Hydration Structure of Glycine Molecules in Concentrated Aqueous Solutions

Yasuo KAMEDA,* Hidekazu EBATA, Takeshi USUKI, Osamu UEMURA, and Masakatsu MISAWA†
Department of Chemistry, Faculty of Science, Yamagata University, Kojirakawa-machi 1-4-12, Yamagata 990
†Department of Chemistry, Faculty of Science, Niigata University, Igarashi-nino-machi 8050, Niigata 950-21
(Received May 16, 1994)

A radial distribution study for aqueous 5 mol% glycine solutions was carried out involving time-of-flight neutron diffraction measurements. An isotopic substitution technique was applied to both nitrogen and hydrogen atoms of the sample in order to determine the hydration structure around the amino group of the glycine molecules in an aqueous solution. It has been clarified that there exist 3.0±0.6 water molecules coordinated to the amino group of a glycine molecule with intermolecular distances of $r_{N\cdots O}$=2.85±0.05 Å and $r_{N\cdots D}$=3.25±0.05 Å. These values suggest that a hydrogen bond is formed between the amino group of a glycine molecule and the nearest-neighbor water molecules in the aqueous glycine solution.

Recently, great interest has been raised to elucidate the structural relationship between amino acid molecules and the neighboring water molecules in an aqueous solution, which gives a hint of some fundamental understanding in the field of biochemical science, e.g., the reaction dynamics on protein biosynthesis and the 'so-called' protein folding problem,[1] which predicts a compact three-dimensional structure resulting from a sequence of amino-acid monomers in an aqueous solution. In addition, such structural information plays a certain role in the synthesis mechanism of metal complexes containing an amino acid as a chelate agent in the aqueous solution.[2] The object of the present work was to investigate the hydration structure of the glycine molecule in an aqueous solution through neutron-diffraction measurements. The structural feature of the simplest amino acid, glycine (NH_2CH_2COOH) has been extensively studied under various states according to its biochemical significance as well as a wide variety of applications to chemical industry.

Glycine exists in a molecular form, NH_2CH_2COOH, in the gaseous state. It has been exhibited by electron diffraction[3] and microwave spectrum measurements[4] that the molecular skeleton of isolated glycine is planar, and that the amino and hydroxyl groups within a molecule are in an anti-position with respect to each other.[3] A new conformer having amino hydrogen atoms hydrogen-bonded to the carbonyl oxygen[5] has also been reported to exist in gaseous glycine by a rotational spectrum measurement. The structure of molecular glycine has been theoretically studied by means of CNDO[6] and ab initio[7,8] calculations.

Solid glycine is composed of zwitterions, $NH_3{}^+CH_2COO^-$. The intra- and inter-molecular geometries of the zwitterion have been determined in detail by X-ray[9] and neutron-diffraction[9,10] measurements using a single crystal. In these results, crystalline glycine forms a three-dimensional network structure due to strong hydrogen bonds between neighboring molecules.[10]

The structure of glycine in an aqueous solution has mainly been studied from the viewpoint of the complex formation of a glycinate ion and various metal ions. For example, the structure of some chelate complexes consisting of glycine and a divalent transition metal ion (Ni^{2+}, Cu^{2+}, and Zn^{2+}) in an aqueous solution has been investigated by means of X-ray diffraction[11—13] and extended X-ray absorption fine-structure[14] techniques. Nevertheless, there have been few reports, at present, concerning the hydration structure of glycine, itself, which is in a zwitterionic form in solution. In practice, it is considerable difficult to deduce any reliable structural information concerning the glycine–water correlation in an aqueous solution by a conventional X-ray diffraction experiment alone, because the contribution of the glycine–water correlation to the observed total diffraction intensities is relatively small and a serious overlap in the distribution function occurs between this correlation and other correlations, such as the correlation between solvent water molecules. Then, a structural analysis of the partial distribution function level should be indispensable to determine the hydration structure of the glycine molecule in solution. In this respect, neutron diffraction adopting the isotopic substitution technique is one of the most available experimental methods, which can supply quantitative information concerning the local atomic configuration around an isotopically substituted atom.

In the present paper we describe the results of time-of-flight (TOF) neutron-diffraction measurements for four kinds of aqueous 5 mol% glycine solutions, in which both nitrogen and hydrogen atoms are isotopically exchanged. The difference function (${}^{D}\Delta_N(Q)$) from two isotopically substituted solutions, $(^{14}ND_2CH_2COOD)_{0.05}(D_2O)_{0.95}$ and $(^{15}ND_2CH_2COOD)_{0.05}(D_2O)_{0.95}$, in conjunction with that, ${}^{0_H}\Delta_N(Q)$, from two solutions, $(^{14}N^0H_2CH_2COO^0H)_{0.05}(^0H_2O)_{0.95}$ and $(^{15}N^0H_2CH_2COO^0H)_{0.05}(^0H_2O)_{0.95}$, gives information concerning two partial structure factors, $a_{NH}(Q)$ and to a good approximation, $a_{NO}(Q)$, which relate to the hydration structure of the glycine molecule in solution. In the latter two solutions the mean coherent scattering length of exchangeable hydrogen atoms was set to zero by the coexistence of the required amounts of H and D(^{0}H).

Experimental

Materials. Isotopically enriched $^{15}NH_2CH_2COOH$ (99.8% ^{15}N, Isotec Inc.) and natural $^{14}NH_2CH_2COOH$ (99.6% ^{14}N, Nacalai tesque, guaranteed grade) were deuterated by dissolving them repeatedly into D_2O (99.9% D, Aldrich Chemical Co., Inc.), followed by dehydration in vacuo. The required amounts of enriched glycine were dissolved into D_2O or H_2O–D_2O mixtures so as to prepare four kinds of aqueous 5 mol% glycine solutions with different isotopic compositions of both nitrogen and hydrogen atoms. Since any intensity contribution from H–X (X=H, N, C, and O) pairs disappears in a solution containing ^0H, the use of a "null mixture" for hydrogen atoms can give approximately direct information concerning the N–O partial structure factor through the $^{0H}\Delta_N(Q)$ intensity function.

Neutron Diffraction Measurements. The sample solution was sealed in vacuo into a cylindrical quartz cell (7.3 mm in inner diameter and 0.5 mm in thickness). TOF neutron-diffraction measurements were carried out at 60 °C using a newly constructed HIT-II instrument[16] with an infrared image furnace installed at the pulsed spallation neutron source (KENS) of the National Laboratory for High Energy Physics, Tsukuba, Japan. Scattered neutrons were detected by 104 pieces of ^3He counters, which covered scattering angles of $10 \leqq 2\theta \leqq 157°$. The data-accumulation time was ca. 4h for the respective samples. Diffraction measurements were made in advance for an empty quartz cell, background and a vanadium rod of 8 mm in diameter.

Data Reduction. The scattering intensities from detectors set up at the same scattering angle on both the right- and left-hand sides of the sample were summed up, and followed such data corrections as the background intensity, for the absorption of both the sample and cell,[17] and for multiple[18] and incoherent scattering. The coherent scattering length as well as the scattering and absorption cross sections for the constituent nuclei were respectively referred to based on those tabulated by Sears.[19] The sample parameters used are listed in Table 1. Since the TOF neutron-diffraction technique employs neutrons with a wide wavelength range of $0.1 \leqq \lambda \leqq 3$ Å, the λ-dependence of the total cross section (σ_t) should be estimated to sufficient precision for the absorption correction. Under the present experimental condition, the following equations were applied to the λ-dependence of σ_t for H and D nuclei:

$$\sigma_{t,H}(\lambda) = 15.0 + 18.8\lambda$$

and

$$\sigma_{t,D}(\lambda) = 2.7 + 1.38\lambda. \quad (1)$$

The coefficients in the equations were determined based on the observed total cross sections for liquid H_2O and D_2O.[20] The observed count rate of the sample was converted to the absolute scattering cross section ($(d\sigma/d\Omega)^{obsd}$) by using the scattering intensities from a vanadium rod. The difference function[21,22] ($\Delta_N(Q)$) is defined as the numerical difference in the normalized scattering cross sections between two aqueous glycine solutions which are identical in all respects except for the isotopic composition of the nitrogen atom. $\Delta_N(Q)$ does not include any pair correlations which are independent of the nitrogen atom, because these are completely canceled out through subtraction. Therefore, the Fourier transform of $\Delta_N(Q)$ ($G_N(r)$) gives the distribution of atoms around the nitrogen atom in the solution. In addition, this subtraction has an advantage in that the inelasticity distortion effect arising from the self-scattering contribution of H and D atoms is eliminated in $\Delta_N(Q)$.[21,23] In the present work, two sets of $\Delta_N(Q)$s were derived through the difference in the scattering cross sections between two solutions having common hydrogen isotopes and different nitrogen isotopes, as in the following equations:

$$^D\Delta_N(Q) = (d\sigma/d\Omega)^{obsd}(\text{for } ^{14}N\text{–D}) - (d\sigma/d\Omega)^{obsd}(\text{for } ^{15}N\text{–D})$$

and

$$^{0H}\Delta_N(Q) = (d\sigma/d\Omega)^{obsd}(\text{for } ^{14}N\text{–}^0H) - (d\sigma/d\Omega)^{obsd}(\text{for } ^{15}N\text{–}^0H). \quad (2)$$

Here, the superscript 0 corresponds to the isotopic composition of the null mixture for the hydrogen atom. Since the respective $^D\Delta_N(Q)$s obtained from 66 sets of detectors located at $2\theta=10$—$51°$ and 14 sets at $2\theta=75$—$97°$ agree well with each other within the statistical error, we combined these $^D\Delta_N(Q)$s at a given Q-value selected adequately, and used them for a subsequent data analysis. Similarly, the intensity data from 38 sets of detectors at $2\theta=10$—$20°$ and those from 18 sets at $2\theta=42$—$78°$ were combined to obtain a whole functional form of $^{0H}\Delta_N(Q)$. Both $^D\Delta_N(Q)$ and $^{0H}\Delta_N(Q)$ for aqueous 5 mol% glycine solutions determined by this way are shown in Figs. 1a and 2a, respectively.

$\Delta_N(Q)$ for an aqueous glycine solution can be expressed as a linear combination of the following five partial structure factors related to the nitrogen atom,

$$\Delta_N(Q) = A[a_{NO}(Q) - 1] + B[a_{NH}(Q) - 1] + C[a_{NN}(Q) - 1] + D[a_{NC}(Q) - 1] + E[a_{NH'}(Q) - 1], \quad (3)$$

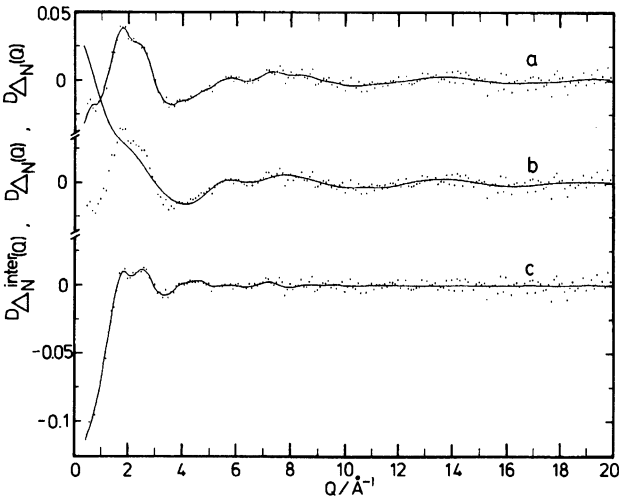

Fig. 1. a) Dots: The observed difference function, $^D\Delta_N(Q)$, for the 5 mol% ND_2CH_2COOD solution in D_2O. Solid line: Smoothed $^D\Delta_N(Q)$ used for the Fourier transform (Fig. 3a). b) Dots: The observed $^D\Delta_N(Q)$. Solid line: The intramolecular intreference function, $I^{intra}(Q)$. c) Dots: The intermolecular contribution, $^D\Delta_N{}^{inter}(Q)$. Solid line: The inverse Fourier transform of $^D\Delta_N{}^{inter}(Q)$ shown in Fig. 3b.

Table 1. Isotopic Compositions and Mean Scattering Lengths, b_N and b_H, of Nitrogen and Hydrogen Atoms, Total Cross Sections and the Number Densities Scaled in the Stoichiometric Unit $(NH_2CH_2COOH)_{0.05}(H_2O)_{0.95}$, σ_t and ρ, Respectively, for the Sample Used in the Neutron Diffraction Measurement

Sample	^{14}N/%	^{15}N/%	H/%[a]	D/%[a]	$b_N/10^{-12}$ cm	$b_H/10^{-12}$ cm	σ_t/barns[b]	ρ/Å^{-3}
$(^{14}ND_2CH_2COOD)_{0.05}(D_2O)_{0.95}$	99.6	0.4	0.3	99.7	0.936	0.666	15.33	0.03080
$(^{15}ND_2CH_2COOD)_{0.05}(D_2O)_{0.95}$	0.2	99.8	0.3	99.7	0.645	0.666	14.96	
$(^{14}N^0H_2CH_2COO^0H)_{0.05}(^0H_2O)_{0.95}$	99.6	0.4	64.1	35.9	0.936	0.000	44.15	
$(^{15}N^0H_2CH_2COO^0H)_{0.05}(^0H_2O)_{0.95}$	0.2	99.8	64.1	35.9	0.645	0.000	43.38	

a) For exchangeable hydrogen atoms. b) For the incident wavelength of 1.0 Å.

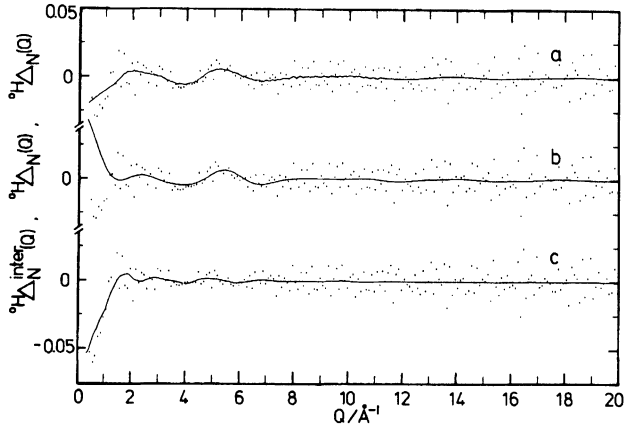

Fig. 2. Same notations as Fig. 1, except for the 5 mol% $N^0H_2CH_2COO^0H$ solution in ^0H_2O, where ^0H denotes the isotopic mixture with the average scattering length of hydrogen atom, $b_H=0$.

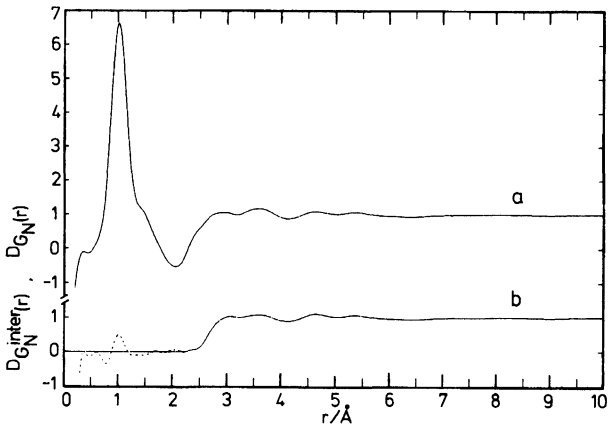

Fig. 3. a) The total and b) intermolecular distribution functions around the nitrogen atom, $^DG_N(r)$ and $^DG_N{}^{inter}(r)$, truncated at $Q_{max}=20.0$ Å^{-1}, for the 5 mol% ND_2CH_2COOD solution in D_2O.

where,

$$A = 2c_Nc_Ob_O(b_{^{14}N} - b_{^{15}N}), \quad B = 2c_Nc_Hb_H(b_{^{14}N} - b_{^{15}N}),$$
$$C = c_N{}^2(b^2{}_{^{14}N} - b^2{}_{^{15}N}), \quad D = 2c_Nc_Cb_C(b_{^{14}N} - b_{^{15}N}),$$
$$E = 2c_Nc_{H'}b_{H'}(b_{^{14}N} - b_{^{15}N}), \text{ respectively.}$$

H′ and H, respectively, denote the hydrogen atom of the methylene group in the glycine molecule and the remaining hydrogen atoms exchanged isotopically. c_i is the number of atom i in the stoichiometric unit $(^*N^*H_2CH_2COO^*H)_{0.05}(^*H_2O)_{0.95}$. The weighting factors (A, B, C, D, and E) in Eq. 3 are numerically listed in Table 2. The distribution function around the nitrogen atom ($G_N(r)$) can also be represented as

$$G_N(r) = 1 + (A+B+C+D+E)^{-1}(2\pi^2\rho r)^{-1} \times \int_0^{Q_{max}} Q\cdot\Delta_N(Q)\sin(Qr)dQ$$
$$= [Ag_{NO}(r) + Bg_{NH}(r) + Cg_{NN}(r) + Dg_{NC}(r) + Eg_{NH'}(r)] \times (A+B+C+D+E)^{-1}, \quad (4)$$

where ρ is the number density scaled in the stoichiometric unit $(^*N^*H_2CH_2COO^*H)_{0.05}(^*H_2O)_{0.95}$. The upper limit of the Fourier integral (Q_{max}) was set to 20.0 Å^{-1} in the present work. The distribution functions ($^DG_N(r)$ and $^{0H}G_N(r)$) given by the Fourier transforms of $^D\Delta_N(Q)$ and $^{0H}\Delta_N(Q)$ are shown in Figs. 3a and 4a, respectively. $G_N(r)$ for an aqueous glycine solution is mainly dominated by the $g_{NO}(r)$ and $g_{NH}(r)$ terms, because weighting factors A and B are much greater than C, D, and E. Moreover, $^{0H}G_N(r)$ in

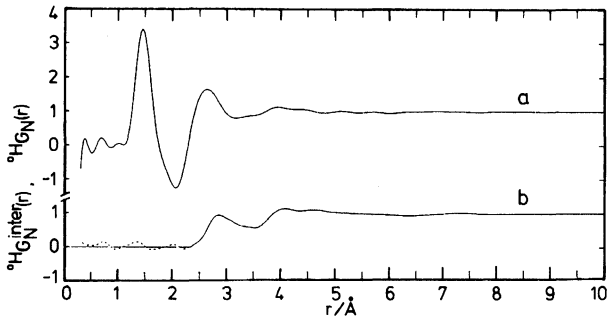

Fig. 4. Same notations as Fig. 3, except for the 5 mol% $N^0H_2CH_2COO^0H$ solution in ^0H_2O.

which the N–H pairs disappear, can be roughly regarded as being the $g_{NO}(r)$ term, itself, to a fairly good approximation. When a sufficiently resolved peak in $G_N(r)$ is assigned well to a particular N–α pair in the solution, the coordination number of the atom (α) around the nitrogen atom ($n_{N\alpha}$) can be obtained to a good approximation by the following integration over the range between r_1 and r_2:

$$n_{N\alpha} = 4\pi c_\alpha\rho\int_{r_1}^{r_2} r^2G_N(r)dr\cdot(A+B+C+D+E)/A_\alpha, \quad (5)$$

where A_α corresponds to the weighting factor for the N–α pair. The N–H partial structure factor ($a_{NH}(Q)$) and its Fourier transform ($g_{NH}(r)$) are derived by the second-order difference between two $\Delta_N(Q)$s, in which the isotopic composition of hydrogen atoms is changed, that is to say

Table 2. Values of the Coefficients of $a_{ij}(Q)$ in Eq. 1

Difference function	A/barns	B/barns	C/barns	D/barns	E/barns
${}^{D}\Delta_N(Q)$	0.0177	0.0392	0.0012	0.0019	−0.0011
${}^{0_H}\Delta_N(Q)$	0.0177	0	0.0012	0.0019	−0.0011

$$ {}^{D}\Delta_N(Q) - {}^{0_H}\Delta_N(Q) = 2c_N c_H(b_D - b_{0_H})(b_{14_N} - b_{15_N})[a_{NH}(Q) - 1] \quad (6) $$

and

$$ g_{NH}(r) = 1 + (2\pi^2\rho r)^{-1}\int_0^{Q_{max}} Q[a_{NH}(Q) - 1]\sin(Qr)dQ. \quad (7) $$

Results and Discussion

A dominant first peak located at $r\approx1$ Å in ${}^{D}G_N(r)$ (Fig. 3a) is assigned to an intramolecular N–D interaction within the amino group of the glycine molecule. By integrating from 0.5 to 1.2 Å in ${}^{D}G_N(r)$ the number of deuteron atoms united with the nitrogen atom was found to be close to three, suggesting that glycine molecules exist in the zwitterionic form in the solution. A higher-r side shoulder ($r\approx1.5$ Å) of the first peak and a negative peak at $r\approx2$ Å may possibly be ascribed to intramolecular N–C and N···H′ interactions (H′ : methylene hydrogen), respectively, on the basis of information concerning the molecular structure of glycine in the crystalline state.[9,10] The intramolecular N···H′ interaction appears as a negative peak in $G_N(r)$, due to the negative coherent scattering length of the methylene hydrogen. Since intra- and inter-molecular correlations at $r>2.5$ Å considerably overlap each other due to a larger glycine molecule, it is necessary to separate both contributions in the total $\Delta_N(Q)$. The intramolecular contribution from the N···α pair in Q-space ($I^{intra}(Q)$) is theoretically defined by

$$ I^{intra}(Q) = \sum 2c_N b_\alpha(b_{14_N} - b_{15_N}) \times\exp(-l_{N\alpha}{}^2Q^2/2)\sin(Qr_{N\alpha})/(Qr_{N\alpha}), \quad (8) $$

where, $l_{N\alpha}$ and $r_{N\alpha}$ denote the root mean-square amplitude and the internuclear distance for N···α pair, respectively. These structural parameters can, in principle, be determined through a least-squares fit of Eq. 8 to the observed $\Delta_N(Q)$ in the high-Q region.[24,25] However, it is practically unreasonable to determine these parameters in this way considering the limited statistical accuracy of the present $\Delta_N(Q)$ at $Q>10$ Å^{-1}. It is well known that the intramolecular vibrational frequencies of the glycine molecule in an aqueous solution[26] are nearly close to those in the crystalline state,[27] which implies that the intramolecular structure of glycine in the aqueous solution can be well approximated by that in the crystalline state. We thus attempted to evaluate $I^{intra}(Q)$ using literature values of $r_{N\alpha}$ and $l_{N\alpha}$ for crystalline glycine, given by neutron and X-ray diffraction measurements,[9,10] and by the calculation of Iijima et al,[3] respectively. The intramolecular contributions calculated by using the literature values for $r_{N\alpha}$ and $l_{N\alpha}$ are shown in Figs. 1b and 2b. The Fourier transform of ${}^{D}\Delta_N{}^{inter}(Q)$ (${}^{D}G_N{}^{inter}(r)$) is given in Fig. 3b. Here, the difference function in Q-space (${}^{D}\Delta_N{}^{inter}(Q)$) was obtained by subtracting the theoretical $I^{intra}(Q)$ from the observed ${}^{D}\Delta_N(Q)$ (Fig. 1c). In this calculating procedure, the overall normalization factor for the observed ${}^{D}\Delta_N(Q)$ was estimated to be 0.9±0.1 in the range of $4\leqq Q\leqq20$ Å^{-1} from a least-squares fit by the SALS program,[28] indicating that the present normalization process was reasonably carried out. The intermolecular distribution function (${}^{D}G_N{}^{inter}(r)$) reflects the distribution of water molecules around the nitrogen atom of the glycine molecule. An almost featureless functional form of ${}^{D}G_N{}^{inter}(r)$ in the $2.5\leqq r\leqq4$ Å range seems to imply that there is a considerable overlap between the intermolecular nearest-neighbor N···O and N···D contributions. It is therefore necessary to separate individually partial N–O and N–D distribution functions, in order to discuss more quantitatively the hydration structure of the glycine molecule in a solution.

The observed ${}^{0_H}\Delta_N(Q)$ and its Fourier transform (${}^{0_H}G_N(r)$) are now available for obtaining information concerning the intermolecular N–O correlation, since the contribution from the N–H pair in these functions completely disappears and, in addition, contributions from other than the N–O pair are much smaller due to their small weighting factors (Table 2). Therefore, the present ${}^{0_H}G_N(r)$ can directly supply information concerning the N–O correlation, particularly in the high-r region with $r>2.5$ Å. The first peak at $r\approx1.5$ Å in ${}^{0_H}G_N(r)$ (Fig. 4a) is attributed to the intramolecular N–C correlation within the glycine molecule. The negative peak at $r\approx2$ Å is due to the intramolecular N···H′ correlation. Intramolecular non-bonded N···C and N···O correlations may possibly be involved in the positive peak at $r\approx2.5$ Å. The intramolecular interference function ($I^{intra}(Q)$) can be calculated using Eq. 8 through the same procedure as described in the case of ${}^{D}\Delta_N(Q)$. The overall normalization factor for the observed ${}^{0_H}\Delta_N(Q)$ determined from a least-squares fit in the range of $4\leqq Q\leqq20$ Å^{-1} was computed to be 1.0±0.2, corresponding to an experimental uncertainty of ca. 20%, which is mainly due to the present counting statistics. The Fourier transform of the difference function (${}^{0_H}\Delta_N{}^{inter}(Q)$ (Fig. 2c)) obtained by subtracting the theoretical $I^{intra}(Q)$ from the observed ${}^{0_H}\Delta_N(Q)$ gives the intermolecular distribution function (${}^{0_H}G_N{}^{inter}(r)$), which is described in Fig. 4b. As mentioned above, the position and area of the first peak

in ${}^{0H}G_N^{inter}(r)$ can be regarded, to a good approximation, as being intermolecular distance, $r_{N\cdots O}$, and the coordination number, $n_{N\cdots O}$, between the nitrogen atom of the glycine molecule and the nearest-neighbor water molecules. The structural parameter, $r_{N\cdots O}=2.85\pm0.05$ Å, is determined from a Gaussian fit of the first peak of the $r\cdot {}^{0H}G_N^{inter}(r)$ curve. This value of $r_{N\cdots O}$ is in good agreement with the average hydrogen-bond distance, $r_{N-H\cdots O}=2.89$ Å, given in various organic crystals.[29] The integration of the first peak over the range of $2.3\leqq r\leqq3.6$ Å gives the coordination number, $n_{N\cdots O}=3.0\pm0.6$, in which the limit of the error depends mainly on the uncertainty in the overall normalization constant for the observed ${}^{0H}\Delta_N(Q)$. The present result of the intermolecular N–O correlation implies that three water molecules are hydrogen-bonded to the amino group of a glycine molecule. This is also consistent with the result of a recent Monte-Carlo (MC) simulation by Mezei et al, $n_{N\cdots OH_2}=3.2$.[15] On the other hand, the MC result for the nearest-neighbor distance, $r_{N\cdots OH_2}=2.6$ Å, seems to be too short when compared with the average value for the N–H···O hydrogen-bond distance (2.89 Å).[29]

Figure 5a represents the observed N–H partial structure factor in an aqueous glycine solution ($a_{NH}(Q)$) derived from the second-order difference between ${}^{D}\Delta_N(Q)$ and ${}^{0H}\Delta_N(Q)$. The Fourier transform of $a_{NH}(Q)$ yields the partial pair-distribution function ($g_{NH}(r)$ (Fig. 5b)) which reflects the distribution of hydrogen atoms belonging to water molecules surrounding the nitrogen atom of the amino group. The substantial fluctuation appearing in the less-pronounced form of $g_{NH}(r)$ may possibly be related to the coordination geometry between the amino group and the neighboring water molecules in the solution. If this is so, the nearest-neighbor N···H distance, $r_{N\cdots H}=3.25\pm0.05$ Å, can be deduced from a Gaussian fit of the $r\cdot g_{NH}(r)$ peak. This value also exhibits that the angle ϕ between the N···O axis and the molecular plane of a water molecule is $63\pm13°$, with the help of knowledge concerning the intramolecular structure of liquid D_2O.[30] Since ϕ can be expected to be 55° under the assumption of the linear direction of the hydrogen bond and the tetrahedral orientation of lone-pair electrons in the oxygen atom, the present value of ϕ in aqueous 5 mol% glycine solution may be considered to suggest the formation of a linear hydrogen bond between the amino group and the nearest-neighbor water molecules.

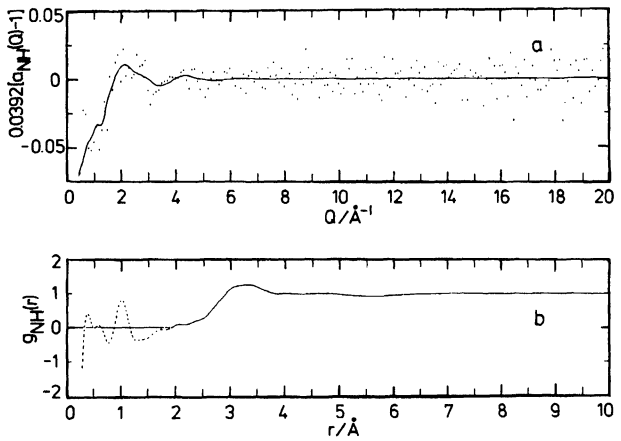

Fig. 5. a) The partial structure factor, $a_{NH}(Q)$, (dots) and b) the partial pair correlation function, $g_{NH}(r)$, for aqueous 5 mol% glycine solution. The solid line in (a) is given by the inverse Fourier transform of the solid line in (b).

It is of interest to compare the hydration structure around the amino group of the glycine molecule with that around the ammonium ion, NH_4^+, in an aqueous solution. According to a neutron-diffraction measurement the $^{14}N/^{15}N$ isotopic substitution previously reported, the distribution function for the nitrogen atom of ND_4^+ in liquid D_2O ($G_N(r)$) has poorly resolved intermolecular peaks located at $r=2.86$—3.0 Å and 3.3—3.4 Å, which correspond respectively to the nearest-neighbor N···O and N···D interactions.[31—33] These intermolecular distances agree well with the present result in an aqueous glycine solution. This suggests that the hydration structure of a zwitterionic glycine molecule and a NH_4^+ ion in the aqueous solution, is roughly similar to each other.

The authors would like to thank Drs. Toshiharu Fukunaga (Nagoya University) and Toshio Yamaguchi (Fukuoka University) for their help during the course of the neutron-diffraction measurement. All calculations were carried out with the ACOS S3600 computer at the Computing Center of Yamagata University.

References

1) H. S. Chan and K. A. Dill, *Phys. Today*, **46**, 24 (1993).
2) S. H. Laurie, "Comprehensive Coordination Chemistry," ed by G. Wilkinson, Pergamon Press, New York (1987), Vol. 2, p. 739.
3) K. Iijima, K. Tanaka, and S. Onuma, *J. Mol. Struct.*, **246**, 257 (1991).
4) R. D. Brown, P. D. Godfrey, J. W. V. Storey, and M-P. Bassez, *J. Chem. Soc., Chem. Commun.*, **1978**, 547.
5) R. D. Suenram and F. J. Lovas, *J. Am. Chem. Soc.*, **102**, 7180 (1980).
6) A. Imamura, H. Fujita, and C. Nagata, *Bull. Chem. Soc. Jpn.*, **42**, 3118 (1969).
7) A. G. Császár, *J. Am. Chem. Soc.*, **114**, 9568 (1992).
8) K. Zhang, D. M. Zimmerman, A. C-Phillips, and C. J. Cassady, *J. Am. Chem. Soc.*, **115**, 10812 (1993).
9) J. Almlöf, Å. Kvick, and J. O. Thomas, *J. Chem. Phys.*, **59**, 3901 (1973).
10) P-G. Jönsson and Å. Kvick, *Acta Crystallogr., Sect. B*, **B28**, 1827 (1972).
11) K. Ozutsumi and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **56**, 3635 (1983).
12) K. Ozutsumi, T. Yamaguchi, H. Ohtaki, K. Tohji, and Y. Udagawa, *Bull. Chem. Soc. Jpn.*, **58**, 2786 (1985).

13) K. Ozutsumi and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **57**, 2605 (1984).
14) K. Ozutsumi and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **58**, 1651 (1985).
15) M. Mezei, P. K. Mehrotra, and D. L. Beveridge, *J. Biomol. Struct. Dyn.*, **2**, 1 (1984).
16) T. Fukunaga, M. Misawa, I. Fujikawa, and S. Satoh, "KENS REPORT-IX," (1993), p. 16.
17) H. H. Paalman and C. J. Pings, *J. Appl. Phys.*, **33**, 2635 (1962).
18) I. A. Blech and B. L. Averbach, *Phys. Rev.*, **137**, A1113 (1965).
19) V. F. Sears, "Thermal-Neutron Scattering Length and Cross Sections for Condensed-Matter Research," Atomic Energy of Canada Ltd., AECL-8490 (1984).
20) J. R. Granada, V. H. Gillete, and R. E. Mayer, *Phys. Rev. A*, **36**, 5594 (1987).
21) A. K. Soper, G. W. Neilson, J. E. Enderby, and R. A. Howe, *J. Phys. C: Solid State Phys.*, **10**, 1793 (1977).
22) J. E. Enderby and G. W. Neilson, "WATER, A Comprehensive Treatise," ed by F. Franks, Plenum Press, New York (1979), Vol. 6, p. 1.
23) K. Ichikawa, Y. Kameda, T. Matsumoto, and M. Misawa, *J. Phys. C: Solid State Phys.*, **17**, L725 (1984).
24) Y. Kameda, H. Arakawa, K. Hangai, and O. Uemura, *Bull. Chem. Soc. Jpn.*, **65**, 2154 (1992).
25) Y. Kameda, H. Saitoh, and O. Uemura, *Bull. Chem. Soc. Jpn.*, **66**, 1919 (1993).
26) S. A. S. Ghazanfar, D. V. Myers, and J. T. Edsall, *J. Am. Chem. Soc.*, **86**, 3439 (1964).
27) I. Laulicht, S. Pinchas, D. Samuel, and I. Wasserman, *J. Phys. Chem.*, **70**, 2719 (1966).
28) T. Nakagawa and Y. Oyanagi, "Recent Developments in Statistical Inference and Data Analysis," ed by K. Matusita, North Holland (1980), p. 221.
29) L. N. Kuleshova and P. M. Zorkii, *Acta Crystallogr., Sect. B*, **B37**, 1363 (1981).
30) Y. Kameda and O. Uemura, *Bull. Chem. Soc. Jpn.*, **65**, 2021 (1992).
31) N. A. Hewish and G. W. Neilson, *Chem. Phys. Lett.*, **84**, 425 (1981).
32) P. A. M. Walker, D. G. Lawrence, G. W. Neilson, and J. Cooper, *J. Chem. Soc., Faraday Trans. 1*, **85**, 1365 (1989).
33) A. K. Adya and G. W. Neilson, *J. Chem. Soc., Faraday Trans.*, **87**, 279 (1991).