Structure of Concentrated Aqueous NH_4Cl Solutions Studied by Neutron Diffraction with ${}^{14}N/{}^{15}N$ and H/D Isotopic Substitution Technique

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Neutron diffraction measurements have been carried out on 14 N/ 15 N and H/D isotopically substituted aqueous 8 mol% *N*H₄Cl solutions to obtain detailed structural information concerning intermolecular hydrogen bond in the solution. Observed scattering cross sections were combined to deduce partial structure factors, $a_{NO}(Q)$, $a_{NH}(Q)$, $a_{HH}(Q)$, $a_{XH}(Q)$, and $a_{XX}(Q)$ (X: O, N and Cl). The interatomic distances between NH₄ and the nearest neighbor H₂O molecules were determined to be $r_{NO} = 2.87(1)$ Å and $r_{NH} = 3.44(2)$ Å, from the least squares fitting analysis to the observed $a_{NO}(Q)$ and $a_{NH}(Q)$, respectively. The average number of H₂O molecules within the first hydration shell of the NH₄⁺ was obtained to be 3.9(1), suggesting a tetrahedral hydration geometry of NH₄⁺. Structural parameters on intermolecular hydrogen bonds between solvent molecules were determined to be $r_{HH} = 2.42(1)$ Å, $r_{OH} = 1.91(1)$ Å, and $r_{OO} = 2.78(1)$ Å, respectively.

KEYWORDS: ¹⁴N/¹⁵N isotopic substitution, neutron diffraction, ammonium chloride, structure factor

§1. Introduction

Ammonium Chloride (NH₄Cl) is one of the most important compounds in extensive fields of fundamental and applied chemistry. Despite considerable effort to elucidating the hydration property of NH_4^+ in aqueous solution, the hydration number reported in the literature is widely spread from 4 to $11.^{1)}$ The difficulty in determining the hydration structure of NH_4^+ from a single X-ray diffraction measurement arises from the fact that the scattering power of NH_4^+ is roughly equivalent to that of solvent water molecule. Neutron diffraction with ¹⁴N/¹⁵N isotopic substitution method is considered to be one of the most suitable experimental technique. The first attempt has been carried out for ^{14}N and ^{15}N isotopically substituted 9.1 mol% *ND₄Cl in D₂O solutions by Hewish and Neilson,²⁾ however, the number of water molecule in the first hydration shell of ND_4^+ was not determined unambiguously due to considerable overlap of the nearest neighbor N—O and N—D peak in the observed distribution function, $G_N(r)$. Obviously, further experiments employing a combination of $^{14}N/^{15}N$ and H/D isotope substitution are necessary to deduce partial distribution functions $g_{\rm NO}(r)$ and $g_{\rm NH}(r)$.

In this paper, we describe results of neutron diffraction measurements on aqueous 8 mol% *N*H₄Cl-*H₂O solutions with different isotopic ratio for nitrogen and hydrogen atoms. Observed intermolecular interference terms for respective samples were combined to determine partial structure factors, $g_{\rm NO}(r)$ and $g_{\rm NH}(r)$. The structural information on hydrogen bonds among solvent water molecules are obtained from the observed $g_{\rm HH}(r)$, $g_{\rm XH}(r)$, and $g_{\rm XX}(r)$ (X: O, Cl, and N) functions.

§2. Experimental

Weighed amounts of ¹⁴N- and ¹⁵N-enriched *N*H₄Cl were dissolved into D_2O or D_2O/H_2O mixtures to prepare five kinds of aqueous 8 mol% *N*H₄Cl solutions with different isotopic compositions, I $({}^{14}ND_4Cl)_{0.08}(D_2O)_{0.92}$, II $({}^{15}ND_4Cl)_{0.08}(D_2O)_{0.92}$, III $(^{14}N^{0}H_{4}Cl)_{0.08}(^{0}H_{2}O)_{0.92}, IV (^{15}N^{0}H_{4}Cl)_{0.08}(^{0}H_{2}O)_{0.92}, and V (^{14}N^{0-2}H_{4}Cl)_{0.08}(^{0-2}H_{2}O)_{0.92}.$ The superscript "0" and "0 - 2" denote isotopic mixtures with the mean scattering lengths of hydrogen atoms $b_{\rm H} = 0$ and $b_{\rm D}/2$, respectively. Neutron diffraction measurements were carried out at 25 °C using the ISSP 4G diffractometer installed at the JRR-3M research reactor in JAERI, Tokai, Japan. The incident neutron wave length of $\lambda = 1.105 \pm 0.003$ Å was employed. Scattered neutrons from the sample solution were collected over the angular range of $3 \leq 2\theta \leq 115^{\circ}$, which corresponds to $0.30 \leq Q \leq 9.59$ Å⁻¹. After corrections for background scattering and absorption within the sample and cell, the observed count rates were converted to the absolute scale using corrected intensities from the vanadium rod. The self scattering term involving both the inelasticity contribution and the multiple scattering one was approximated by a polynomial function of Q, and then subtracted from the observed total scattering cross section.

The first order difference functions³⁾ around the nitrogen atom within NH_{4}^{+} , $^{\mathrm{D}}\Delta_{\mathrm{N}}(Q)$ and $^{\mathrm{OH}}\Delta_{\mathrm{N}}(Q)$, between normalized scattering cross sections scaled at the stoichiometric unit, $(*\mathrm{N}^{*}\mathrm{H}_{4}\mathrm{Cl})_{x}(*\mathrm{H}_{2}\mathrm{O})_{1-x}$, for sample solutions with the same isotopic state for hydrogen atoms and different one for nitrogen atoms, can be expressed as follows,

$$\Delta_{\rm N}(Q) = A[a_{\rm NO}(Q) - 1] + B[a_{\rm NH}(Q) - 1]$$

+C[
$$a_{\rm NCl}(Q) - 1$$
] + D[$a_{\rm NN}(Q) - 1$] (2.1)

where

$$\begin{aligned} \mathbf{A} &= 2x(1-x)b_{\mathrm{O}}(b_{14\mathrm{N}} - b_{15\mathrm{N}}),\\ \mathbf{B} &= 4x(1+x)b_{\mathrm{H}}(b_{14\mathrm{N}} - b_{15\mathrm{N}}),\\ \mathbf{C} &= 2x^2b_{\mathrm{Cl}}(b_{14\mathrm{N}} - b_{15\mathrm{N}}), \text{ and}\\ \mathbf{D} &= x^2(b_{14\mathrm{N}}^2 - b_{15\mathrm{N}}^2), \text{ respectively.} \end{aligned}$$

Since magnitudes of coefficients C and D are much smaller than those of A and B in the present experimental condition, the observed $\Delta_N(Q)$ is dominated by the contribution from NH_4^+ —water correlation. The present $^{OH}\Delta_N(Q)$, corresponding to the difference in observed cross sections between the sample III and IV, is well approximated by $a_{NO}(Q) - 1$. The N—H partial structure factor, $a_{NH}(Q)$, is directly derived by subtracting $^{OH}\Delta_N(Q)$ from the observed $^{D}\Delta_N(Q)$ function, in which intramolecular N—D contribution within the ND₄⁺ has already been eliminated,

$$^{\mathrm{D}}\Delta_{\mathrm{N}}(Q) - {}^{0\mathrm{H}}\Delta_{\mathrm{N}}(Q) = 4x(1+x)b_{\mathrm{D}}(b_{1^{4}\mathrm{N}} - b_{1^{5}\mathrm{N}}) \times [a_{\mathrm{NH}}(Q) - 1].$$
(2.2)

Partial structure factors, $a_{\rm HH}(Q)$, $a_{\rm XH}(Q)$, and $a_{\rm XX}(Q)$ (X: O, Cl and N) are derived from the combination of the intermolecular interference terms, $(d\sigma/d\Omega)^{\rm inter}$, for three sample solutions, I(¹⁴N - D), III(¹⁴N - ⁰H), and V(¹⁴N-⁰⁻²H), as follows:

$$(d\sigma/d\Omega)^{\text{inter}}(\text{for I}) + (d\sigma/d\Omega)^{\text{inter}}(\text{for III}) -2(d\sigma/d\Omega)^{\text{inter}}(\text{for V}) = 2(1+2)^2 b_D^2[a_{\text{HH}}(Q) - 1],$$
(2.3)
$$4(d\sigma/d\Omega)^{\text{inter}}(\text{for V}) - (d\sigma/d\Omega)^{\text{inter}}(\text{for I}) -3(d\sigma/d\Omega)^{\text{inter}}(\text{for III}) = 4(1+x)\{x(b_N + b_{\text{Cl}}) + (1-x)b_O\}b_D[a_{\text{XH}}(Q) - 1],$$
(2.4)

$$(d\sigma/d\Omega)^{\text{inter}}(\text{for I}) = \{x(b_{\text{N}} + b_{\text{Cl}}) + (1-x)b_{\text{O}}\}^{2}[a_{\text{XX}}(Q) - 1].$$
(2.5)

Quantitative analysis of the observed partial structure factor was carried out through a least-squares fit of the calculated structure factor, $a_{ij}(Q)$, involving contributions from the short- and long-range intermolecular interactions,

$$a_{ij}(Q) = \sum \beta_{ij} n_{ij} \exp(-l_{ij}^2 Q^2/2) \sin(Qr_{ij}) / (Qr_{ij}) + 4\pi \rho (-l_0^2 Q^2/2) [Qr_0 \cos(Qr_0) - \sin(Qr_0)] Q^{-3},$$
(2.6)

where β_{ij} denote the weighting factor of the partial structure factor. ρ is the number density. Short-range parameters, n_{ij} , l_{ij} and r_{ij} , corresponds to the coordination number, root-mean-square amplitude, and the interatomic distance for i–j pair, respectively. The longrange parameter, r_0 denotes the distance beyond which the continuous distribution of atoms is assumed. The parameter l_0 describes the sharpness of the boundary at r_0 . The fitting was made in the range of $1.00 \le Q \le 9.59$ Å⁻¹.

The partial distribution, $g_{ij}(r)$, was derived by the Fourier transform of the observed $a_{ij}(Q)$,

$$g_{ij}(r) = 1 + (2\pi^2 \rho r)^{-1} \int_0^{Q_{\text{max}}} Q[a_{ij}(Q) - 1] \sin(Qr) dQ,$$
(2.7)

The upper limit of the integral was taken to be Qmax = 9.59 Å⁻¹.

§3. Results and Discussion

3.1 Hydration structure of NH_4^+

Observed ${}^{0H}\Delta_{N}(Q) \ (\approx a_{NO}(Q)-1)$ and $a_{NH}(Q)$ functions with the best fit of the calculated interference terms and shown in Fig. 1. In the preliminary analysis, it was found that at least two shot-range interactions should be involved in the calculated interference term to reproduce the observed ${}^{0H}\Delta_{N}(Q)$ and $a_{NH}(Q)$ functions. Distribution functions ${}^{0H}G_{N}(r)$ and $g_{NH}(r)$ are represented in Fig. 2. The nearest neighbor N···O interaction can



Fig. 1. Difference function, ${}^{0H}\Delta_{N}(Q)$, and N—H partial structure factor, $a_{NH}(Q)$ observed for 8 mol%*N*H₄Cl solution (circles). The best-fit of calculated interference terms are indicated by solid lines. The residual function, $\delta(Q)$, is shown below.

clearly be observed as a well resolved first peak in the present ${}^{0H}G_{\rm N}(r)$, indicating the stability of the first hydration shell of NH_4^+ . The present value of the nearest neighbor N···O distance, $r_{\rm NO} = 2.87(1)$ Å, is in good agreement with the average value of hydrogen bonded N— $H \cdots O$ distance (2.89Å) derived from structure data for various organic crystals.⁴⁾ The nearest neighbor $N \cdots O$ coordination number was determined to be 3.9(1), implying that the NH_4^+ forms hydrogen bonds with on the average four water molecules in the first hydration shell. The tilt angle between the $N \cdots O$ axis and the molecular plane of the nearest neighbor water molecule is determined to be $40(6)^{\circ}$, which is calculated from the observed values for the nearest neighbor $N \cdots O$ and N···H distances and known molecular geometry of water molecule in the liquid state.⁵⁾

The present value of the nearest neighbor N···H coordination number, $n_{\rm NH} = 13(1)$, is somewhat larger than the value, $n_{\rm NH} = 8$, which is expected from the present



Fig.2. Circles: Difference function, ${}^{0H}G_{\rm N}(r)$, and N—H partial distribution function, $g_{\rm NH}(r)$, observed for the aqueous 8 mol% ${}^*{\rm N}{}^*{\rm H}_4{\rm Cl}$ solution. Solid lines: The Fourier transform of the solid lines in Fig. 1. Contributions from both the short- and long-range interactions are denoted by broken lines.



Fig.3. Observed H—H, X—H and X—X (X:O, Cl and N) partial structure factors for the aqueous 8 mol% *N*H₄Cl solution (dots). The best-fit of calculated interference terms are denoted by solid lines. The residual function, $\delta(Q)$, is shown below.

analysis for the ${}^{0}G_{\rm N}(r)$ function. This discrepancy is considered to arise from a significant overlap between the first and second nearest neighbor N···H interactions as seen in Fig. 2b. The value $n_{\rm NO} = 3.9(1)$ is therefore considered to be more reliable value for the hydration number of NH₄⁺. Hewish and Neilson reported much larger hydration number for NH₄⁺ (10—11) derived from the integration of the observed $G_{\rm N}(r)$ in which both contributions from $g_{\rm NO}(r)$ and $g_{\rm NH}(r)$ are involved. It is now obvious that the contribution from the second neighbor N···H interaction should be involved at the distance beyond $r \gtrsim 4$ Å. The present result is therefore considered to be more reliable.

3.2 Intermolecular hydrogen-bonded structure

Partial structure factors, $a_{\rm HH}(Q)$, $a_{\rm XH}(Q)$ and $a_{\rm XX}(Q)$ (X: O, N and Cl) observed for aqueous 8 mol% *N*H₄Cl solutions, and the best-fit of the calculated $a_{ij}(Q)$ functions are represented in Fig. 3. Observed partial distri-



Fig. 4. The H—H, X—H, and X—X (X: O, Cl, and N) partial distribution functions for aqueous 8 mol% *N*H₄Cl solution (solid lines). Contributions from both the short- and long-range interactions are denoted by broken lines.

bution functions, $g_{\text{HH}}(r)$, $g_{\text{XH}}(r)$ and $g_{\text{XX}}(r)$, are shown in Fig. 4.

The first peak located at r = 2.4 Å in the present $g_{\rm HH}(r)$ is assigned to the nearest neighbor $\rm H\cdots \rm H$ interaction between water molecules. The resolved first peak at $r \simeq 2$ Å in $g_{\rm XH}(r)$ is attributable to the sum of contributions from the nearest neighbor $\rm O\cdots \rm H$ and $\rm Cl\cdots \rm H$ interactions.

In the fitting procedure for observed $a_{XX}(Q)$, structural parameters for the nearest neighbor N···O interaction have been fixed at the values determined from the present analysis of ${}^{0H}\Delta_N(Q)$ as described above. Present values of interatomic distances for the nearest neighbor hydrogen-bonded water-water interaction, $r_{\rm H\cdots H} = 2.42(1)$ Å, $r_{\rm O\cdots H} = 1.91(1)$ Å, and $r_{\rm O\cdots O} =$ 2.78(1) Å, are in good agreement with those reported for pure liquid water,⁶⁻⁸⁾ implying that the intermolecular hydrogen-bonded network remains in the present concentrated aqueous NH₄Cl solutions. The hydration number of Cl⁻ in the 8 mol% NH₄Cl solution has been determined to be 5.3(5).

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