Hydration Structure around a Formyl-Hydrogen Atom Studied by Neutron Diffraction with H/D Isotopic Substitution Method

Yasuo Kameda,* **Atsunari Sayama, Motoya Sasaki, Yuko Amo, and Takeshi Usuki**

Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, Yamagata 990-8560

Received June 14, 2004; E-mail: kameda@sci.kj.yamagata-u.ac.jp

Time-of-Flight (TOF) neutron diffraction measurements were carried out for 12 mol% $^*HCOO^7Li$ solutions in D_2O. The H/D isotopic substitution technique was applied to the formyl-hydrogen atom of the formate ion in order to determine both the hydration structure around the formyl-hydrogen atom and the intramolecular structure of $HCOO^-$ in the aqueous solution. The hydration structure around the formyl-hydrogen atom was analyzed by applying a least-squares refinement procedure to the observed intermolecular difference function. The intramolecular distances within the formate ion were determined to be $r(H_f–C) = 1.072(2)$ Å and $r(H_f\cdots O_f) = 2.015(8)$ Å.

The hydration structure of the formate ion has received considerable attention because of its significant importance in various fields of chemical and biological science. Despite its importance, there have been limited structural studies concerning hydration of the formate ion itself. Earlier Raman and IR spectroscopic studies[1–3] examined the vibrational frequencies of the formate ion in aqueous HCOONa and DCOONa solutions. The existence of a Fermi resonance between the C–H stretching and C–H in-plane bending modes has been reported.[3] The structural properties of concentrated aqueous HCOOTl solutions have been investigated by the X-ray diffraction method.[4] In an aqueous 10.77 $\mathrm{mol\,dm^{-3}}$ HCOOTl solution, a tetramer, $Tl_4(O_2CH)_4$, was found. The result of a Monte Carlo simulation study indicated that the number of water molecules neighboring the carboxyl-oxygen and the formyl-group of the formate ion are 3.4 and 4.5, respectively.[5] X-ray and neutron diffraction studies have revealed that 4.4(2) water molecules are hydrogen-bonded to the carboxyl-oxygen atoms within the formate ion with an intermolecular distance of $r(O_f\cdots H_2O) = 2.82(1)$ Å.[6] More recently, the concentration dependence of the hydration number of the formate ion in aqueous HCOOK solutions was investigated by means of ATR-IR double-difference spectroscopy.[7] The hydration number of the formate ion, $n_{HCOO^-\cdots H_2O} = 4.6$ for an aqueous 1 mol% HCOOK solution, decreased to $n_{HCOO^-\cdots H_2O} = 1.6$ for a 40 mol% HCOOK solution.[7] The value of $n_{HCOO^-\cdots H_2O}$ obtained from the ATR-IR method can be regarded as the number of the nearest neighbor water molecules interacting with the carboxyl-oxygen atoms within the formate ion.[8] The structural properties of the contact ion pair, $HCOO^-\cdots Li^+$, were investigated by our neutron diffraction experiments on $^6Li/^7Li$ and H/D isotopic substituted 12 mol% $^*HCOO^*Li$ solutions in D_2O.[9] However, the hydration structure around the formyl-hydrogen atom within the formate ion has not yet been examined.

In this report, we describe results concerning TOF neutron diffraction measurements on H/D isotopically substituted aqueous 12 mol% $^*HCOO^7Li$ solutions in D_2O. The difference function, $\Delta_H(Q)$, between the scattering cross sections observed for $(DCOO^7Li)_{0.12}(D_2O)_{0.88}$ and $(HCOO^7Li)_{0.12}(D_2O)_{0.88}$ solutions, gives information concerning the hydration structure around the formyl-hydrogen atom within the formate ion. In the present study, ^7Li-enriched samples were employed in order to avoid large absorption by the ^6Li nucleus involved in the natural Li, which may prevent us from obtaining favorable statistical accuracies in the observed difference function.

Experimental

Materials. ^7Li-enriched lithium formate was prepared by reacting $^7LiOH\cdot H_2O$ (99.94% ^7Li, Tomiyama Chemical Co. Ltd) with concentrated HCOOH (natural abundance, Nacalai Tesque, Guaranteed grade) and DCOOD (99.5% D, Merck), to obtain $HCOO^7Li$ and $DCOO^7Li$, respectively. The product solutions were carefully dehydrated by heating at 80 °C under a vacuum. The required amounts of enriched anhydrous $HCOO^7Li$ and $DCOO^7Li$ were dissolved in D_2O (99.9% Aldrich Chemical Co., Inc.) to prepare 12 mol% $^*HCOO^7Li$ heavy water solutions. The sample parameters used in this study are listed in Table 1.

Neutron Diffraction Measurements. The sample solution was sealed into a cylindrical fused quartz cell (7.3 mm in inner di-

Table 1. Isotopic Composition and Mean Scattering Length, b_{H_f}, of the Formyl-Hydrogen Atom, Total Cross Section and Number Density Scaled in the Stoichiometric Unit, $(^*HCOO^7Li)_{0.12}(D_2O)_{0.88}$, σ_t and ρ, Respectively

	Sample	H_f/%	D_f/%	$b_{H_f}/10^{-12}$ cm	$\sigma_t{}^{a)}$/barns	ρ/Å^{-3}
I	$(DCOO^7Li)_{0.12}(D_2O)_{0.88}$	0.5	99.5	0.662	13.375	0.03115
II	$(HCOO^7Li)_{0.12}(D_2O)_{0.88}$	100	0	−0.374	16.924	

a) For incident neutron wavelength of 1.0 Å.

Published on the web March 11, 2005; DOI 10.1246/bcsj.78.413

ameter and 0.5 mm in thickness). TOF neutron diffraction measurements were carried out at 25 °C using a HIT-II spectrometer[10] installed at the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. Scattered neutrons were detected by 104 ^{3}He counters covering scattering angles of $10 \le 2\theta \le 157°$. The data acquisition time for the sample solution was ca. 8 h. Measurements were made in advance for an empty cell, instrumental background, and a vanadium rod of 8 mm in diameter, respectively.

Data Reduction. The observed scattering intensities from the sample were corrected for the background, absorption of both sample and cell,[11] and for multiple[12] and incoherent scatterings. The coherent scattering lengths, scattering and absorption cross sections for the constituent nuclei were referred to those tabulated by Sears.[13] The wavelength dependence of the total cross sections for H and D nuclei was estimated from the observed total cross sections for liquid H_2O and D_2O, respectively.[14] The corrected scattering intensity was converted to the absolute scattering cross section using the corrected scattering intensity from the vanadium rod. The inelasticity correction was applied using the scattering cross section observed for liquid ^0H_2O, in which the average scattering length of the hydrogen atom was set to be zero.[15]

The first-order difference function, $\Delta_H(Q)$,[16,17] was derived from the numerical difference between the fully corrected scattering cross sections observed for I. $(DCOO^7Li)_{0.12}(D_2O)_{0.88}$, and II. $(HCOO^7Li)_{0.12}(D_2O)_{0.88}$, which are identical in all except for different isotopic composition of the formyl-hydrogen atom within the formate ion,

$$\begin{aligned}\Delta_H(Q) = {} & (d\sigma/d\Omega)^{obs} \text{ (for sample I)} \\ & - (d\sigma/d\Omega)^{obs} \text{ (for sample II)}. \end{aligned} \tag{1}$$

Since the difference functions from 62 sets of forward angle detectors located at $10 \le 2\theta \le 51°$ agree well within the statistical uncertainties, they were combined at a Q-interval of 0.1 Å^{-1}, and used for the subsequent analysis. The $\Delta_H(Q)$ scaled at the stoichiometric unit, $(^*HCOO^7Li)_x(D_2O)_{1-x}$, can be described as a linear combination of partial structure factors relating with the formyl-hydrogen atom,

$$\begin{aligned}\Delta_H(Q) = {} & A[a_{H_fH_f}(Q) - 1] + B[a_{H_fC}(Q) - 1] \\ & + C[a_{H_fO_f}(Q) - 1] + D[a_{H_fLi}(Q) - 1] \\ & + E[a_{H_fO_W}(Q) - 1] + F[a_{H_fD_W}(Q) - 1], \end{aligned} \tag{2}$$

where

$$A = x^2({b_{D_f}}^2 - {b_{H_f}}^2), \quad B = 2x^2(b_{D_f} - b_{H_f})b_C,$$
$$C = 4x^2(b_{D_f} - b_{H_f})b_O, \quad D = 2x^2(b_{D_f} - b_{H_f})b_{Li},$$
$$E = 2x(1-x)(b_{D_f} - b_{H_f})b_O, \text{ and } F = 4x(1-x)(b_{D_f} - b_{H_f})b_{D_W}.$$

H_f and O_f are the formyl-hydrogen and the carboxyl-oxygen atoms within the formate ion, respectively. Water-hydrogen and water-oxygen atoms are denoted by D_W and O_W, respectively. Numerical values of the weighting factors in Eq. 2, A–F, are listed in Table 2. The distribution function, $G_H(r)$, around the formyl-hydrogen atom is given by the Fourier transform of $\Delta_H(Q)$:

$$\begin{aligned}G_H(r) = {} & 1 + (A+B+C+D+E+F)^{-1}(2\pi^2\rho r)^{-1} \\ & \times \int_0^{Q_{max}} Q\Delta_H(Q)\sin(Qr)dQ \\ = {} & [Ag_{H_fH_f}(r) + Bg_{H_fC}(r) + Cg_{H_fO_f}(r) \\ & + Dg_{H_fLi}(r) + Eg_{H_fO_W}(r) + Fg_{H_fD_W}(r)] \\ & \times (A+B+C+D+E+F)^{-1}. \end{aligned} \tag{3}$$

The upper limit of the integral, Q_{max}, was set to 20 Å^{-1} in the present study.

The intramolecular structural parameters for H_f–C and $H_f \cdots O_f$ interactions within the formate ion were determined from a least squares refinement of the observed $\Delta_H(Q)$ in the range of $8 \le Q \le 20$ Å^{-1}, where the contribution from the intramolecular interference term is dominant. The intramolecular interference term involved in the $\Delta_H(Q)$ is given by

$$\begin{aligned}{I_H}^{intra}(Q) = {} & \beta \cdot \sum 2c_{H_f}(b_{D_f} - b_{H_f})b_\alpha \\ & \times \exp(-{l_{H_f\alpha}}^2Q^2/2)\sin(Qr_{H_f\alpha})/(Qr_{H_f\alpha}), \end{aligned} \tag{4}$$

where β is the normalization factor. c_{H_f} denotes the number of formyl-hydrogen atoms in the stoichiometric unit. $l_{H_f\alpha}$ and $r_{H_f\alpha}$ stand for the root-mean-square amplitude and the internuclear distance for the $H_f \cdots \alpha$ pair, respectively. The fitting procedure was performed by using the SALS program,[18] assuming that the statistical uncertainties distribute uniformly. ${I_H}^{intra}(Q)$ was then subtracted from the total $\Delta_H(Q)$ to obtain the intermolecular difference function, ${\Delta_H}^{inter}(Q)$,

$${\Delta_H}^{inter}(Q) = \Delta_H(Q) - {I_H}^{intra}(Q). \tag{5}$$

The intermolecular distribution function, ${G_H}^{inter}(r)$, was obtained by a Fourier transform of the ${\Delta_H}^{inter}(Q)$ using Eq. 3 with the upper limit of the integral, $Q_{max} = 20$ Å^{-1}. Since the magnitudes of coefficients E and F were much larger than those of A–D under the present experimental condition, the observed ${\Delta_H}^{inter}(Q)$ was dominated by the contribution from the $H_f \cdots D_2O$ correlation.

The hydration parameters concerning the formyl-hydrogen atom were determined through a least squares fitting procedure for the observed ${\Delta_H}^{inter}(Q)$ employing a model function, ${\Delta_H}^{model}(Q)$, involving both the short- and long-range contributions:[19–21]

$$\begin{aligned}{\Delta_H}^{model}(Q) = {} & \sum 2c_{H_f}n_{H_f\alpha}(b_{D_f} - b_{H_f})b_\alpha \\ & \times \exp(-{l_{H_f\alpha}}^2Q^2/2)\sin(Qr_{H_f\alpha})/(Qr_{H_f\alpha}) \\ & + 4\pi\rho(A+B+C+D+E+F)\exp(-{l_0}^2Q^2/2) \\ & \times [Qr_0\cos(Qr_0) - \sin(Qr_0)]Q^{-3}, \end{aligned} \tag{6}$$

where, $n_{H_f\alpha}$ denotes the coordination number of α atoms around the H_f atom. The long-range parameter, r_0, stands for the distance beyond which the continuous distribution of atoms around the H_f atom can be assumed. The parameter, l_0, describes the sharpness of the boundary at r_0. The structural parameters ($n_{H_f\alpha}$, $l_{H_f\alpha}$, $r_{H_f\alpha}$, l_0, and r_0) were respectively determined from least squares fits to the observed ${\Delta_H}^{inter}(Q)$. The fitting procedure was carried out in the range of $0.4 \le Q \le 20$ Å^{-1} with the SALS program.[18]

Table 2. Values of the Coefficients of $a_{ij}(Q)$ in Eq. 2

A/barns	B/barns	C/barns	D/barns	E/barns	F/barns
0.0043	0.0198	0.0347	−0.0066	0.1271	0.2917

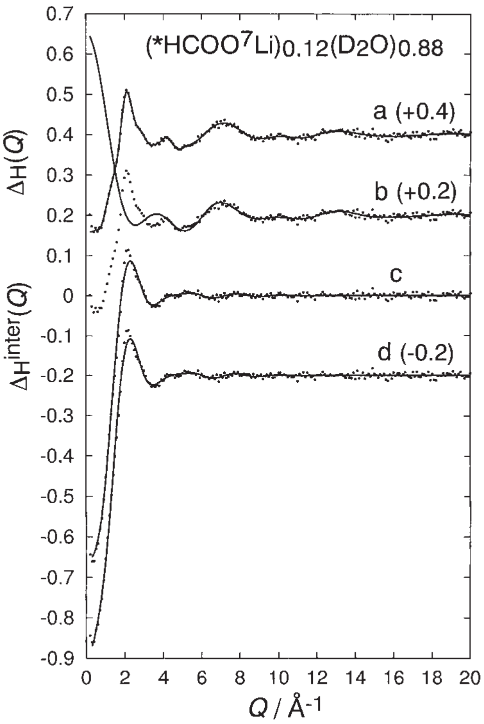

Fig. 1. a) The observed difference function, $\Delta_\mathrm{H}(Q)$, for aqueous 12 mol% lithium formate solutions (dots). Smoothed $\Delta_\mathrm{H}(Q)$ used for the Fourier transform (solid line). b) The observed $\Delta_\mathrm{H}(Q)$ (dots). The intramolecular contribution within the formate ion, $I_\mathrm{H}{}^\mathrm{intra}(Q)$ (solid line). c) Intermolecular difference function, $\Delta_\mathrm{H}{}^\mathrm{inter}(Q)$ (dots). The best fit of the $\Delta_\mathrm{H}{}^\mathrm{model}(Q)$ calculated by the model function in which the nearest neighbor $\mathrm{H_f\cdots D_2O}$ interaction was treated as a single interaction (solid line). d) The same notations as for c) but the solid line indicates the result using the model function in which the nearest neighbor $\mathrm{H_f\cdots O_W}$ and $\mathrm{H_f\cdots D_W}$ interactions were treated independently.

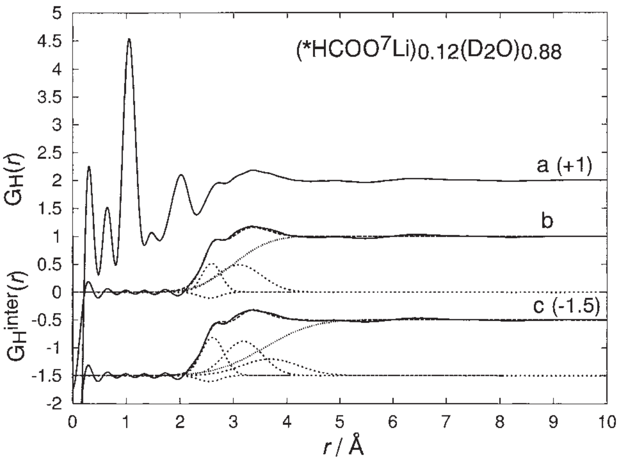

Fig. 2. a) Total distribution function around the formyl-hydrogen atom, $G_\mathrm{H}(r)$, observed for aqueous 12 mol% lithium formate heavy water solutions. b) Observed intermolecular distribution function, $G_\mathrm{H}{}^\mathrm{inter}(r)$ (solid line), and the Fourier transform of the calculated $\Delta_\mathrm{H}{}^\mathrm{model}(Q)$ (Fig. 1c) is shown by the broken line. Short- and long-range contributions are denoted by dotted lines. c) The same notations as for b) but the Fourier transform of the calculated $\Delta_\mathrm{H}{}^\mathrm{model}(Q)$ (Fig. 1d) is shown by the broken line. Short- and long-range contributions are denoted by dotted lines.

Results and Discussion

Intramolecular Structure of the Formate Ion. The observed $\Delta_\mathrm{H}(Q)$ function, represented in Fig. 1a, exhibits a well-defined first diffraction peak at $Q \approx 2$ Å^{-1} with a shoulder at the higher-Q side. The interference oscillations extend over the higher Q region, which mainly involves contributions from intramolecular $\mathrm{H_f}$–C and $\mathrm{H_f\cdots O_f}$ interactions within the formate ion. The distribution function around the formyl-hydrogen atom, $G_\mathrm{H}(r)$, is represented in Fig. 2a. The dominant first peak at $r \approx 1.1$ Å is attributable to the intramolecular $\mathrm{H_f}$–C interaction. The intramolecular $\mathrm{H_f\cdots O_f}$ interaction can be indicated as the second peak at $r \approx 2.0$ Å. Because a broadened peak located at $r \approx 3.2$ Å with a shoulder at around $r \approx 2.6$ Å cannot be ascribed to any intramolecular interaction within the formate ion, these structural features indicate an intermolecular interaction between the $\mathrm{H_f}$ atom and water molecules in the first hydration shell.

In order to determine the intramolecular structure parameters, a least squares fit of the calculated intramolecular interference term by Eq. 4 was applied to the observed $\Delta_\mathrm{H}(Q)$ in the range of $8 \le Q \le 20$ Å^{-1} (Fig. 1b). The parameters for the internuclear distances and their root-mean-square displacements for $\mathrm{H_f}$–C and $\mathrm{H_f\cdots O_f}$ interactions are refined independently. The final results are listed in Table 3. The present values of intramolecular distances, $r_{\mathrm{H_f–C}} = 1.072(2)$ Å and $r_{\mathrm{H_f\cdots O_f}} = 2.015(8)$ Å, are in excellent agreement with those determined by our previous neutron diffraction study on an aqueous 15 mol% DCOONa solution in D_2O ($r_{\mathrm{H_f–C}} = 1.07(1)$ Å and $r_{\mathrm{H_f\cdots O_f}} = 2.04(3)$ Å).[6] On the other hand, the $r_{\mathrm{H_f–C}}$ value obtained from a recent ab initio calculation[8] is ca. 0.05 Å longer than that from the experiment. The normalization factor, β, in Eq. 4 was determined to be $\beta = 1.07(6)$, implying that the present data correction and normalization procedures were adequately carried out; the overall normalization error in the $\Delta_\mathrm{H}(Q)$ is roughly estimated to be within 7%.

Table 3. Intramolecular Parameters for the Formate Ion in Aqueous 12 mol% $\mathrm{^*HCOO^7Li}$ Solutions in D_2O[a)]

i–j	r_ij/Å	l_ij/Å
$\mathrm{H_f}$–C	1.072(2)	0.079(5)
$\mathrm{H_f\cdots O_f}$	2.015(8)	0.124(4)

a) Estimated standard deviations are given in parentheses.

Hydration Structure around the Formyl-Hydrogen Atom. The calculated $I_\mathrm{H}{}^\mathrm{intra}(Q)$ was subtracted from the observed $\Delta_\mathrm{H}(Q)$ to obtain the intermolecular difference function, $\Delta_\mathrm{H}{}^\mathrm{inter}(Q)$, which is shown in Fig. 1c. The corresponding intermolecular distribution function, $G_\mathrm{H}{}^\mathrm{inter}(r)$, is represented in Fig. 2b. The $G_\mathrm{H}{}^\mathrm{inter}(r)$ function exhibits a considerably broadened feature, indicating a very weak interaction between the formyl-hydrogen atom and the nearest neighbor water molecule. The structural features appearing at $r = 2.6$ and 3.2 Å in the $G_\mathrm{H}{}^\mathrm{inter}(r)$, are very similar to those observed in the total

$G_H(r)$ function, which suggests that these features reflect real structures. This implies that the first and second hydration shells are present around the formyl-hydrogen atom.

In order to obtain structural parameters concerning the hydration around the formyl-hydrogen atom, the least squares fitting analysis was applied to the observed $\Delta_H{}^{inter}(Q)$. Since it would be difficult to distinguish contributions from the $H_f \cdots O_W$ (O_W: water oxygen atom) and the $H_f \cdots D_W$ (D_W: water deuterium atom) interactions in the present difference functions, the least squares refinement procedure was carried out with two different assumptions in evaluating the theoretical interference term. In a preliminary analysis, the nearest neighbor $H_f \cdots D_2O$ interaction was treated as a single interaction. The following assumptions were adopted for evaluating the theoretical $\Delta_H{}^{model}(Q)$: a) The first nearest neighbor $H_f \cdots D_2O$ interaction was treated as a single interaction with the coherent scattering length in Eq. 6, b_α, being $2b_D + b_O$. The structural parameters, $r_{H_f \cdots D_2O}$, $l_{H_f \cdots D_2O}$, and $n_{H_f \cdots D_2O}$, were refined independently. b) The second nearest neighbor $H_f \cdots D_2O$ interaction was taken into account, and treated as a single interaction. c) The contribution from the nearest neighbor $H_f \cdots Li^+$ interaction was involved in the present model function with the fixed structural parameters, $r_{H_fLi} = 2.57$ Å, $l_{H_fLi} = 0.20$ Å, and $n_{H_fLi} = 1.2$, which were determined from our previous neutron diffraction study.[9] d) The parameters of a continuous long-range random distribution of atoms, r_0 and l_0, were refined independently.

The best-fit result is compared with the observed $\Delta_H{}^{inter}(Q)$ in Fig. 1c. A satisfactory agreement is obtained in the range of $0.4 \le Q \le 20$ Å^{-1}. The observed and calculated $G_H{}^{inter}(r)$ (Fig. 2b) also agree well with each other. The contribution from the $H_f \cdots Li^+$ interaction appears as a negative peak due to the negative scattering length of ^7Li. The final results of the least squares refinement are summarized in Table 4. The present value of the nearest neighbor $H_f \cdots D_2O$ distance, $r_{H_f \cdots D_2O} = 2.60(1)$ Å, is close to the sum of the van der Waals radius of the hydrogen atom (1.2 Å) and radius of the water molecule in aqueous solutions (1.4 Å),[22] implying that the interaction between the formyl-hydrogen atom and the water molecule in the first hydration shell is weak. The number of water molecules within the first hydration shell was determined to be 0.60(2).

Table 4. Hydration Parameters around the Formyl-Hydrogen Atom (H_f) Observed for Aqueous 12 mol% *HCOO^{7}Li Solutions in D_2O Obtained Using the Model Interference Function in Which the Nearest Neighbor $H_f \cdots D_2O$ Contribution Was Treated as a Single Interaction[a)]

Interaction	i–j	r_{ij}/Å	l_{ij}/Å	n_{ij}
$H_f \cdots D_2O(I)^{b)}$	$H_f \cdots D_2O$	2.60(1)	0.18(1)	0.60(2)
$H_f \cdots D_2O(II)^{c)}$	$H_f \cdots D_2O$	3.16(1)	0.42(1)	2.0(1)
$H_f \cdots Li^+$	$H_f \cdots Li^+$	2.57$^{d)}$	0.20$^{d)}$	1.2$^{d)}$
		r_0/Å	l_0/Å	
Long-range	$H_f \cdots X$	3.10(3)	0.53(1)	

a) Estimated standard deviations are given in parentheses. b) The first nearest neighbor $H_f \cdots D_2O$ interaction. c) The second nearest neighbor $H_f \cdots D_2O$ interaction. d) Fixed at values reported in Ref. 9.

Recently, the hydration structure around the methyl group of the alanine molecule was investigated by neutron diffraction with the H/D isotopic substitution method.[23] Water molecules within the first hydration shell of the methyl-hydrogen atom take a preferred orientation in which the oxygen atom of each water molecule faces towards the methyl-hydrogen atom (H_M) with an intermolecular distance of $r_{H_M \cdots O_W} = 2.58(1)$ Å,[23] which is in good agreement with the position of the first peak found in the present $G_H{}^{inter}(r)$. If water molecules within the first hydration shell of the formyl-hydrogen atom also take a similar orientation as that observed for the methyl-hydrogen atom of the alanine molecule, it can be considered that the first peak of the present $G_H{}^{inter}(r)$ mainly involves the contribution from the nearest neighbor $H_f \cdots O_W$ interaction. Thus, we next attempted a least squares fitting analysis in which the orientation of the water molecules around the formyl-hydrogen atom was taken into account. In evaluating the theoretical interference term, contributions from the nearest neighbor $H_f \cdots O_W$ and $H_f \cdots D_W$ interactions were treated as separated ones. The following assumptions were adopted: a) The parameters for the nearest neighbor $H_f \cdots D_2O$ interaction ($r_{H_f \cdots O_W}$, $l_{H_f \cdots O_W}$, $r_{H_f \cdots D_W}$, $l_{H_f \cdots D_W}$, and $n_{H_f \cdots O_W}$) were refined independently. b) The second nearest neighbor $H_f \cdots D_2O$ interaction was taken into account, and treated as a single interaction. c) The contribution from the nearest neighbor $H_f \cdots Li^+$ interaction was involved with the fixed parameters, as mentioned above. d) The parameters for the long-range random distribution of atoms, r_0 and l_0, were independently refined.

The best-fit result is compared with the observed $\Delta_H{}^{inter}(Q)$ in Fig. 1d. A satisfactory agreement is again obtained. The observed and calculated $G_H{}^{inter}(r)$ (Fig. 2c) also agree well with each other. The final results of the least squares refinement are summarized in Table 5. The present value of the nearest neighbor $H_f \cdots O_W$ distance, $r_{H_fO_W} = 2.63(1)$ Å, is very close to the sum of the van der Waals radii of the hydrogen and oxygen atoms, which implies that the interaction between the formyl-hydrogen atom and the nearest neighbor water molecule is weak. The present $r_{H_fO_W}$ value agrees well with the values, $r_{H_M'O_W} = 2.64(1)$ Å (H_M': methylene-hydrogen atom) and $r_{H_MO_W} = 2.58(1)$ Å (H_M: methyl-hydrogen atom), which were determined for aqueous 4 mol% glycine[24] and 3 mol% alanine

Table 5. The Same Notations as Table 4 but Results Obtained by Using the Model Function in Which the Nearest Neighbor $H_f \cdots O_W$ and $H_f \cdots D_W$ Were Treated as Separate Interactions[a)]

Interaction	i–j	r_{ij}/Å	l_{ij}/Å	n_{ij}
$H_f \cdots D_2O(I)^{b)}$	$H_f \cdots O_W$	2.63(1)	0.21(1)	3.19(2)
	$H_f \cdots D_W$	3.23(1)	0.36(1)	6.38$^{c)}$
$H_f \cdots D_2O(II)^{d)}$	$H_f \cdots D_2O$	3.77(5)	0.53(4)	2.1(4)
$H_f \cdots Li^+$	$H_f \cdots Li^+$	2.57$^{e)}$	0.20$^{e)}$	1.2$^{e)}$
		r_0/Å	l_0/Å	
Long-range	$H_f \cdots X$	3.72(7)	0.71(3)	

a) Estimated standard deviations are given in parentheses. b) The first nearest neighbor $H_f \cdots D_2O$ interaction. c) Fixed at the value $2n_{H_fO_W}$. d) The second nearest neighbor $H_f \cdots D_2O$ interaction. e) Fixed at values reported in Ref. 9.

solutions,[23] respectively. The nearest neighbor $H_f \cdots D_W$ distance was determined to be 3.23(1) Å. The average angle between the $H_f \cdots O_W$ axis and the molecular plane of the water molecule was estimated to be 37(4)°, employing the known molecular geometry of D_2O in the liquid state ($r_{OD} = 0.983$ Å and $r_{DD} = 1.55$ Å).[25,26] The results indicate that the orientation of the water molecules within the first hydration shell around the formyl-hydrogen atom is not completely random. The present value of the nearest neighbor $H_f \cdots O_W$ coordination number, $n_{H_fO_W} = 3.19(2)$, is much larger than that, 0.60(2), determined from an analysis employing a model function in which the nearest neighbor $H_f \cdots D_2O$ interaction was treated as a single interaction. The present value of $n_{H_fO_W}$ is larger than that observed for the methylene-hydrogen atom of the glycine molecule ($n_{H_{M'}O_W} = 0.86(3)$)[24] and that observed for the methyl-hydrogen atom of the alanine molecule ($n_{H_MO_W} = 0.62(1)$).[23]

In order to obtain more detailed information concerning the first hydration shell of the formyl-hydrogen atom, it is necessary to deduce the partial structure factors, $a_{H_fO_W}(Q)$ and $a_{H_fH_W}(Q)$. This requires additional measurements on solutions with different H/D ratios of the water molecule, and will be a future research subject. The present results indicate that the distribution of water molecules around the formyl-hydrogen atom of the formate ion is not random. The existence of a hydration shell around the formyl-hydrogen atom has been confirmed.

The authors would like to acknowledge Prof. Toshiharu Fukunaga (Kyoto University) and Dr. Keiji Itoh (Kyoto University) for their help during the course of neutron diffraction measurements. All calculations were carried out with a S7/7000U computer at the Yamagata University Computing Service Center. This work was supported in part by Grants-in-Aid for Scientific Research on Priority Areas (No. 16041205) and Scientific Research (C) (No. 16550049) from the Ministry of Education, Culture, Sports, Science and Technology.

References

1 K. Ito and H. J. Bernstein, *Can. J. Chem.*, **34**, 170 (1956).

2 E. Spinner, *J. Chem. Soc. B*, **1967**, 879.

3 R. J. Bartholomew and D. E. Irish, *Can. J. Chem.*, **71**, 1728 (1993).

4 K. Ozutsumi, H. Ohtaki, and A. Kusumegi, *Bull. Chem. Soc. Jpn.*, **57**, 2612 (1984).

5 W. L. Jorgensen and J. Gao, *J. Phys. Chem.*, **90**, 2174 (1986).

6 Y. Kameda, T. Mori, T. Nishiyama, T. Usuki, and O. Uemura, *Bull. Chem. Soc. Jpn.*, **69**, 1495 (1996).

7 Y. Kameda, K. Fukuhara, K. Mochiduki, H. Naganuma, T. Usuki, and O. Uemura, *J. Non-Cryst. Solids*, **312–314**, 433 (2002).

8 K. Leung and S. B. Rempe, *J. Am. Chem. Soc.*, **126**, 344 (2004).

9 Y. Kameda, T. Usuki, and O. Uemura, *High Temp. Mater. Proc.*, **18**, 27 (1999).

10 T. Fukunaga, M. Misawa, I. Fujikura, and S. Satoh, "KENS REPORT-IX," (1993), p. 16.

11 H. H. Paalman and C. J. Pings, *J. Appl. Phys.*, **33**, 2635 (1962).

12 I. A. Blech and B. L. Averbach, *Phys. Rev.*, **137**, A1113 (1965).

13 V. F. Sears, *Neutron News*, **3**, 26 (1992).

14 J. R. Granada, V. F. Gillete, and R. E. Mayer, *Phys. Rev. A*, **36**, 5594 (1987).

15 Y. Kameda, M. Sasaki, T. Usuki, T. Otomo, K. Itoh, K. Suzuya, and T. Fukunaga, *J. Neutron Res.*, **11**, 153 (2003).

16 A. K. Soper, G. W. Neilson, J. E. Enderby, and H. A. Howe, *J. Phys. C: Solid State Phys.*, **10**, 1793 (1977).

17 J. E. Enderby and G. W. Neilson, "Water, A Comprehensive Treatise," Plenum Press, New York (1979), Vol. 6, p. 1.

18 T. Nakagawa and Y. Oyanagi, "Recent Development in Statistical Inference and Data Analysis," North-Holland (1980), p. 221.

19 A. H. Narten, M. D. Danford, and H. A. Levy, *Discuss. Faraday Soc.*, **43**, 97 (1967).

20 R. Caminiti, P. Cucca, M. Monduzzi, G. Saba, and G. Crisponi, *J. Chem. Phys.*, **81**, 543 (1984).

21 H. Ohtaki and N. Fukushima, *J. Solution Chem.*, **21**, 23 (1992).

22 I. Marcus, *Chem. Rev.*, **88**, 1475 (1988).

23 Y. Kameda, K. Sugawara, T. Usuki, and O. Uemura, *Bull. Chem. Soc. Jpn.*, **76**, 935 (2003).

24 M. Sasaki, Y. Kameda, M. Yaegashi, and T. Usuki, *Bull. Chem. Soc. Jpn.*, **76**, 2293 (2003).

25 J. G. Powles, *Mol. Phys.*, **42**, 757 (1981).

26 Y. Kameda and O. Uemura, *Bull. Chem. Soc. Jpn.*, **65**, 2021 (1992).