4^+$ in both solutions. It should be noted that the size of NH_4^+ is similar to that of H_2O, and thus NH_4^+ is replaced by a water molecule in bulk structure without significant perturbation of water structure.[21] In the difference RDF thus obtained (Figure 2) the water−water and Cl^-−water interactions are almost canceled out. As is observed in the figure there are two distinct peaks at about 215 and 410 pm, corresponding to the $Sc^{3+}-H_2O$ interactions in the first and second hydration shells, respectively. In addition, a shoulder appears at ∼260 pm, showing the presence of the $Sc^{3+}-Cl^-$ contact ion pairs in the 1.6 M $ScCl_3$ solution.

The experimental structure functions for the 3 and 1 M aqueous $Sc(ClO_4)_3$ solutions at various temperatures are shown in Figures 3 and 4, respectively. The corresponding RDFs are depicted in Figures 5 and 6.

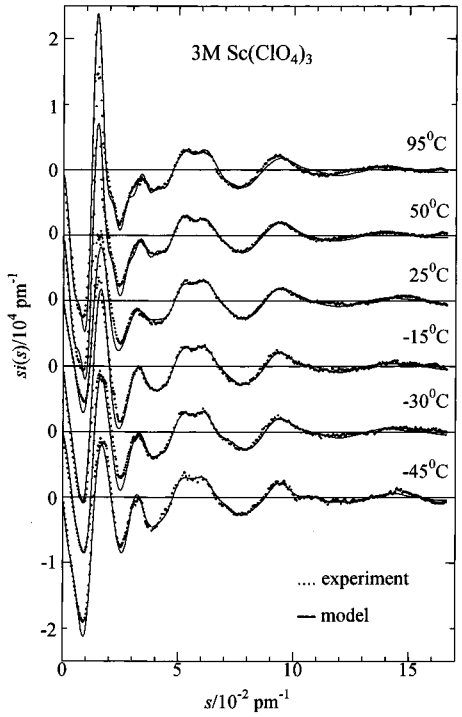

Figure 3. Structure functions $i(s)$ multiplied by s for the 3 M $Sc(ClO_4)_3$ aqueous solution at various temperatures. The experimental values are given by dots and those calculated with the parameter values in Table 3 by solid lines.

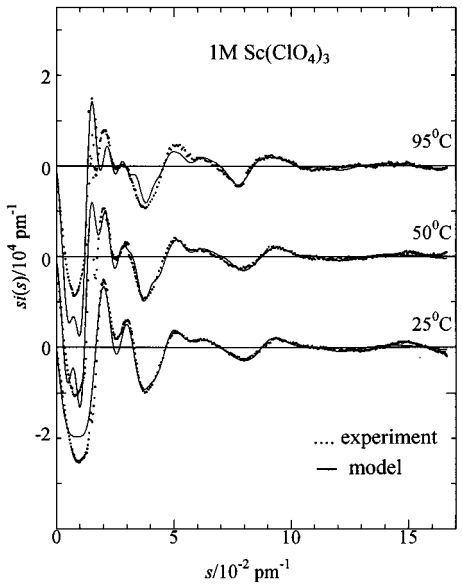

Figure 4. Structure functions $i(s)$ multiplied by s for the 1 M $Sc(ClO_4)_3$ aqueous solution at various temperatures. The experimental values are given by dots and those calculated with the parameter values in Table 4 by solid lines.

All of these RDFs have almost the same set of peaks. The first sharp peak at 143 pm arises from the Cl−O interactions within the perchlorate ion.[7−13] The next peak at ∼225 pm is ascribed to the $Sc^{3+}-H_2O$ bonds due to the cation hydration. The interactions between the oxygen atoms within the tetrahedral perchlorate ion fall at 237 pm and are thus included partly in this peak. The next peak at 280−290 pm appears due to the H_2O-H_2O hydrogen bonds in the bulk water,[20] to the interactions between water molecules bound to Sc^{3+} in the first coordination shell, to those between the water molecules in the first and outer shells, and to those between the oxygen atoms

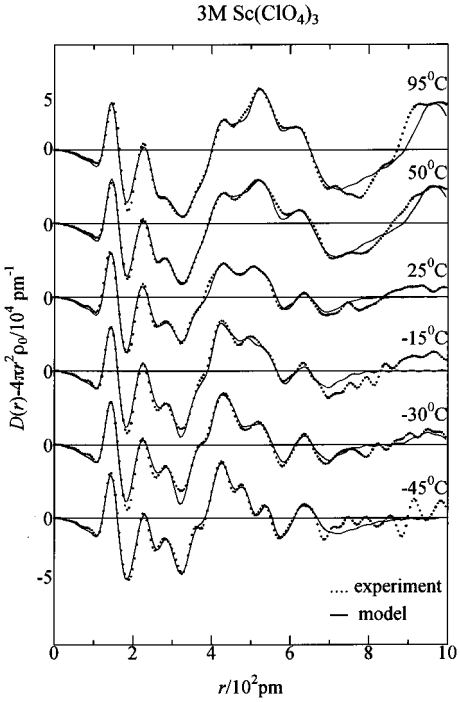

Figure 5. RDFs in the form of $D(r) - 4\pi r\rho_0$ for the 3 M $Sc(ClO_4)_3$ aqueous solution at various temperatures. Shown are experimental (dots) and calculated (solid lines) values, which are obtained by Fourier transform of the values in Figure 3.

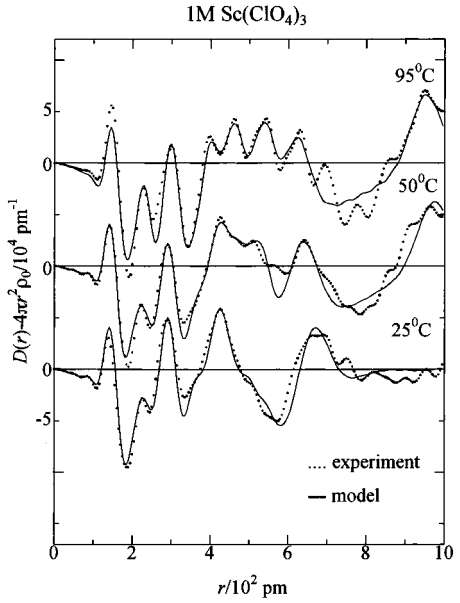

Figure 6. RDFs in the form of $D(r) - 4\pi r^2\rho_0$ for the 1 M $Sc(ClO_4)_3$ aqueous solution at various temperatures. Shown are experimental (dots) and calculated (solid lines) values, which are obtained by Fourier transform of the values in Figure 4.

of the perchlorate ion and its weakly hydrated water molecules ($O_{ClO_4^-}$ $-H_2O$). The well-observed shoulder at ~360 pm in Figure 6 arises from the interactions between the perchlorate Cl atom and the surrounding water molecules due to the anion hydration ($Cl_{ClO_4^-} - H_2O$).[8−13] The broad peak at ~420−450 pm is ascribed to the second-neighbor distances in the bulk water at ~450 pm[20] and to the distances between the cation and its second coordination shell at ~410 pm as discussed above for the $ScCl_3$ aqueous solutions.

In the RDF of the 3 M $Sc(ClO_4)_3$ aqueous solution, a broad peak is observed at around 500 pm at room temperature and is

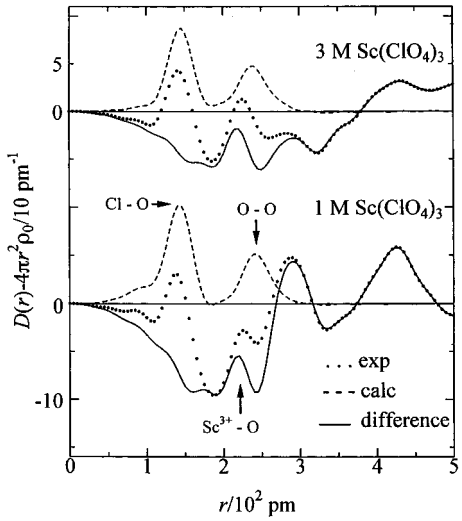

Figure 7. Contributions of the Cl−O and O−O interactions within the perchlorate ion (dashed lines) to the experimental RDFs (dots) of the 1 and 3 M $Sc(ClO_4)_3$ aqueous solutions at room temperature. The differential functions are shown with the solid lines.

sharpened at elevated temperatures. It should be noted in Figure 2 that the corresponding peak is absent in the RDF of the $ScCl_3$ solution of a similar concentration at room temperature. This suggests that the 500 pm peak is ascribed to perchlorate ion-related interaction, most probably the solvent-separated ion pairs between Sc^{3+} and ClO_4^-. The enhancement of the peak with rising temperature does show that the ion pair formation is more favorable at higher temperatures.

A large peak centered at 650−660 pm, which has also been observed for the aqueous $ScCl_3$ solutions, includes many different contributions, but the main contribution can be ascribed to water-related interactions.

With cooling of the solutions, all water-originated peaks at 290, 450, and 650 pm become more and more intensive. This finding shows the evolution of partial intrinsic water structure caused by strengthened hydrogen bonds at low temperatures as observed for other supercooled aqueous solutions of LiX (X = Cl, Br, and I),[5,14,22] $Ca(NO_3)_2$,[6] and $ZnBr_2$.[23]

On dilution of the solution to 1 M, the peaks at 290, 450, and 650 pm become enhanced since the contribution from the bulk water is dominant. The peak at ~500 pm almost disappears, in contrast with the case for the 3 M $Sc(ClO_4)_3$ solution; this suggests a decrease in the amount of the solvent-separated ion pairs with dilution.

Model Fitting. To analyze the X-ray diffraction data quantitatively, a model fitting procedure was applied to the experimental structural functions (Figures 1, 3, and 4) as has previously been described in detail.[14,16] All calculations were performed with the program NLPLSQ.[24] In the present calculations, the perchlorate ion was treated as a tetrahedral moiety with Cl−O and O−O distances of 143 and 237 pm and temperature factors of 2 and 3 pm^2, respectively.[7−13] To illustrate the contributions of the perchlorate ion and the Sc^{3+}−H_2O interactions to the 225 pm peak, the theoretical peaks of the ClO_4^- ion were calculated and subtracted from the experimental RDFs for 1 and 3 M solutions at room temperature (Figure 7). The differential functions show the contribution of the Sc^{3+}−H_2O interactions, which is large enough for quantitative analysis. The following complete model fitting procedure was then performed. The interatomic distance r, the temperature factor b, and the number of interactions n were treated as variables. All interactions discussed in the previous section were

TABLE 2: Important Structural Parameter Values Obtained by the Model Fitting for the 1.6 and 2.8 M $ScCl_3$ Aqueous Solutions at Room Temperature[a]

interaction	parameter	1.6 M	2.8 M
$Sc^{3+}-H_2O$	*r*	218 (2)	218 (2)
	b/10	3	3
	n	6.2 (2)	6.7 (2)
$Sc^{3+}-Cl^-$	*r*	265 (2)	263 (2)
	b/10	7	7
	n	1.2 (2)	1.6 (2)
H_2O-H_2O	r	283 (2)	287 (2)
	b/10	9	9
	n	3.1 (1)	2.0 (1)
Cl^-H_2O	*r*	315 (2)	315 (2)
	b/10	16	16
	n	4.7 (2)	5.4 (2)
$Sc^{3+}-H_2O$	*r*	416 (3)	415 (3)
	b/10	16	16
	n	9.0 (3)	7.4 (3)
H_2O-H_2O	*r*	457 (3)	455 (3)
	b/10	18	18
	n	1.0 (2)	1.7 (2)
O−O	*r*	665 (4)	650 (4)
	b/10	60	60
	n	0.9 (1)	1.45 (1)

[a] Interatomic distance *r* (pm), temperature factor *b* (pm^2), number of interactions *n*. The values in parentheses are their estimated standard deviations.

taken into account and are summarized with their optimized values finally obtained in Tables 2−4. Theoretical structure functions and RDFs based on the models are shown in Figures 1−6 and are in good agreement with the experimental values.

In the $ScCl_3$ solutions, as can be seen in Table 2, Sc^{3+} forms contact ion pairs with Cl^- and has ∼6 water molecules and ∼1.3 Cl^- with $Sc^{3+}-H_2O$ and $Sc^{3+}-Cl^-$ distances of 218 and 263 pm, respectively, in the first coordination shell. The second coordination shell of Sc^{3+} is formed with an $Sc^{3+}-H_2O$ distance of 416 pm. The number of water molecules around Cl^- is ∼5, slightly smaller than 6 as usually observed for aqueous chloride solutions[14,15] because of the formation of the contact ion pairs.

In the case of the $Sc(ClO_4)_3$ aqueous solutions the model analysis was initiated from the 3 M solution at room temperature. To determine the hydration number of Sc^{3+}, different models of the aqua Sc^{3+} with hydration numbers of 6−9 were examined; a good agreement between the experimental and theoretical functions has been obtained for the hydration number 7 and the $Sc^{3+}-OH_2$ distance 215 pm. This result is in good accordance with conclusions in the previous work.[2] In the 3 M $Sc(ClO_4)_3$ solution, the cation builds up the second coordination shell from ∼16 water molecules and/or perchlorate O atoms with the $Sc^{3+}-O_{II}$ distance of ∼410 pm; this suggests that ∼2 water molecules and/or the perchlorate O atoms are connected with one water molecule in the first coordination shell.

When the aqueous 3 M $Sc(ClO_4)_3$ solution is supercooled, the hydration number of Sc^{3+} slightly increases from 7.2 at 25 °C to 7.6 at −45 °C. This can be interpreted as follows. At subzero temperatures the hydrogen bonds among water molecules are strengthened; thus, the intrinsic water structure is partially recovered, as has been seen for aqueous supercooled solutions of mono- and divalent cations and halide ions.[5,14,16,22,23] On the other hand, the hydration shell of Sc^{3+} is rigid and should be stable at a temperature as low as −45 °C because of highly positive charge. The partially recovered water structure and stable aqua Sc^{3+} probably compromise on a slight increase in coordination number of Sc^{3+} as has been observed in the crystal structure of $[Sc(H_2O)_9](CF_3SO_3)_3$. The solution structure at −45 °C for the aqueous 3 M $Sc(ClO_4)_3$ solution is likely to reflect the initial step of crystallization of the solution. On the other hand, when the temperature is elevated to +95 °C, the hydration number of the Sc^{3+} decreases to 6.7. One of the reasons will be large thermal motion of water molecules coordinated to Sc^{3+}, followed by partial dehydration of the cation.

The solvent-separated ion pairs between Sc^{3+} and ClO_4^- are characterized by $Sc^{3+}-O$ (410 pm), $Sc^{3+}-Cl$ (500−510 pm), and $Sc^{3+}-O$ (535−540 pm) distances. The orientation of the perchlorate ion toward Sc^{3+} was difficult to uniquely determine in the present X-ray analysis. The formation of the ion pairs appears to be favorable at both elevated and supercooled

TABLE 3: Important Structural Parameter Values Obtained by the Model Fitting for the 3 M $Sc(ClO_4)_3$ Aqueous Solution at Various Temperatures[a]

interaction	parameter	−45 °C	−30 °C	−15 °C	25 °C	50 °C	95 °C
$Sc^{3+}-H_2O$	*r*	215 (2)	215 (2)	215 (2)	215 (2)	215 (2)	214 (2)
	b/10	3	3	3	3	3	3
	n	7.6 (2)	7.5 (2)	7.4 (2)	7.2 (2)	6.8 (2)	6.7 (2)
H_2O-H_2O	*r*	285 (2)	287 (2)	286 (2)	284 (2)	284 (2)	286 (2)
$O_{ClO_4^-}-H_2O$	*b*/10	9	9	9	9	9	9
	n	5.3 (1)	4.8 (1)	4.12 (1)	4.0 (1)	3.8 (1)	3.6 (1)
H_2O-H_2O	*r*	450 (3)	450 (3)	450 (3)	450 (3)	455 (3)	455 (3)
$O_{ClO_4^-}-H_2O$	*b*/10	22	22	22	22	22	22
	n	2.7 (2)	2.40 (2)	2.30 (2)	2.2 (2)	2.6 (2)	2.5 (2)
$Sc^{3+}-H_2O_{II}$	*r*	410 (3)	410 (3)	410 (3)	410 (3)	410 (3)	414 (3)
	b/10	19	19	19	19	19	19
	n	22 (3)	18 (3)	18 (3)	16 (3)	18 (3)	18 (3)
$Cl_{ClO_4}-H_2O$	*r*	360 (2)	360 (2)	360 (2)	362 (2)	365 (2)	365 (2)
	b/10	16	16	16	16	16	16
	n	6.8 (3)	6.0 (3)	5.8 (3)	5.5 (3)	5.6 (3)	5.7 (3)
$Sc^{3+}-Cl_{ClO_4^-}$	*r*	500 (3)	515 (3)	500 (3)	503 (3)	505 (3)	507 (3)
	b/10	30	30	30	30	30	30
	n	3.2 (2)	3.0 (2)	2.8 (2)	2.5 (2)	3.5 (2)	4.0 (2)
$Sc^{3+}-O_{ClO_4^-}$	*r*	540 (4)	538 (4)	537 (4)	537 (4)	535 (4)	540 (4)
	b/10	40	40	40	40	40	40
	n	9.9 (3)	9.5 (3)	8.9 (3)	7.6 (3)	9.5 (3)	12 (3)
O−O	*r*	629 (4)	628 (4)	626 (4)	628 (4)	618 (4)	614 (4)
	b/10	50	50	50	50	50	50
	n	2.4 (1)	2.1 (1)	1.9 (1)	1.9 (1)	1.85 (1)	1.83(1)

[a] Interatomic distance *r* (pm), temperature factor *b* (pm^2), number of interactions *n*. The values in parentheses are their estimated standard deviations.

TABLE 4: Important Structural Parameter Values Obtained by the Model Fitting for the 1 M $Sc(ClO_4)_3$ Aqueous Solution at Various Temperatures[a]

interaction	parameter	25 °C	50 °C	95 °C
$Sc^{3+}-H_2O$	*r*	216 (2)	214 (2)	216 (2)
	b/10	3	3	3
	n	7.2 (2)	6.9 (2)	6.8 (2)
H_2O-H_2O	*r*	289 (2)	289 (2)	295 (2)
$O-H_2O$	*b*/10	9	9	9
	n	4.2 (1)	4.1 (1)	3.8 (1)
H_2O-H_2O	*r*	450 (3)	445 (3)	450 (3)
$O-H_2O$	*b*/10	22	22	22
	n	1.65 (2)	1.62 (2)	1.6 (2)
$Sc^{3+}-H_2O_{II}$	*r*	410 (3)	410 (3)	405 (3)
	b/10	19	19	19
	n	16.2 (3)	16.5 (3)	16.0 (3)
$Cl_{ClO_4}-H_2O$	*r*	360 (2)	363 (2)	365 (2)
	b/10	16	16	16
	n	7.3 (3)	6.0 (3)	4.6 (3)
$Sc^{3+}-Cl_{ClO_4}$	*r*	506 (3)	509 (3)	510 (3)
	b/10	30	30	30
	n	1.8 (2)	2.3 (2)	2.8 (2)
$Sc^{3+}-O_{ClO_4}$	*r*	536 (4)	540 (4)	540 (4)
	b/10	40	40	40
	n	5.6 (3)	6.9 (3)	8.4 (3)
O−O	*r*	660 (4)	630 (4)	610 (4)
	b/10	50	50	50
	n	1.5 (1)	1.5 (1)	1.4 (1)

[a] Interatomic distance *r* (pm), temperature factor *b* (pm^2), number of interactions *n*. The values in parentheses are their estimated standard deviations.

temperatures. At elevated temperatures, the dielectric constant of water decreases with increasing temperature;[25] hence, the solvent-separated ion pair formation is favored with increasing temperature. In addition, enhanced thermal motions of water molecules around the cation and anion will lead to partial dehydration and thereby promote the ion association. On the contrary, the present finding of increasing ion association in the supercooled solutions is not expected from the dielectric constant. As we have discussed previously, in the supercooled state, the bulk water structure is partially recovered due to reinforced hydrogen bonds. Under this condition, microheterogeneity will occur in the solution, followed by local condensation of the electrolyte solution and promotion of ion association. The increase in contact ion pairing in going from ambient temperature to supercooled and glassy states has been evidenced from Raman and infrared spectroscopic measurements of dilute (0.02−0.5 M) aqueous solutions of alkaline earth nitrates by Fleissner et al.[26,27] The authors have reasoned that the increase in ion pairing in the dilute supercooled and glassy solutions is caused by structural changes toward a more open, fully hydrogen bonded tetrahedral network in its supercooled and glassy state. The present study has demonstrated that a similar phenomenon takes place even in concentrated supercooled electrolyte solutions. It should be added that the relative permittivity of a concentrated solution with a composition $LiCl{\cdot}6.72H_2O$ decreases with lowering temperature in the supercooled state.[28]

The hydration of the perchlorate ion is characterized at room temperature by 5.5 water molecules at 362 pm. With lowering temperature the number of water molecules around the perchlorate ion increases. It is likely that the water molecules around the structure-breaking perchlorate ion take part in forming local water structure at subzero temperatures.

With dilution of the perchlorate solution to 1 M, the hydration number of Sc^{3+} and the amount of water molecules in the second coordination shell remain the same as for the concentrated solution, the hydration number of the perchlorate ion increases, and the amount of solvent-separated ion pairs decreases. These trends are well explained by an increase in free water molecules in the diluted solution. The structural change in the 1 M solution with increasing temperature is almost the same as for the concentrated solution; that is, the coordination numbers of Sc^{3+} and ClO_4^- decrease with raising temperature, and the amount of solvent-separated ion pairs increases (Table 4).

Conclusions

X-ray diffraction measurements on 1 and 3 M aqueous $Sc(ClO_4)_3$ solutions over a wide temperature range have revealed a temperature-dependent hydration number of Sc^{3+}; at room temperature Sc^{3+} has about seven water molecules in the first coordination shell with the $Sc^{3+}-H_2O$ distance at 215 pm and the second coordination shell at the distance of ∼410 pm. The number of water molecules bound to Sc^{3+} slightly increases with lowering temperature. The perchlorate ion has its coordination shell around 360 pm, and the number of water molecules in the shell increases from 5.7 to 6.8 with decreasing temperature. Solvent-separated ion pairs are present in the aqueous perchlorate solutions, and the number of ion pairs increases with both cooling and heating of the solution. Dilution of the solution leads to decreasing degree of the ion pairs. The partial recovery of ice-like water−water interactions is observed in the solutions with lowering temperature. In the aqueous 1.6 (2.8) M $ScCl_3$ solutions at room temperature contact ion pairs between Sc^{3+} and Cl^- are formed; the coordination shell of Sc^{3+} consists of 6.2 (6.7) water molecules at 218 (218) pm and 1.2 (1.6) Cl^- at 265 (263) pm as average species.

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