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X-ray diffraction study of calcium nitrate tetrahydrate melt at 328 K

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The hydration structure of calcium nitrate tetrahydrate, $Ca(NO_3)_2 \cdot 4.1H_2O$, melt at 328 K has been investigated by X-ray scattering and correlation method. Analysis of the radial distribution function and model fitting revealed that in the hydrate melt, a Ca^{2+} ion is surrounded by about six oxygen atoms, 4.1 of which come from water molecules at the average distance of 0.241 nm, 2.0 coming from the nitrate ions at the average distance of 0.254 nm. In the first coordination shell of the melt, the formation of a direct Ca^{2+}–NO_3^- correlation, such as contact ion pairs, was suggested. The hydration structure of the melt analysed was compared with that of $Ca(NO_3)_2 \cdot 3.5H_2O$ melt previously reported, and the decrease from nine of the reported melt to six in this melt was observed in the number of the nearest neighbour oxygen atoms around a Ca^{2+} ion. This implies that in the highly concentrated aqueous solution, the structure of the first coordination shell around the cation changes markedly with a small difference in the water molecule content.

1. Introduction

Recently, a ternary mixture aqueous solution of alkali nitrates was noted as a new absorption working pair of an absorption heat pump which provides higher temperature capability, higher lifts, and use of lower-cost construction materials than current working pairs, e.g. $LiBr$–H_2O[1]. This absorbent is characteristically thermally stable to above 530 K and promotes the formation of a passive and protective corrosion-resistant oxide film on both mild steel and all stainless steels. An addition of salt, such as alkaline earth nitrates, to the solution is expected to enhance the capability of the absorbent to lower efficiently the vapour pressure of water. In searching for available salts for the addition, information on the hydration structure of ions in concentrated aqueous solutions is required.

Numerous investigations on the hydration structure around a cation and an anion in aqueous solutions have been carried out using X-ray and neutron diffractions [2–6] and computer simulations such as Monte Carlo and molecular dynamics calculations [7–9]. Most of these works considered solutions of relatively diluted concentration, up to about 4M, but there are a few studies on concentrated solutions, so-called hydrate melts. Yamaguchi *et al.* [10] studied the hydration structure of calcium chloride hydrate melts, $CaCl_2 \cdot RH_2O$, with $R = 4.0$–8.6 by X-ray diffraction analysis and model fitting, and reported that in the solution with $R = 8.6$, a Ca^{2+} ion is surrounded by six water molecules, and with decreasing H_2O concentration a direct Ca^{2+}–Cl^- correlation, due to the formation of contact ion pairs, appears. Furthermore, it was found that in the $CaCl_2 \cdot 6H_2O$ melt, almost one Cl^- ion binds to a Ca^{2+} ion, and in the $CaCl_2 \cdot 4H_2O$ melt, about two Cl^- ions coordinate to a Ca^{2+} ion. Although the counter anion differs, the hydration structure of the more concentrated hydrate melt containing the Ca^{2+} ion was investigated by Caminiti *et al.* [11]. They reported for the $Ca(NO_3)_2 \cdot 3.5H_2O$ melt at room temperature, that a Ca^{2+} ion is coordinated to nine oxygen atoms, partly coming from water molecules, partly from NO_3^- ions.

In connection with the development of a new absorption working pair containing alkali and alkaline earth nitrates, we have already studied thermal characteristics of calcium nitrate tetrahydrate [12] and the molar volume of the molten binary mixture containing anhydrous calcium nitrate [13]. In this work, we report the hydration structure of the calcium nitrate tetrahydrate melt at 328 K, obtained from the analysis of the radial distribution function based on X-ray diffraction measurements and model fitting.

2. Experimental procedure

The hydrate salt used was of analytical reagent grade and was dried under a reduced pressure (200 Pa) at room temperature to remove water adhering to the crystal surface. In this process, attention was paid to avoid excessive evacuation thus promoting the reduction of hydrated water. Because this compound was very deliquescent, all treatments and measurements were performed under a high-purity nitrogen atmosphere. The exact value of the water molecules in the hydrate salt was determined to be 4.1 with thermogravimetric–differential thermal analysis (TG–DTA) and titrations using EDTA and Karl-Fischer reagents, indicating that the melting point of the salt thus prepared was 316 K, which was comparable to the literature value of 315.9 K [14].

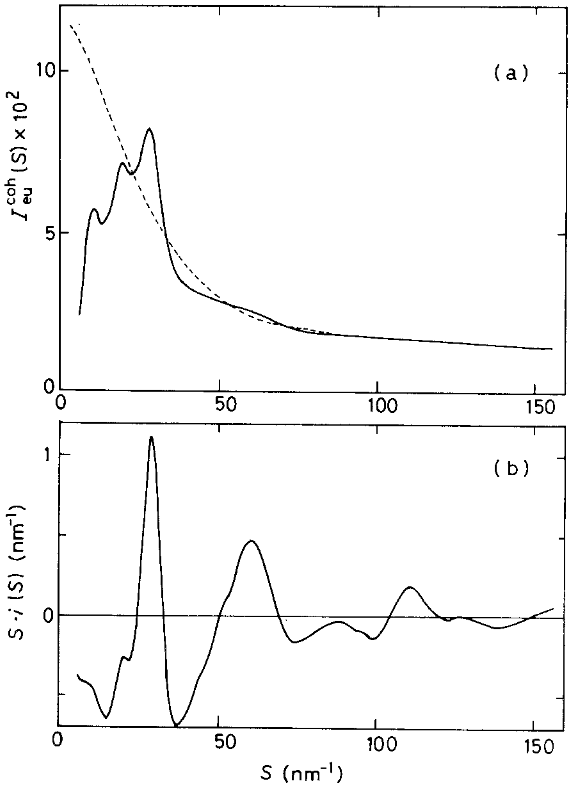

Figure 1 Total coherent intensity, $I_{eu}^{coh}(S)$, and reduced intensity, $S \cdot i(S)$, curves of $Ca(NO_3)_2 \cdot 4.1H_2O$ melt at 328 K. The monotonically decreasing curve in total coherent intensity indicates the calculated self-scattering intensity.

X-ray diffraction (XRD) measurements were performed on a θ–θ X-ray diffractometer with a curved graphite monochromator mounted in the diffracted beam. The diffracted intensities were counted using the step-scanning technique for a fixed count at every interval of 0.25 °. The observable range of scattering angle, θ, was $3° \leq \theta \leq 62°$, corresponding to the range $9.25 \leq S\,\mathrm{nm}^{-1} \leq 156.1$ ($S = 4\pi\sin\theta/\lambda$, $\lambda = 0.071\,0\,7$ nm) for MoK_α radiation. Divergence and scattering silts of $\frac{1}{2}°$–$\frac{1}{2}°$, 1 °–1 °, and 2 °–2 ° were used for the low-angle ($3° \leq \theta \leq 15°$), middle-angle ($13° \leq \theta \leq 35°$), and high-angle ($32° \leq \theta \leq 62°$) regions, respectively. Several runs were made in order to accumulate 5×10^4 counts per datum point in the low scattering and 1×10^5 counts in the middle and high scattering angles. The sample was contained in a small BN vessel (40 mm × 40 mm × 15 mm) with a heater set in a small airtight chamber under a helium atmosphere. Because the $Ca(NO_3)_2 \cdot 4.1\ H_2O$ melt is stable without dehydration from the melting point to 331 K [12], the temperature of the melt was set at 328 K and controlled to within ± 0.2 K throughout the experiments with a programmable temperature device. The intensity data were corrected for background, polarization, absorption and Compton radiation, and were normalized to the independent scattering factor for the stoichiometric unit according to the usual method [15]. Atomic scattering factors and Compton scattering factors were taken from the literature [16–19]. The reduced intensity, $S \cdot i(S)$, the radial distribution function, $D(r)$, and the correlation function, $G(r)$, are given by

$$S \cdot i(S) = \frac{S[I_{eu}^{coh}(S) - \sum_m f_m^2(S)]}{\sum_m f_m^2(S)} \qquad (1)$$

$$D(r) = 4\pi r^2 g_0 + \frac{\sum_m (\bar{K}_m)^2 r}{\pi} \int_0^{S_{max}} S \cdot i(S) \sin(Sr) \mathrm{d}S \qquad (2)$$

$$G(r) = 1 + \frac{\sum_m (\bar{K}_m)^2}{(2\pi^2 g_0 r)} \int_0^{S_{max}} S \cdot i(S) \sin(Sr)\, \mathrm{d}S \qquad (3)$$

$$g_0 = \left(\sum_m \bar{K}_m\right)^2 \rho_0 \qquad (4)$$

where ρ_0 is the number of stoichiometric units per volume, K_m is the effective number of electrons in the atom m, $f_m(S)$ the independent atomic scattering intensity and $I_{eu}^{coh}(S)$ the total coherent intensity function and S_{max} is the maximum value of S reached in the experiments. Summation is over the stoichiometric units for m. The effective electron numbers of respective atoms for this melt were obtained to be 27.280 for the calcium atom, 6.730 for nitrogen, 7.923 for oxygen, and 0.254 for hydrogen. The intensity $S \cdot i(S)$ was corrected by the repeated Fourier transformations [20], to remove ghost peaks or ripples in front of the first peak of $D(r)$. In the calculations, a modification function, which is a damping factor that minimizes the truncation effect of the integral at S_{max}, was not used, because the spurious peaks at the longer distance than the first peak of the $D(r)$ did not appear. The density of the melt was measured dilatometrically under atmospheric pressure, as described elsewhere [21] and was determined to be 1.766×10^3 kg m^{-3} at 328 K, which was a higher value by 2.8% than that of Moynihan and Fratiello [22].

3. Results and discussion

The total coherent intensity, $I_{eu}^{coh}(S)$, and the reduced intensity, $S \cdot i(S)$, for the $Ca(NO_3)_2 \cdot 4.1\ H_2O$ melt at 328 K are shown in Fig. 1a and b, respectively. The coherent intensity curve in the lower region of S consists of characteristic continued three peaks. The peak pattern of the reduced intensity curve obtained in this work was found to be very similar in phase to that of $Ca(NO_3)_2 \cdot 3.5\ H_2O$ melt at room temperature reported previously [11], but not at a peak height of 29.0 nm^{-1} of S.

The $D(r)$ and $G(r)$ curves for the hydrate melt are shown in Fig. 2a and b, respectively. The $G(r)$ curve has peaks at $r = 0.125$, 0.245, 0.295, 0.475, and 0.720 nm. This result was similar to $G(r)$ of the $Ca(NO_3)_2 \cdot 3.5H_2O$ melt [11]. However, on detailed

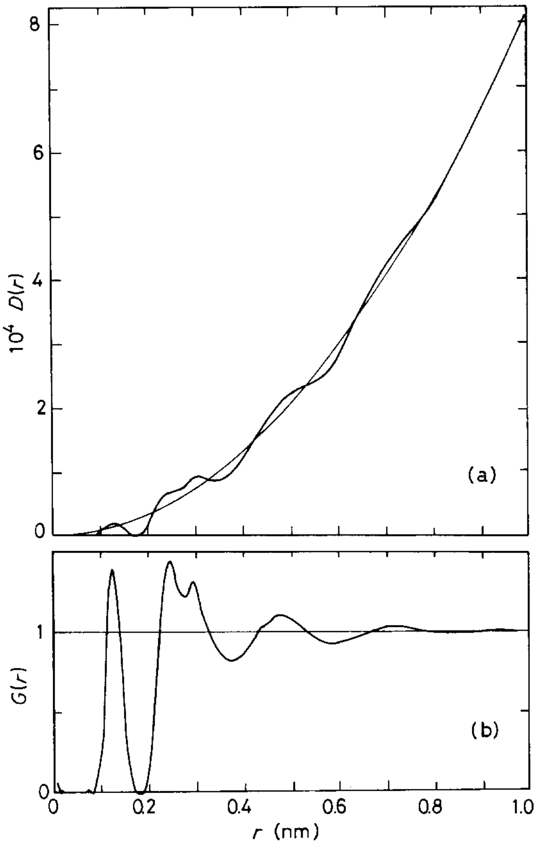

Figure 2 Radial distribution function, $D(r)$, and correlation function, $G(r)$, curves.

observation, small differences were found in the position of the fifth peak and the magnitude of the fall between the second and third peaks. The first peak at 0.125 nm of $G(r)$ corresponds to the N–O intermolecular interactions for the NO_3 ion, an integration of the first peak of the $D(r)$ curve giving 3 as the coordination number of oxygen atoms around a nitrogen atom. The large second peak at 0.245 nm will contain mainly the Ca–O interactions, because it is close to the sum of the radius (0.100 nm) [23] of Ca^{2+} ion and a van der Waals radius (0.140) [24] of the oxygen atom. A contribution from the O–O intermolecular interactions for the NO_3 ion seems to appear at $r = 0.215$ nm, because the shape of the nitrate ion is the plane right triangle with $r = 0.125$ nm in the N–O distance, but it is not resolved because of a neighbouring distance to the large second peak. The third peak at 0.295 nm is thought to be due to the contributions from the interactions such as the water–water molecules and water molecule–nitrate ion.

In a multi-component system with similar nearest neighbour distances of the interactions, it is difficult to separate these correlations from the analysis of $D(r)$ and $G(r)$ curves. In order to determine these correlations quantitatively, the correlation method was applied to the observed $S \cdot i(S)$ curve. The theoretical structure function calculated on the basis of a model is obtained by

$$i(S)_{\text{calcd}} = \left[\sum\sum n_{ij} f_i f_j \frac{\sin(Sr_{ij})}{Sr_{ij}} \exp\left(\frac{-l_{ij}^2}{2} S^2\right)\right] \Big/ \sum f_i^2(S) \qquad (5)$$

where r_{ij} is the interatomic distance, l_{ij} the root mean square displacement, and n_{ij} the number of interactions for atom pairs ij. This equation is related to only the short-range interactions, the term for the contribution of the interactions between a spherical hole and the continuum electron distribution beyond the discrete distance was not included. In this calculation, the scattering intensity from the hydrogen atom was neglected because of a very small contribution. On the basis of the above consideration of the radial distribution function, we constructed the structural model for the hydrate melt as follows. The structural parameters for the N–O and O–O intramolecular interactions of the NO_3^- ion in the melt were fixed and only their root mean square displacements were taken as variables. The first coordination shell of the Ca^{2+} ion consists of both H_2O and NO_3^- ions. The interactions between the water molecules and the NO_3^- ions were taken into account. However, because correlations such as the O_H–O_H and O_H–O_N pairs are difficult to separate exactly, they are treated with one correlation as an O–O atom pair, where the subscripts H and N indicate that the oxygen atoms belong to the H_2O molecule and NO_3^- ion, respectively. The interactions between the Ca^{2+} ion and the oxygen atoms in the second coordination shell was also included as Ca–O_{second}. The quantities, n_{ij}, r_{ij}, and l_{ij} for these interactions can be obtained by a least-squares calculation of the variations in Equation 6 against the observed intensity function $S \cdot i(S)$ beyond $S = 30\ \text{nm}^{-1}$. In the calculation, initial values for the variations of the respective pairs were placed by considering the findings from the $D(r)$ and $G(r)$ curves and the crystal structure of calcium nitrate tetrahydrate [25]. In order to check the goodness of fit of the calculated intensity to the observed one, the quantity, R, was introduced

$$R = \frac{\sum |S \cdot i(S)_{\text{obs}} - S \cdot i(S)_{\text{calcd}}|}{\sum |S \cdot i(S)_{\text{obs}}|} \qquad (6)$$

The parameters of the most probable arrangement obtained in the $Ca(NO_3)_2 \cdot 4.1H_2O$ melt at 328 K are listed in Table I, in which the numbers in parentheses are designated as the presupposed constants. The R value was 0.238 when the calculation converged. The intensity function, $S \cdot i(S)$, calculated using these parameters is compared with the observed one and is presented in Fig. 3. Fig. 4 shows the contribution of each atom pair to the $S \cdot i(S)$ curve calculated for the hydrate melt. It was found that contributions existed from the five atom pairs even in the region beyond

TABLE I Short-range structural parameters

i	j	n_{ij}	r_{ij}	l_{ij}
N	O_N	(3.0)	(0.125)	0.0134
O_N	O_N	(3.0)	(0.215)	0.0145
Ca	O_N	2.0	0.254	0.0176
Ca	O_H	4.1	0.241	0.0167
O	O	6.3	0.296	0.0255
N	O_H	4.1	0.341	0.0258
Ca	N	2.1	0.353	0.0261
Ca	O_{second}	3.8	0.463	0.0396

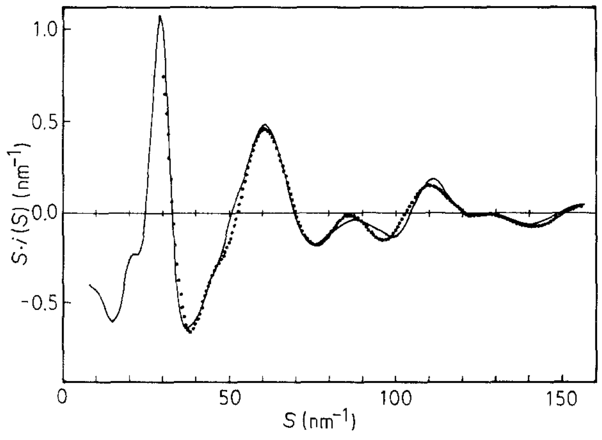

Figure 3 Observed (———) and calculated (· · ·) $S \cdot i(S)$ curves.

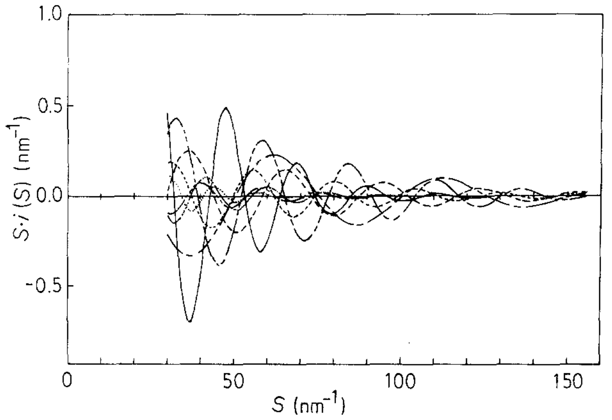

Figure 4 Contribution of each ion pair to the $S \cdot i(S)$ curve calculated. (———) N–O_N pair, (–·–) O_N–O_N, (---) Ca–O_N, (——) Ca–O_H, (——) O–O, (—····—) N–O_H, (------) Ca–N, (· · ·) Ca–O_H.

$S = 100\ nm^{-1}$. The calculated $S \cdot i(S)$ curve was linked with the data of $S \leq 32\ nm^{-1}$ of the observed one at $S = 32\ nm^{-1}$ and $G(r)$ was computed by Fourier transformation of the linked $S \cdot i(S)$ curve. A comparison of the observed $G(r)$ with the computed $G(r)$ curve is shown in Fig. 5. Both curves in the short-range distance less than 0.4 nm, gave good agreement.

As seen in Table I, a Ca^{2+} ion is coordinated to about six oxygen atoms, about four of which come from water molecules at 0.241 nm and two from nitrate ions at 0.253 nm. In these correlations, the distance for the Ca–O_N pair is slightly longer than that of the Ca–O_H. Such a difference is found in the distances between the calcium ion and the water molecules and nitrate ions in the first coordination shell of the tetrahydrate crystal [25]. The two oxygen atoms from the nitrate ion are thought to belong to the two different ions, because the number of Ca–N interactions is almost 2. As is suggested from the investigation by Raman spectroscopy of the calcium nitrate tetrahydrate melt [26], these two nitrate ions in the first coordination shell appeared to make direct correlations, such as contact ion pairs, with the calcium ion. It was observed that the hydration structure of the tetrahydrate melt analysed in this study was analogous to that in the nearest coordination number, that of molten $CaCl_2 \cdot 4H_2O$ [10] measured at 393 K even though the counter anion differed.

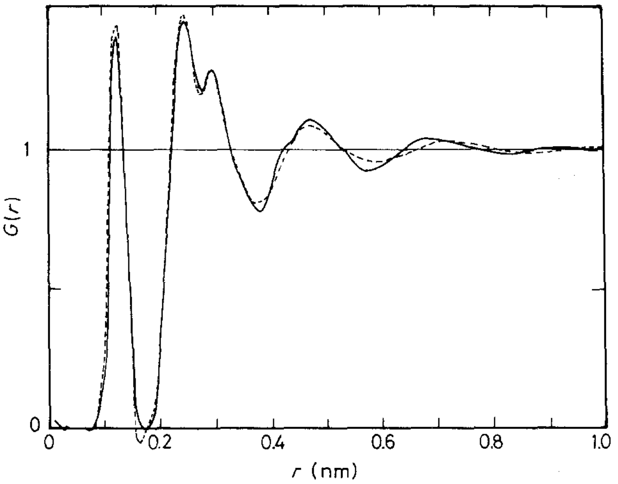

Figure 5 Observed (——) and calculated (---) $G(r)$ curves.

The number of oxygen atoms in the first coordination shell obtained in this work is lower by about 3 than those in the first coordination shells of the $Ca(NO_3)_2 \cdot 3.5\ H_2O$ melt [11] and the tetrahydrate crystal [25]. The density of the crystal is calculated to be $1.9365 \times 10^3\ kg\,m^{-3}$ from the crystal data of the space group P_{z1}/c with $a = 0.6268$, $b = 0.9116$, $c = 1.483$ nm and $\beta = 106.5°$, $Z = 4$ [25]. On the other hand, the density of the hydrate melt at 328 K was $1.766 \times 10^3\ kg\,m^{-3}$. By use of these values, the molar volumes in the solid and molten states were calculated and an increase in volume by 9.6% on melting was observed. Such a volume expansion would lead to decreases in the nearest atom distance and the numbers of atoms in the first coordination shell, as well as alkali halides [27]. The nearest distances between the Ca^{2+} ion and the water molecules and nitrate ions for the melt are obviously shorter than the nearest average ones of those correlations in the crystal. The decrease in the nearest coordination number seemed to occur as the result.

The results of the hydration structures of the $Ca(NO_3)_2 \cdot 4.1\ H_2O$ and $Ca(NO_3)_2 \cdot 3.5\ H_2O$ melts and a series of calcium chloride hydrate melts described in Section 1 suggest that in the highly concentrated aqueous solution, the hydration structure around the cation varies markedly with slightly changing water molecule content.

4. Conclusion

The hydration structure of the $Ca(NO_3)_2 \cdot 4.1H_2O$ melt at 328 K has been investigated by X-ray scattering and correlation. Analysis of the radial distribution function and model fitting revealed that in the hydrate melt, a Ca^{2+} ion is surrounded by about six oxygen atoms, 4.1 of which come from water molecules at the average distance of 0.241 nm, 2.0 coming from the nitrate ions at the distance of 0.254 nm. In the first coordination shell, the existence of the direct Ca^{2+}–NO_3^- correlation, such as contact ion pairs, was suggested. From a comparison with the hydration structure for $Ca(NO_3)_2 \cdot 3.5H_2O$ previously reported, it was found that the number of oxygen atoms around a Ca^{2+} ion reduces from nine in the reported melt, to about six. The result implies that in the highly concentrated aqueous solution, the structure of the first coordination shell for the Ca^{2+} ion changes markedly with a small difference in the water molecule content.

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