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A Structural Study of Saturated Aqueous Solutions of Some Alkali Halides by X-Ray Diffraction

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The structure of nearly saturated or supersaturated aqueous solutions of NaCl [6.18 mol (kg H_2O*)*$^{-1}$*], KCl [4.56 mol (kg* H_2O*)*$^{-1}$*], KF [16.15 mol (kg* H_2O*)*$^{-1}$*] and CsF [31.96 mol (kg* H_2O*)*$^{-1}$*] has been investigated by means of solution X-ray diffraction at 25°C. In the NaCl and KCl solutions about 30% and 60%, respectively, of the ions form ion pairs and the* Na^+*-*Cl^- *and* K^+*-*Cl^- *distances have been determined to be 282 and 315 pm, respectively. The average hydration numbers of* Na^+ *and* Cl^- *ions are 4.6 and 5.3, respectively, in the NaCl solution and those of* K^+ *and* Cl^- *ions in the KCl solution are both 5.8. In the KF solution, clusters containing some cations and anions, besides 1:1 (*K^+*-*F^-*) ion pairs, are formed. The* K^+*-*F^- *interatomic distance has been determined to be 269 pm, and nonbonding* $K^+ \cdots K^+$ *and* $F^- \cdots F^-$ *distances in the clusters are 388 and 432 pm, respectively, and the average coordination numbers* n_{KF}*,* n_{KK} *and* n_{FF} *have been estimated to be 2.3, 1.9, and 1.6, respectively. In the highly supersaturated CsF solution an appreciable amount of clusters containing several caesium and fluoride ions are formed. The* Cs^+*-*F^- *distance in the clusters has been determined to be 312 pm, while the nonbonding* $Cs^+ \cdots Cs^+$ *and* $F^- \cdots F^-$ *distances are estimated to be 442 and 548 pm, respectively, the distances being about* $\sqrt{2}$ *and* $\sqrt{3}$ *times the* Cs^+*-*F^- *distance, respectively. The coordination numbers* n_{CsF}*,* n_{CsCs} *and* n_{FF} *in the first coordination sphere of each ion are 3.3, 2.3 and 5.3, respectively, and the result shows the formation of clusters of higher order than 1:1 and 2:2 ion pairs. These ion pairs and clusters may be regarded as embryos for the formation of nuclei of crystals and the results obtained in the present diffraction study support observations for the nucleation of the alkali halide crystals studied by molecular dynamics simulations previously examined.*

KEY WORDS: Nucleation of crystal; X-ray diffraction; alkali halide; saturated solution; structure of complex; embryo; cluster; ion pair.

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1. Introduction

In the series of the molecular dynamics studies on the dissolution and nucleation processes of alkali halides in water, we have obtained the following results: 1) A chloride ion first dissolved and then some chloride ions were liberated from LiCl and NaCl crystals in water and within 20 ps and no dissolution of the cations was observed.(1-3) 2) Fluoride ions dissolved from a CsF crystal, but no Cs^+ ion was liberated from the crystal within 12 ps.(3) 3) Clusters were formed in supersaturated NaCl and CsF aqueous solutions. The size of the clusters was larger in the CsF solution than the NaCl solutions.(4) In this case the concentration of the former solution was much higher than the latter because of the larger solubility of CsF than NaCl at room temperature.

However, no experimental evidence has been obtained to support the *observation* by the molecular dynamics simulations. The present work has been attempted to provide support for the simulation results by determining the structure of saturated solutions of some alkali halides.

2. Experimental

2.1. Preparations of Sample Solutions

Solutions were prepared from weighed amounts of dried NaCl, KCl, KF and CsF crystals and water. An excess amount of a salt was added in water and the mixture was kept for several days at 25°C with occasionally stirring, and then the supernatant of the mixture was taken as a sample. Crystals used were 99.9% NaCl, 99.9% KCl (Wako, Japan), 99.995% KF (Aldrich) and 99% CsF (Miwa, Japan) without further purification. Concentrations of the salts in the sample solutions were analyzed by using Ion Chromatoanalyzer IC500 (Yokogawa, Japan). Densities were determined by a density meter DA-110 (Kyoto, Japan) for the NaCl, KCl, and KF solutions and by a pycnometer for the CsF solution. The composition of the sample solutions are shown in Table I, together with the concentrations of saturated solutions of these salts at 25°C quoted from the literature.(5)

2.2. X-Ray Diffraction Measurements

Intensities of diffracted X-rays on the surface of the sample solutions were detected by using an NaI-Tl scintillation counter equipped on a θ-θ type (2θ is the scattering angle) X-ray diffractometer (JEOL, Japan). A Johansson type LiF crystal monochromator was positioned between the sample and the detector. Mo $K\alpha$ radiation ($\lambda = 71.07$ nm) was used. Times to obtain 40,000 counts were measured at each angle

Table I. Composition of Sample Solutions at 25°C

Salt	NaCl	Ka	KF	CsF
Concentration[a]	6.18	4.56	16.15	31.96
Molar Ratio[b]	8.98	12.18	3.44	1.74
Density[c]	1.20	1.17	1.50	2.93
Concn. Saturated Solution at 25°C[a]	6.15	4.81	17.50	24.13

[a] Units: mol (kg H_2O)$^{-1}$. [b] Units: H_2O/Salt. [c] Units: g-cm^{-3}.

point and the measurements were repeated twice over the range $\theta = 1° - 72°$. Temperature was kept at 25°C during the measurements.

2.3. Data Treatment

Data treatments were carried out by the techniques previously reported.(6,7) After corrections for polarization in the sample and monochromator, the data were normalized to a stoichiometric unit of volume V containing one cation by comparing observed intensities in the high angle region with calculated values for the total independent coherent scattering.(8,9)

Reduced intensities $i(s)$ were calculated from the scaled observed intensities $I(s)$ according to the following equation

$$i(s) = I(s) - \sum_{j} n_j [\{f_j(s) + \Delta f'_j\}^2 + (\Delta f''_j)^2] \tag{1}$$

Scattering factors $f(s)$ for neutral atoms were corrected for the real $\Delta f'_j$ and imaginary $\Delta f''_j$ parts of the anomalous dispersion. The scattering variable s is $4\pi\lambda^{-1}\sin\theta$ and the summations were taken over all j atoms n_j in the stoichiometric volume V. Experimental $si(s)$ values for the solutions investigated are given in Figs. 1 - 4.

Radial distribution functions $D(r)$ or $G(r) = D(r)/4\pi r^2\rho_0$ were calculated from

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

or

$$G(r) = D(r)/(4\pi r^2\rho_0) = 1 + (2\pi^2 r\rho_0)^{-1}\int_0^{s_{\max}} si(s)M(s)\sin(rs)\mathrm{d}s \tag{3}$$

where ρ_0 is the average scattering density

$$\rho_0 = \sum_j n_j[\{f_j(0) + \Delta f'_j\}^2 + (\Delta f''_j)^2]/V \tag{4}$$

$f(0)$ denotes the scattering factors at $s = 0$, and $M(s)$ a modification function

$$M(s) = \{\sum [n_j f_j(0)]^2 / \sum [n_j f_j(s)]^2\}\exp(-0.01s^2) \tag{5}$$

The same modification function and the lower and upper limits, $s_{\mathrm{min}} = 0$ and $s_{\mathrm{max}} = 0.166$ pm^{-1}, respectively, were used at the Fourier transform for all solutions. Spurious peaks appearing in the smaller r region than 100 pm in the $G(r)$ curves were corrected. The $G(r)$ curves thus calculated are also shown in Figs. 1 - 4.

Theoretical intensity values $i(s)_{\mathrm{theor}}$ were calculated by taking into account the short-range intramolecular $i(s)_{\mathrm{intra}}$ and long-range intermolecular $i(s)_{\mathrm{inter}}$ interactions

$$i(s)_{\mathrm{theor}} = i(s)_{\mathrm{intra}} + i(s)_{\mathrm{inter}} = \sum n_{\mathrm{pq}} c_{\mathrm{pq}}(s) j_0(s r_{\mathrm{pq}}) \exp(-b_{\mathrm{pq}} s^2)$$
$$- (4\pi\rho_0 s^{-1}) \sum n_{\mathrm{p}} n_{\mathrm{q}} c_{\mathrm{pq}}(s) R_{\mathrm{pq}}^2 j_1(s R_{\mathrm{pq}}) \exp(-B_{\mathrm{pq}} s^2) \tag{6}$$

where $c_{\mathrm{pq}}(s) = f_{\mathrm{p}}(s) f_{\mathrm{q}}(s) M(s)$, r_{pq}, b_{pq} and n_{pq} denote the distance, temperature factor which relates to the root-means-square variation by the equation $b_{\mathrm{pq}} = l_{\mathrm{pq}}^2/2$, and frequency factor (or coordination number) of the p-q atom pair, respectively. R_{pq} is the distance beyond which a continuous distribution of q atoms around an atom p is assumed. B_{pq} is a parameter describing the sharpness of the boundary at R_{pq}. $j_{\mathrm{m}}(x)$ stands for the spherical Bessel function of the mth order.

Least-squares (LSQ) refinements of the parameter values in the assumed structural models were carried out by minimizing the error squares sum U

$$U = \sum w(s)[i(s) - i(s)_{\mathrm{theor}}]^2 \tag{7}$$

with the weighting factor $w(s)$ assumed to be s^2. The calculations were carried out by using programs KURVLR(10) and NLPLSQ.(11) The contributions of short-range interatomic interactions finally estimated to the total $G(r)$ function are also represented in Figs. 1 - 4.

3. Results

In these systems some atom pairs have similar interatomic distances and cannot be treated as fully independent parameters. Therefore, we inserted some reliable literature values as the initial values and the LSQ treatment was carried out in a small area around the minimum of the error square sum U defined by Eq. (7).

In the course of the LSQ treatment, the following assumptions were made throughout the work:

1. The O-H and H-H interatomic distances in water were fixed at the values found in the gas phase by taking into account the b values reported by Narten *et al.*(12) Any other literature values for the O-H and H-H atom pairs can be used since the contribution of these atom pairs to the final results is small due to the small atomic number of the hydrogen atom.

2. The O-O interaction between water molecules, r_{OO}, b_{OO}, and n_{OO} were refined as independent parameters. No other intermolecular interactions were taken into account for water-water interactions.

3. Ion-water interactions in the first coordination sphere were taken into account in the course of the data refinement. Bond lengths r_{MO}, r_{XO} temperature factors, b_{MO}, b_{XO}, and hydration numbers n_{MO}, n_{XO} for cation M^+ and anion X^- were refined as independent parameters. Since the M-O, M-X, M-M and X-X distances as well as the O-O distances are rather similar to each other in many cases, the reliable literature values were inserted as the initial values of the parameters to be refined. Therefore, the b values are less reliable compared with those found in systems containing simple hydrated ions.

4. Structural parameters for the M^+-X^- contact were refined as independent parameters for all systems. In solutions where H_2O/salt molar ratios are very small (KF and CsF), non-bonding $M \cdots M$ and $X \cdots X$ interactions were also taken into consideration. The initial values of the M-X

distance of the contact atom pairs were calculated from their ionic radii. If the values were reported in the literature, we used them.

5. The frequency factor n_{pq} is defined as the number of atoms p around an atom q. However, deconvolution of a peak in the radial distribution function into their component peaks may be rather difficult when the peak consists of those arising from similar interatomic distances. Nevertheless, the LSQ procedure has been carried out to find some reasonable values of n_{pq} of a p-q atom pair. Therefore, the n values shown in Tables II - V may contain larger uncertainties than the values indicated as 3σ (σ denotes the standard deviation) in n_{pq} in cases where two or more kinds of atom pairs have similar interatomic distances.

3.1. NaCl Solution

Results obtained for the 6.18 mol (kg H_2O)$^{-1}$ NaCl solution by the LSQ calculations are summarized in Table II.

Agreement between experimentally obtained and theoretically calculated $si(s)$ curves is satisfactory as seen in Fig. 1. The double peak around s = 300 pm^{-1} often appears in aqueous solutions in which some bulk structure of water remains in the solution and the reproduction of the double peak is usually not possible without taking into consideration the complicated bulk water structure, which might be largely distorted compared with that in pure water. In the present study long-range water-water interactions are not taken into account, and thus the double peak in the $si(s)$ curve is not well reproduced, except for the case of the CsF solution where practically no more bulk water structure remains.

The $G(r)$ curve is also well reproduced in terms of the O-H and O-O interactions in water, Na^+-OH_2 and Cl^--H_2O interactions in the first coordination shells of the ions. The contribution of the Na^+-Cl^- ion pairs to the $G(r)$ function is small. However, the U value is improved by the introduction of the assumption of formation of the Na^+-Cl^- contact ion pairs.

The result in Table II showed that the Na^+-O bond length is 241 pm which is close to the sum of the radii of an Na^+ ion and a water molecule as expected from the calculation procedure mentioned previously. The value is also in good agreement with the values obtained by X-ray diffraction measurements(13-15) carried out for solutions

Table II. Bond Lengths, Temperature and Frequency Factors, and Parameters for the Homogeneous Electron Distributions Around Atoms[a]

	r/pm	b/10 pm^2	n
O-H	95.7[b]	10[b]	2.0[b]
H-H	151[b]	28[b]	1.0[b]
O-O	285(1)	85(7)	1.8(1)
Na-O	241(2)	27(7)	4.6(1)
Cl-O	318(2)	20(5)	5.3(1)
Na-Cl	282(17)	45(71)	0.3(1)

	R/pm	B/10 pm^2
H	279(5)	70(42)
O	275(1)	100(11)
Na	361(6)	72(46)
Cl	399(4)	110(32)

[a] 6.18 mol (kg H_2O)$^{-1}$ NaCl aqueous solution at 25°C. [b] Numbers are fixed during the least squares calculations.

containing Na^+ ions, and those found by molecular dynamics(16) and Monte Carlo(17) simulations in dilute NaCl aqueous solutions.

The Cl^--O distance, 318 pm, found in the present work can also be compared with the sum of the radii of these species and with the values determined by means of X-ray diffraction(13,14) and molecular dynamics simulations.(18) The average hydration numbers of Na^+ and Cl^- ions are 4.6 and 5.3, respectively, which are slightly smaller than the value of 6 reported for both ions from X-ray diffraction experiments due, probably, to the formation of Na^+-Cl^- contact ion pairs in solution.

The interatomic Na^+-Cl^- distance 282 pm is close to the sum of the effective ionic radii of the ions (116 pm + 167 pm = 283 pm(19)).

The frequency factor of the Na^+-Cl^- pairs may be rather uncertain due to the small contribution to the $si(s)$ and $G(r)$ functions. However, the value $n_{NaCl} = 0.3$ estimated for the Na^+-Cl^- pair in the LSQ procedure suggests that a certain amount of Na^+ and Cl^- ions form Na^+-Cl^- contact ion pairs in solution.

3.2. KCl Solution

Structural parameters obtained for 4.56 mol (kg H_2O)$^{-1}$ aqueous

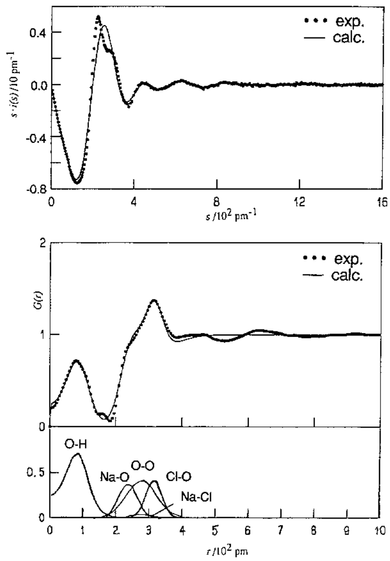

Fig. 1. The structure function *si(s)* (upper) and the radial distribution function *G(r)* (lower) for 6.18 mol (kg H_2O)$^{-1}$ NaCl aqueous solution.

solution are summarized in Table III. The solution is slightly supersaturated and the H_2O/KCl molar ratio is 12.2. This value implies that no bulk water could exist if all ions had six water molecules(15) in their first coordination shells as found in dilute solutions (even larger hydration numbers than 6 have been reported for potassium(20,21) and chloride(22,23) ions). Therefore, the formation of contact ion pairs is expected, and the data given in Table III show the frequency factor n_{KCl} = 0.6, and thus about 60% of the ions form K^+-Cl^- contact ion pairs provided that no more higher aggregates are formed. An assumption of the formation of higher-degree aggregates in the solution did not improve the result significantly.

The value r_{KO} = 281 pm agrees well with the K^+-O bond length (280 pm) reported from an X-ray diffraction method(15) but much longer than the value (260 pm) found by means of neutron diffraction.(24) Monte Carlo(25,26) and molecular dynamics(16,20,21) calculations gave results (276-286 pm) similar to those obtaind by X-ray diffraction. The r_{ClO} value found in this work (322 pm) is slightly longer than the reported value (314 pm)(15) and the distance obtained in the NaCl system (318 pm) as previously shown. The average hydration numbers of K^+ and Cl^- ions are both 5.8 and slightly smaller than 6 given in Ref. 15, probably due to the formation of contact ion pairs.

Table III. Bond Lengths, Temperature and Frequency Factors, and Parameters for the Homogeneous Electron Distribution Around Atoms[a]

	r/pm	b/10 pm^2	n
O-H	95.7[b]	10[b]	2.0[b]
H-H	151[b]	28[b]	1.0[b]
O-O	285(1)	81(6)	1.8(1)
K-O	281(1)	8(3)	5.8(1)
Cl-O	322(1)	11(4)	5.8(1)
K-Cl	315(5)	11(2)	0.6(1)
	R/pm	B/10 pm^2	
H	310(4)	70(33)	
O	310(1)	100(8)	
K	340(5)	250(56)	
Cl	385(6)	1100(125)	

[a] 4.56 mol (kg H_2O)$^{-1}$ KCl aqueous solution at 25°C. [b] Numbers are fixed during the least squares calculations.

The agreement between experimental and calculated *G(r)* curves, as well as *si(s)* curves, is satisfactory as seen in Fig. 2.

3.3. KF Solution

The *si(s)* and *G(r)* experimental curves are shown in Fig. 3. By using the final parameter values given in Table IV, reasonable agreement is obtained between the calculated and experimental *si(s)* and *G(r)* curves except for the double peak around 250 - 300 pm^{-1} in the *si(s)* curve..

The sample solution (16.15 mol (kg H_2O)$^{-1}$) was slightly unsaturated [the concentration of the saturated solution is 17.50 mol (kg H_2O)$^{-1}$]. However, since the concentration of the solution is so high, higher aggregates than 1:1 contact ion pairs can be expected to be formed. In fact, the values of n_{KF}, n_{KK}, and n_{FF} were found to be 2.3, 1.9 and 1.6, respectively, and the results suggested the formation of ionic aggregates or clusters in the solution, although the n_{FF} value given in Table IV might contain a larger uncertainty than the estimated 3σ value.

The K^+-O distance was determined to be 282 pm in reasonable agreement with the sum of the ionic radius of K^+ ion (152 pm for the six-coordinated ion(19)) and the size of a water molecule (140 pm). The

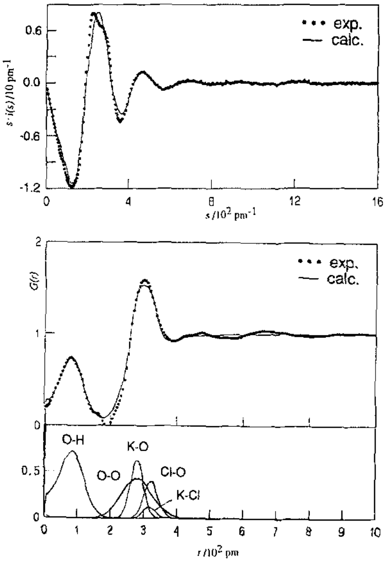

Fig. 2. The structure function *si(s)* (upper) and the radial distribution function *G(r)* (lower) for 4.56 mol (kg H_2O)$^{-1}$ KCl aqueous solution.

F^--O interatomic distance was found to be 268 pm, which is slightly longer than the value reported by Terekhova *et al.* (262 pm)$^{(23)}$ but agrees fairly well with the value obtained by molecular dynamics simulations.$^{(21)}$

The K^+-F^- distance was found to be 269 pm, which agrees well with the sum of the effective radii of the ions (155 pm + 119 pm = 271 pm$^{(21)}$). The nonbonding $K^+ \cdots K^+$ and $F^- \cdots F^-$ distances are 388 pm and 432 pm, respectively, and these values are about 2 and 1.6 (= $(\sqrt{2} + \sqrt{3})/2$) times the r_{KF} value. This suggests that the clusters may be fragments of a face-centered-cubic structure.

The hydration number of the K^+ ion was 3.3, which is very small compared with the values so far reported for aqueous solutions, and the small value showed that a part of the water molecules in the hydration sphere of a potassium ion was replaced by F^- ions in the formation of ion clusters. The same explanation may be applied to the small hydration number of the F^- ion (n_{FO} = 4.0). Since the n_{KK} and n_{FF} values found in the present work were 1.9 and 1.6, respectively, we might say that clusters containing two to three cations and anions were formed, besides 1:1 ion pairs, although the composition of the clusters could not be determined from this experiment. The conclusion derived from the

Table IV. Bond Lengths, Temperature and Frequency Factors, and Parameters for the Homogeneous Electron Distributions Around Atoms[a]

	r/pm	b/10 pm^2	n
O-H	95.7[b]	10[b]	2.0[b]
H-H	151[b]	28[b]	1.0[b]
O-O	289(3)	27(10)	1.4(1)
K-O	282(1)	14(4)	3.3(1)
F-O	268(2)	18(8)	4.0(1)
K-F	269(2)	33(7)	2.3(1)
K-K	388(2)	120(12)	1.9(1)
F-F	432(9)	48(39)	1.6(2)
	R/pm	B/10 pm^2	
H	314(7)	60(58)	
O	301(2)	50(13)	
K	416(2)	407(32)	
F	389(6)	587(86)	

[a] 16.15 mol (kg H_2O)$^{-1}$ KF aqueous solution at 25°C. [b] Numbers are fixed during the least squares calculations.

coordination numbers n_{KF}, n_{KK} and n_{FF} is consistent with that from the bond distances, r_{KF}, r_{KK} and r_{FF}.

3.4. CsF Solution

The sample solution was highly supersaturated, but was stable for several weeks and no precipitates were formed during the X-ray diffraction experiment. The *si(s)* and *G(r)* curves obtained from the experiment agreed well with calculated values as seen in Fig. 4. The structural parameters thus obtained are shown in Table V.

The r_{CsF} value (312 pm) found in this work is an intermediate value between the sums of the ionic radii r_F (119 pm)(19) + r_{Cs} (181 pm; six-coordination)(19) and r_F + r_{Cs} (202 pm; 12-coordination).(19)

The r_{CsO} value (321 pm) agrees well with the expected values from their sizes (181 pm + 140 pm = 321 pm(19)). The value is slightly smaller than that found in an X-ray diffraction measurement,(27) but agrees satisfactorily with the result from a molecular dynamics simulation.(28)

The r_{FO} value obtained (271 pm) seems to be larger than that ex-

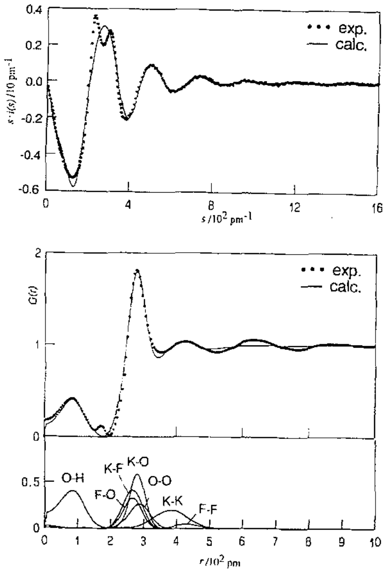

Fig. 3. The structure function *si(s)* (upper) and the radial distribution function *G(r)* (lower) for 16.15 mol (kg H_2O)$^{-1}$ KF aqueous solution.

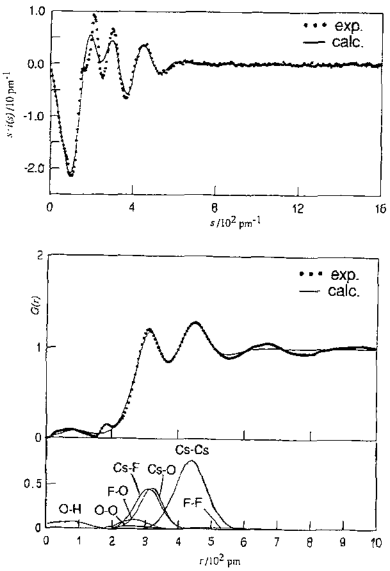

Fig. 4. The structure function *si(s)* (upper) and the radial distribution function *G(r)* (lower) for 31.96 mol (kg H_2O)$^{-1}$ CsF aqueous solution.

Table V. Bond Lengths, Temperature and Frequency Factors, and Parameters for the Homogeneous Electron Distributions Around Atoms[a]

	r/pm	b/10 pm^2	n
O-H	95.7[b]	10[b]	2.0[b]
H-H	151[b]	28[b]	1.0[b]
O-O	280(25)	104(136)	1.2(3)
Cs-O	321(2)	32(6)	3.6(1)
F^-O	271(8)	45(34)	4.1(5)
Cs-F	312(2)	53(7)	3.3(1)
Cs-Cs	442(7)	105(3)	2.3(1)
F^-F	548(30)	450(268)	5.3(11)

	R/pm	B/10 pm^2
H	309(28)	170[b]
O	330(7)	318(86)
Cs	490(1)	254(13)
F	393(12)	1143(235)

[a] 31.96 mol (kg H_2O)$^{-1}$ CsF aqueous solution at 25°C. [b] Numbers are fixed during the least squares calculations.

pected (119 pm + 140 pm = 259 pm$^{(19)}$) but agrees with the value found in the KF solution (269 pm).$^{(21)}$ However, the value may be rather uncertain, and thus, the discussion is not conclusive.

The nonbonding $Cs^+ \cdots Cs^+$ and $F^- \cdots F^-$ distances appeared at 442 and 548 pm, respectively, which corresponds to about $\sqrt{2}$ and $\sqrt{3}$ times the r_{CsF} value, respectively, although the r_{FF} value is very uncertain. The $Cs^+ \cdots Cs^+$ interactions are clearly seen in the *G(r)* curve because of a significant contribution of the interaction to the radial distribution function due to their large scattering ability.

The average hydration numbers of Cs^+ and F^- ions were found to be 3.6 and 4.1, respectively, which are fairly small compared with the values reported in many aqueous solutions. The frequency factor for the Cs^+-F^- pairs was 3.3, which suggested the formation of clusters of a higher order of aggregation in the solution.

4. Discussion

The results obtained in the present study can be compared with those obtained from our previous molecular dynamics simulation of the nucleation of NaCl and CsF crystals(4).

4.1. NaCl System

Concentrations of the solutions examined in the simulation studies(4) were 9.25 [solution (a)] and 15.42 mol (kg $H_2O)^{-1}$ [solution (b)] and were higher than that of the solution in the present diffraction work. According to the results from simulation, ion pairs and clusters with a relatively low degree of aggregation are formed in solution (a) and the cluster formation is slowed down and seems to reach an equilibrium after about 12 ps. The frequency factor n_{NaCl} in the region of the first coordination shell ($r \leq 282.5$ pm) is 0.55 but it is 2.43 when we covered the coordination sphere to the second shell ($r \leq 488.5$ pm). The n_{NaNa} and n_{ClCl} values within the second-coordination-sphere region are 2.84 and 2.25, respectively. In solution (b) which was highly supersaturated, a higher order aggregation seems to occur in the solution. Also, the average frequency factor for the Na^+-Cl^- contact in the first-coordination-shell region is 1.25 and did not change significantly from 6 to 18 ps. The factor is 3.76 at 18 ps in the second-coordination-shell region. The n_{NaNa} and n_{ClCl} values within the second-coordination-shell region are 4.66 and 4.25, respectively, at 18 ps.

The NaCl solution investigated in the present work was 6.18 mol (kg $H_2O)^{-1}$, which was much lower than those examined by the molecular dynamics simulations, but the frequency factor n_{NaCl} obtained from the diffraction study (0.3) is close to the value calculated for system (a) (0.55). In the X-ray diffraction study no information for higher aggregation of the ions was obtained, but the discrepancies between the experimental and calculated $G(r)$ curves in the range $r > 400$ pm suggest that long-range ordering of ions must exist in the solution, which implies the formation of clusters or nuclei of NaCl crystals.

4.2. CsF System

Solution (c) used in the molecular dynamics study was 36.34 mol (kg $H_2O)^{-1}$,(4) which is close to that examined in the present X-ray diffraction study [31.96 mol (kg $H_2O)^{-1}$]. According to the X-ray diffraction results, n_{CsF} is 3.3, which is between the two values, 1.90 and 5.85, within the first ($r \leq$ 301.5 pm)- and second ($r \leq$ 521.5 pm)-coordination-shell regions, respectively, and the growth of nuclei seemed to reach an equilibrium after 12 ps according to the simulations.

The conclusion derived in the present X-ray diffraction measurement is similar to that obtained by the simulations with respect to the size of the clusters formed in the supersaturated solutions, and thus, the X-ray diffraction study detects clusters predicted by the molecular dynamics simulations.

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