

Selected Paper

Local Structure around the Amino Group of Glycine Carbamate in Concentrated Aqueous Solutions

Yasuo Kameda,* Yuko Amo, and Takeshi Usuki

Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, 1-4-12 Kojirakawa-machi, Yamagata 990-8560

Received June 18, 2009; E-mail: kameda@sci.kj.yamagata-u.ac.jp

Neutron diffraction measurements were carried out on aqueous alkaline 2 mol % glycine heavy water solutions absorbing CO_2. $^{14}N/^{15}N$ isotopic substitution was applied to obtain information on the molecular structure of glycine carbamate formed in the solution and the hydration structure around the nitrogen atom of the carbamate molecule. The least-squares fitting analysis of the higher-Q region of the observed first-order difference function $\Delta'_N(Q)$ between ^{14}N- and ^{15}N-enriched sample solutions revealed that the intramolecular distances within the carbamate molecule, $r(N–C_C) = 1.58(1)$ Å and $r(C_C–O_C) = 1.25(1)$ Å, where C_C and O_C denote the carbamate carbon and oxygen atoms, respectively. It was shown that on the average 2.1(2) D_2O molecules were hydrogen-bonded to the amino-hydrogen atoms of the carbamate molecule with the intermolecular distances of $r(N\cdots O_W) = 2.86(3)$ Å and $r(N\cdots D_W) = 3.18(5)$ Å (O_W: water oxygen, D_W: water deuterium atoms), respectively.

In recent years, there has been a growing interest in concentrated aqueous solutions involving amine compounds to capture CO_2 gas emitted from thermal power plants.[1] The captured CO_2 forms a chemical bond with the amino nitrogen atom to build up the carbamate molecule and captured CO_2 can readily be recovered by heating the solution. In order to understand the molecular mechanism of chemical reaction which occurs in the amine–H_2O–CO_2 system, structural investigation by ab initio,[2–6] NMR,[7–9] and vibrational spectroscopic[3] methods have been carried out. Concentrated aqueous MEA (monoethanolamine, $NH_2CH_2CH_2OH$) solution is typically applied as a CO_2-absorbing medium, however the relatively large amount of thermal energy required for recovering gaseous CO_2 from the solution has long been a problem. In order to reduce the CO_2 recovering energy, the reaction mechanism of CO_2 with secondary amines such as DEA (diethanolamine, $NH(CH_2CH_2OH)_2$) and with other amine compounds has been extensively investigated.[2,4–9] The chemical reaction to form the amine carbamate molecule has also been a matter of discussion. Ab initio calculations by da Silva and Svendsen have shown that the total energy of the CO_2–MEA system as a function of the C(CO_2)–N(MEA) bond length strongly depends on the solvation environment of the MEA molecule,[4] which indicates that detailed information concerning the hydration structure of both amine and amine carbamate molecules is essential.

Amino acids are known to act like amine compounds under basic conditions to form carbamate molecules. The reaction mechanism of the amino acids with CO_2 has fundamental importance in biological systems such as the neurotoxicity of carbamates[10,11] and carbonate transportation.[12] However, direct experimental information concerning the intramolecular structure as well as the hydration structure of amine carbamates in aqueous solution has not yet been reported. Neutron diffraction with $^{14}N/^{15}N$ isotopic substitution is considered to be one of the most suitable experimental techniques to obtain direct information on both the intramolecular and intermolecular structure around the amino nitrogen atom within the carbamate molecule in the aqueous solution.

In the present paper, we describe the results of time-of-flight (TOF) neutron diffraction measurements on aqueous alkaline 2 mol % glycine heavy water solutions absorbing CO_2, $(^*ND_2CH_2COOD)_{0.02}(KOD)_{0.02}(D_2O)_{0.96}(CO_2)_{0.012}$, in which $^{14}N/^{15}N$ isotopic composition has been changed. The observed first-order difference function, $\Delta_N(Q)$, between sample solutions with different $^{14}N/^{15}N$ ratio, was analyzed in terms of the intra- and intermolecular structure around the amino nitrogen atom of the glycine carbamate molecule.

Experimental

Materials. Isotopically enriched $^{15}NH_2CH_2COOH$ (98.0% ^{15}N) and natural $^{14}NH_2CH_2COOH$ (99.6% ^{14}N) were deuterated by dissolving them in D_2O (99.9% D), followed by the drying under vacuum. The required amounts of enriched glycine and KOD were dissolved into D_2O to prepare aqueous alkaline 2 mol % glycine heavy water solutions with different $^{14}N/^{15}N$ isotopic compositions. Gaseous CO_2 was absorbed into the glycine solution by bubbling the CO_2 in the solution. The molar quantity of the absorbed CO_2 was determined by using a total carbon analyzer (TOC-Vc, SHIMADZU Co.) and revealed to be 60% of the molar quantity of glycine, $(^*ND_2CH_2COOD)_{0.02}(KOD)_{0.02}(D_2O)_{0.96}(CO_2)_{0.012}$. The D content of the sample solutions was determined to be 99.8% D from the integrated absorption intensity of the O–H stretching vibrational band observed with a JASCO FT/IR-410 spectrometer with the ATR-500M attachment. The mole fraction of the glycine carbamate was determined to be 0.46 from the ratio of the integrated intensity of the ^1H NMR absorption peaks for the methylene protons of the glycine and glycine carbamate molecules observed at the resonance frequency of

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Table 1. Isotopic Composition and Average Scattering Length, b_N, Total Cross Section, σ_t, and Number Density of the Stoichiometric Unit, $(^*ND_2CH_2COOD)_x(KOD)_x(D_2O)_{1-2x}(CO_2)_y$

Sample	^{14}N/%	^{15}N/%	$b_N/10^{-12}$ cm	σ_t/barns[a)]	ρ/Å^{-3}
$(^{14}ND_2CH_2COOD)_{0.02}(KOD)_{0.02}(D_2O)_{0.96}(CO_2)_{0.012}$	99.6	0.4	0.936	14.652	0.03539
$(^{15}ND_2CH_2COOD)_{0.02}(KOD)_{0.02}(D_2O)_{0.96}(CO_2)_{0.012}$	2.0	98.0	0.650	14.508	

a) For incident neutron wavelength of 1 Å.

400 MHz. From these results, the composition of the sample solution is estimated to be, glycine carbamate:glycine:HCO_3^- = 0.0092:0.0108:0.0028, in which the CO_2 molecules not bound to the glycine molecules are assumed to form bicarbonate ion.[7] Each sample solution was sealed in a cylindrical Ti–Zr null alloy cell (8.0 mm in inner diameter and 0.3 mm in thickness) and used for the neutron diffraction measurements. Sample parameters are listed in Table 1.

Neutron Diffraction Measurements. TOF neutron diffraction measurements were carried out at 25 °C using the HIT-II spectrometer[13] installed at the spallation neutron source (KENS) in the High Energy Accelerator Organization (KEK), Tsukuba, Japan. Scattered neutrons were detected by 104 ^{3}He counters covering the scattering angles of $10 \leq 2\theta \leq 157°$. The data acquisition time was 12 h for each sample. Measurements of an empty cell, background, and vanadium rod of 8 mmϕ, were made in advance.

Data Reduction. Observed scattering intensities for the sample were corrected for instrumental background, absorption of sample and cell,[14] and multiple[15] and incoherent scatterings. The coherent scattering lengths as well as the scattering and absorption cross sections for the constituent nuclei were referred to those tabulated by Sears.[16] 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.[17] The corrected intensities were converted to the absolute scale using the corrected scattering intensities from the vanadium rod.

The first-order difference function, $\Delta_N(Q)$,[18,19] was derived from the numerical difference between scattering cross sections observed for sample solutions. $\Delta_N(Q)$ scaled at the stoichiometric unit, $(^*ND_2CH_2COOD)_x(KOD)_x(D_2O)_{1-2x}(CO_2)_y$, is written as a linear combination of partial structure factors involving contribution from the N···α pair:

$$\begin{aligned}\Delta_N(Q) = {} & A[a_{NO}(Q) - 1] + B[a_{ND}(Q) - 1] \\ & + C[a_{NC}(Q) - 1] + D[a_{NH}(Q) - 1] \\ & + E[a_{NK}(Q) - 1] + F[a_{NN}(Q) - 1] \end{aligned} \quad (1)$$

where, $A = 2x(1 + x + 2y)\Delta b_N b_O$, $B = 4x\Delta b_N b_D$, $C = 2x(2x + y)\Delta b_N b_C$, $D = 4x^2\Delta b_N b_H$, $E = 2x^2\Delta b_N b_K$, and $x^2(b_{14N}^2 - b_{15N}^2)$, and $\Delta b_N = b_{14N} - b_{15N}$. The weighting factors $A - F$ are listed in Table 2. The contribution from the N–O and N–D pairs occupies 98% of the observed $\Delta_N(Q)$ under the present experimental conditions, $\Delta_N(Q)$ can be regarded as involving information on the hydration structure around the nitrogen atom of the amino group. Since the difference functions from 64 sets of forward angle detectors located at $10 \leq 2\theta \leq 51°$ agree well within the statistical uncertainties, they were combined at the Q-interval of 0.1 Å^{-1}, and used for the subsequent analysis.

The present difference function involves contributions from $\Delta_N(Q)$ for the glycine molecule in alkaline aqueous solution and that for the glycine carbamate molecules. The $\Delta''_N(Q)$ for the glycine molecule was approximated by the $\Delta_N(Q)$ reported for the aqueous alkaline 2 mol % glycine solution.[20] The difference function for the glycine carbamate molecules, $\Delta'_N(Q)$, was deduced by,

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

A/mbarn	B/mbarn	C/mbarn	D/mbarn	E/mbarn	F/mbarn
6.93	15.25	0.39	−0.25	0.08	0.18

$$\Delta'_N(Q) = \Delta_N(Q) - (1 - f)\Delta''_N(Q) \quad (2)$$

where f denotes the mole fraction of the glycine carbamate molecule. $\Delta'_N(Q)$ and $\Delta''_N(Q)$ represent the difference functions for the glycine carbamate and glycine molecules, respectively. In the present analysis, $f = 0.46$ was employed, which had been determined from the ^{1}H NMR data as mentioned above. The distribution function, $G'_N(r)$, around the amino nitrogen atom within the glycine carbamate molecule was obtained by the Fourier transform of the observed $\Delta'_N(Q)$.

$$\begin{aligned} G'_N(r) &= 1 + (A + B + C + D + E + F)^{-1} f^{-1} (2\pi^2\rho r)^{-1} \\ &\quad \times \int_0^{Q_{max}} Q\Delta'_N(Q)\sin(Qr)\mathrm{d}Q \\ &= [Ag_{NO}(r) + Bg_{ND}(r) + Cg_{NC}(r) \\ &\quad + Dg_{NH}(r) + Eg_{NK}(r) + Fg_{NN}(r)] \\ &\quad \times (A + B + C + D + E + F)^{-1} f^{-1} \end{aligned} \quad (3)$$

The upper limit of the integral, Q_{max}, was set to be 20 Å^{-1} in the present study. The intramolecular contribution involved in the $\Delta'_N(Q)$ can be evaluated by

$$I_N^{intra}(Q) = \Sigma 2fx\Delta b_N b_\alpha \exp(-l_{N\alpha}{}^2 Q^2/2)\sin(Qr_{N\alpha})/(Qr_{N\alpha}) \quad (4)$$

where, $l_{N\alpha}$ and $r_{N\alpha}$ denote the root-mean-square (rms) displacement and internuclear distance for the N···α pair, respectively. The observed $\Delta'_N(Q)$ consists of the intra- and intermolecular interference contributions. The preliminary results of the present difference function have been presented in the experimental report of the KENS facility[21] in which the employed intramolecular interference term was evaluated from the molecular orbital calculation. In the present analysis, the intramolecular structural parameters for the glycine carbamate molecule was directly determined from the least-squares fit of the observed difference function. Since the oscillational amplitude for the intermolecular interference term decreases much faster than that for the intramolecular interference term with increasing Q value, oscillational appearing in the high-Q region of the $\Delta'_N(Q)$ is dominated by the intramolecular interference term. In order to obtain information on the intramolecular structure of the glycine carbamate in the aqueous solution, the least-squares fitting procedure was adopted for the observed $\Delta'_N(Q)$ in the range of $5 \leq Q \leq 20$ Å^{-1}. In the fitting procedure, four intramolecular bond lengths, r(N–C$_\alpha$), r(N–C$_C$), r(N–D), and r(C$_C$–O$_C$) (C$_\alpha$: α-carbon atom), and one bond angle $\angle$N–C$_C$–O$_C$, were treated as independent parameters. The normalization factor, γ, defined by $\Delta'_N(Q) = \gamma \times I_N^{intra}(Q)$, was also allowed to vary independently. The other intramolecular N···α distances within the carbamate were calculated by using the

value of the independent parameter, r(N–C$_\alpha$), and known molecular geometry of the glycine molecule.[22,23] Values of the rms amplitude were fixed to those reported for the gaseous glycine molecule.[23] The fitting procedure was performed using the SALS program.[24]

The intermolecular difference function, $\Delta'_N{}^{inter}(Q)$, was obtained by subtracting $I_N{}^{intra}(Q)$ calculated for the carbamate molecule from the observed $\Delta'_N(Q)$, which contains information concerning the hydration structure of the amino group of the carbamate molecule.

$$\Delta'_N{}^{inter}(Q) = \Delta'_N(Q) - I_N{}^{intra}(Q) \quad (5)$$

The intermolecular distribution function, $G'_N{}^{inter}(r)$, was evaluated by the Fourier transform of $\Delta'_N{}^{inter}(Q)$. Structural parameters concerning the hydration shell of the amino group of the carbamate molecule were obtained through the least-squares fitting procedure applying the following model function, involving short- and long-range interactions.[25–27]

$$\begin{aligned}\Delta'_N{}^{model}(Q) &= \Sigma 2fxn_{N\alpha}\Delta b_N b_\alpha \exp(-l_{N\alpha}{}^2Q^2/2)\sin(Qr_{N\alpha})/(Qr_{N\alpha}) \\ &\quad + 4\pi\rho f(A+B+C+D+E+F) \\ &\quad \times \exp(-l_0{}^2Q^2/2)[Qr_0\cos(Qr_0) - \sin(Qr_0)]Q^{-3} \end{aligned} \quad (6)$$

where, $n_{N\alpha}$ is the coordination number of α atom around the N atom. The long-range parameter, r_0, denotes the distance beyond which the continuous distribution of atoms around the N atom can be assumed. The parameter, l_0, describes the sharpness of the boundary at r_0. Structural parameters, $n_{N\alpha}$, $l_{N\alpha}$, $r_{N\alpha}$, l_0, and r_0, were determined from the least-squares fit to the observed $\Delta'_N{}^{inter}(Q)$. The fitting procedure was performed in the range of $0.3 \le Q \le 12.0$ Å^{-1} with the SALS program[24] assuming that the statistical uncertainties distribute uniformly. Prior to the fitting analysis, correction for the low-frequency systematic error involved in the observed $\Delta'_N{}^{inter}(Q)$ was adopted.[28]

Results and Discussion

Intramolecular Structure of Glycine Carbamate Molecule. The first-order difference function, $\Delta_N(Q)$, obtained from the difference in the scattering cross sections between the sample solutions containing ^{14}N and ^{15}N, is shown in Figure 1a. The present $\Delta_N(Q)$ involves both interference contributions from 46% glycine carbamate and 54% glycine as determined from NMR data. The difference function $\Delta'_N(Q)$ for the glycine carbamate molecule was obtained by subtracting contribution from the aqueous alkaline glycine solution, $\Delta''_N(Q)$, from the observed $\Delta_N(Q)$ (eq 2). The contribution from the glycine molecule involved in the present $\Delta_N(Q)$ was approximated as the $\Delta''_N(Q)$ observed for aqueous alkaline 2 mol % glycine heavy water solution[20] (Figure 1a). The data points of $\Delta'_N(Q)$ for the glycine carbamate seems somewhat scattered due to statistical uncertainties, the first diffraction peak at $Q \approx 2$ Å^{-1} and oscillatory features extending to the higher-Q region are conspicuously observed (Figure 1b). The Fourier transform of the observed $\Delta'_N(Q)$ gives the distribution function, $G'_N(r)$, around the N atom within the glycine carbamate molecule, which is represented in Figure 2. The dominant first peak at $r \approx 1$ Å in the $G'_N(r)$ is assigned to the intramolecular N–D interaction. The coordination number n_{ND} has been estimated to be ca. 2 from the integration value of the first peak, which implies that two D atoms are bonded to the amino nitrogen atom. The second peak at $r \approx 1.5$ Å should involve the N–C$_\alpha$ and N–C$_C$ interactions within the carbamate molecule. The intramolecular interaction between the N and hydrogen atoms bonded to the α-carbon atom can appear as a negative peak at $r \approx 2$ Å, reflecting negative neutron scattering length of methylene hydrogen atoms. A positive peak at $r \approx 2.3$ Å is attributable to the sum of N···C$_a$ (C$_a$: carboxyl carbon atom) and N···O$_C$ interactions within the carbamate molecule.

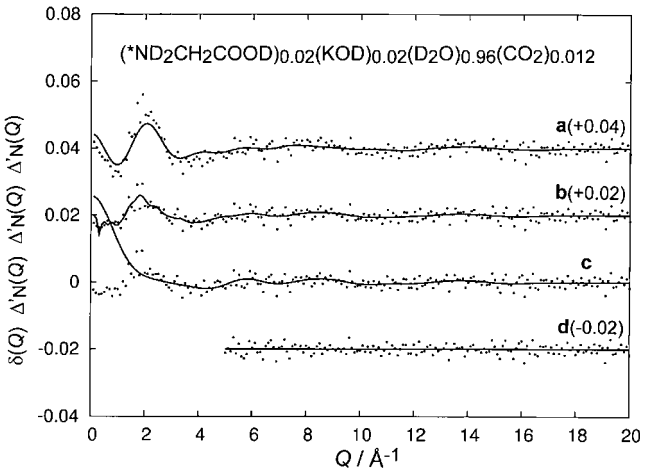

Figure 1. a) Observed difference function, $\Delta_N(Q)$, for aqueous alkaline 2 mol % glycine heavy water solutions absorbing CO_2 (dots). The $\Delta_N(Q)$ reported for aqueous alkaline 2 mol % glycine heavy water solutions[17] multiplied by 0.54 (solid line). b) Difference function $\Delta'_N(Q)$, observed for glycine carbamate heavy water solutions (dots). Back Fourier transform of $G'_N(r)$ denoted by the solid line in Figure 2a (solid line). c) Observed $\Delta'_N(Q)$ (dots), and the best-fit of the calculated intramolecular interference term for glycine carbamate (solid line). d) The residual function, $\delta(Q)$ (dots).

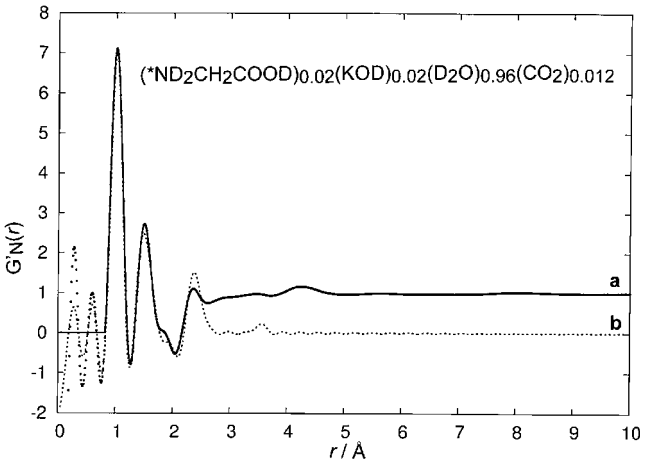

Figure 2. a) Total distribution function around the amino nitrogen atom of glycine carbamate, $G'_N(r)$, observed for aqueous alkaline 2 mol % glycine heavy water solutions absorbing CO_2 (solid line). b) Fourier transform of calculated intramolecular interference term, $I_N{}^{intra}(Q)$ (dotted line).

Table 3. Results of the Least-Squares Refinement of the Intramolecular Structural Parameters of Glycine Carbamate Obtained from the Difference Function, $\Delta'_N(Q)$, for the Aqueous Alkaline 2 mol % Glycine Heavy Water Solutions Absorbing CO_2[a)]

Parameters	Refined value
r(N–C_α)/Å	1.47(1)
r(N–C_C)/Å	1.58(1)
r(N–D)/Å	1.02(1)
r(C_C–O_C)/Å	1.25(2)
∠N–C_C–O_C/°	105(2)
γ[b)]	0.93(3)

a) Estimated errors are given in parentheses. b) Normalization factor defined by $\Delta'_N(Q) = \gamma \times I_N^{intra}(Q)$.

In order to determine the intramolecular structure of the carbamate molecule in the aqueous solution, the least-squares fitting analysis was carried out for the observed $\Delta'_N(Q)$ in the range of $5 \leq Q \leq 20$ Å^{-1}, where the intramolecular interference contribution is dominant. Although the S/N of the observed data does not seem sufficiently good, all independent structural parameters have been successfully determined through the least-squares fitting procedure. The final results of the independent parameters are listed in Table 3. The present N–C_α distance (1.47(1) Å) is in good agreement with that in the glycine molecule obtained from the single crystalline neutron diffraction study (1.476 Å)[22] in which the glycine molecule exists as the zwitterionic form. The value of the present r(N–C_α) also agrees well with that reported for isolated neutral glycine molecule in the gaseous state (1.469(1) Å)[23] determined by electron diffraction method, indicating that the N–C_α bond length remains almost unchanged despite the ionization state of the amino group of the glycine molecule, and formation of the carbamate in the aqueous solution. The present N–D distance (1.02(1) Å) is in good agreement with that determined for the zwitterionic glycine in the crystalline state (1.04 Å)[22] and that observed from the gas-phase electron diffraction study (1.014 Å).[23] The N–C_C distance (1.58(2) Å) determined in the present study is significantly longer than the value 1.376(4) Å found in diaqua-bis(ethylenediamine)copper(II) salts of carbamic acid anion[29] in which the nitrogen atom of the carbamate anion is bound to one hydrogen atom, which may reflect the difference in the hybridization state of the nitrogen atom between in the crystalline state and in the aqueous solution. The present value of the C_C–O_C bond length within the carbamate group (1.25(2) Å) agrees well with that observed for the formate ion (1.272(7) Å)[30] and for the acetate ion (1.24(1))[31] in the aqueous solution, which indicates the carbamate group of the glycine carbamate molecule is ionized.

Hydration Structure around Amino Nitrogen Atom of Glycine Carbamate Molecule. The calculated $I_N^{intra}(Q)$ involving contributions from all possible N···α pairs within the carbamate molecule, was subtracted from the observed $\Delta'_N(Q)$ to deduce the intermolecular difference function, $\Delta'_N{}^{inter}(Q)$, which is shown in Figure 3a. The Fourier transform of the $\Delta'_N{}^{inter}(Q)$, $G'_N{}^{inter}(r)$, is represented in Figure 4. Although the present $G'_N{}^{inter}(r)$ seems rather featureless, a broadened first intermolecular peak at $r \approx 3$ Å can be identified. This structural

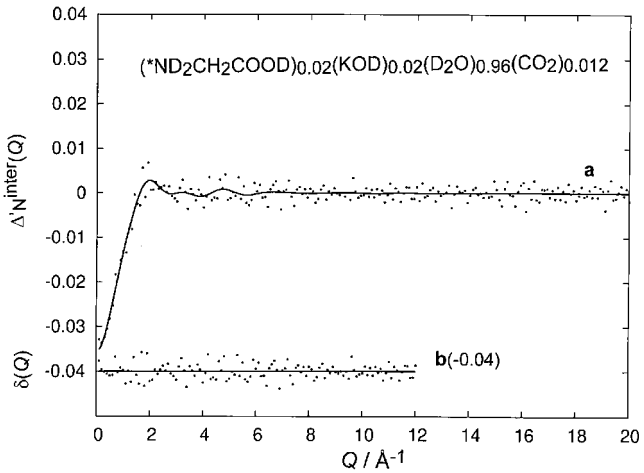

Figure 3. a) Intermolecular difference function, $\Delta'_N{}^{inter}(Q)$ (dots). The best-fit of the calculated intermolecular interference term, $\Delta'_N{}^{model}(Q)$, is shown by the solid line. b) The residual function, $\delta(Q)$ (dots).

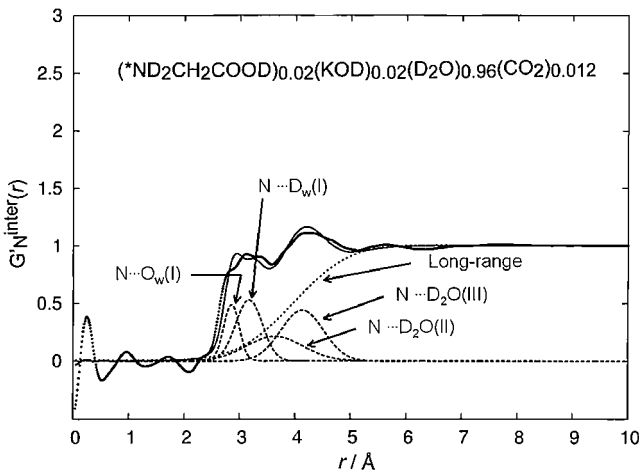

Figure 4. Observed intermolecular distribution function, $G'_N{}^{inter}(r)$, around the amino nitrogen of glycine carbamate (thick solid line). Fourier transform of the calculated $\Delta'_N{}^{model}(Q)$ is shown by the thin solid line. The contributions from the short- and long-range interactions are denoted by the broken- and dotted lines, respectively.

feature is very similar to that observed for aqueous glycine solutions in neutral[32] and acidic[33] conditions, in which the nearest neighbor water molecules around the amino group form N(–D)···OD_2 hydrogen bonds. Therefore, the first peak of the present $G'_N{}^{inter}(r)$ should involve contributions from the nearest neighbor N···O_W and N···D_W interactions. An indication of further structural feature can be recognized as a much broadened second peak at $r \approx 4.2$ Å. This may indicate the existence of the second hydration shell of the amino group, which has not been observed for the aqueous glycine solutions.[32,33]

In order to obtain structural parameters concerning the hydration around the amino group of the glycine carbamate molecule, the least-squares fitting analysis was applied to the observed $\Delta'_N{}^{inter}(Q)$. The following assumptions were adopted in evaluating the theoretical interference term. a) Structural

Table 4. Results of the Least-Squares Fitting Refinement of the Intermolecular Difference Function, $\Delta'_N{}^{inter}(Q)$, Observed for an Aqueous Alkaline 2 mol % Glycine Solution Absorbing CO_2, $(^*ND_2CH_2COOD)_{0.02}(KOD)_{0.02}(D_2O)_{0.96}(CO_2)_{0.012}$[a]

Interaction		i···j	r_{ij}/Å	l_{ij}/Å	n_{ij}
Short-range	N···D_2O(I)[b]	N···O	2.86(3)	0.14(4)	2.1(2)
		N···D	3.18(5)	0.24(3)	(4.2)[c]
	N···D_2O(II)[d]	N···D_2O	3.70(5)	0.51(2)	1.7(1)
	N···D_2O(III)[e]	N···D_2O	4.16(1)	0.38(4)	3.4(8)
			r_0/Å	l_0/Å	
Long-range	N···X[f]		4.12(1)	0.77(7)	

a) Estimated errors are given in parentheses. b) The first nearest neighbor N(–D)···D_2O interaction. c) Fixed to the value $2n_{NO}$. d) The second nearest neighbor N(–D)···D_2O interaction. e) The third nearest neighbor N(–D)···D_2O interaction. f) X: O, D, H, C, N, and K.

parameters for the first nearest neighbor N···D_2O interaction, r_{NO}, r_{ND}, l_{NO}, l_{ND}, and n_{NO}, were independently refined. In the fitting procedure, n_{ND} was fixed to the value, $2 \times n_{NO}$. b) In the preliminary analysis, it was found that at least two more intermolecular N···D_2O interactions at around $r \approx 3.7$ and 4.2 Å are necessary to reproduce the observed $\Delta'_N{}^{inter}(Q)$.[21] Then, intermolecular contributions from the second and third nearest neighbor N···D_2O interactions were taken into account in the present model function, in which each contribution was treated as a single interaction with the coherent scattering length in eq 6, b_α, being $2b_D + b_O$. c) Structural parameters for the long-range random distribution of atoms, l_0 and r_0, were treated as independent parameters.

The best-fit result is compared with the observed $\Delta'_N{}^{inter}(Q)$ in Figure 3a. A satisfactory agreement is obtained in the range of $0.3 \leq Q \leq 12.0$ Å^{-1}. The observed and calculated $G'_N{}^{inter}(r)$ functions (Figure 4) also agree well with each other. A small difference appears in the intensity between the observed and calculated $G'_N{}^{inter}(r)$ functions. However, it should be noted that uncertainties mainly arising from the statistical fluctuations in the observed $\Delta'_N{}^{inter}(Q)$ as well as the truncation errors associated with the Fourier transform are involved in the observed $G'_N{}^{inter}(r)$. Therefore, reliable structural parameters can be determined through the least-squares fitting analysis of the observed $\Delta'_N{}^{inter}(Q)$. The final results of the least-squares refinement are summarized in Table 4. The present value of the N(–D)···O_W distance, $r_{NO} = 2.86(3)$ Å, is in good agreement with those reported for aqueous glycine solutions in neutral ($r_{NO} = 2.85(5)$ Å)[32] and acidic ($r_{NO} = 2.90(2)$ Å)[33] conditions. The present r_{NO} also agrees well with the average value of the N(–H)···O hydrogen bond length found in various organic crystals ($r_{NO} = 2.89$ Å).[34] The present coordination number, $n_{NO} = 2.1(2)$, is consistent with the molecular structure of the glycine carbamate already determined from the analysis of the intramolecular interference term as described in the previous section. The present nearest neighbor N–O coordination number is also consistent with the hydrogen-bonded structure between the amino hydrogen atoms and the nearest neighbor D_2O molecule. The intermolecular distance for the second nearest neighbor N···D_2O interaction was obtained as 3.70(5) Å. The assignment of this interaction is rather unclear at present however it is supposed that oxygen atoms of the carbamate group should form hydrogen bonds with the neighboring D_2O molecules. This second nearest neighbor N···D_2O contribution may be attributable to the interaction between the amino nitrogen atom and water molecules hydrogen-bonded to the carbamate oxygen atoms. The third N···D_2O interaction located at $r_{N\cdots D2O} = 4.16(1)$ Å is attributable to the water molecules in the second hydration shell of the amino group, that are hydrogen bonded to the water molecules in the first hydration shell. This N···D_2O interaction for the second hydration shell of the amino group was not observed in the intermolecular $G_N{}^{inter}(r)$ functions for the glycine molecule in the aqueous solutions with neutral,[32] acidic,[33] and alkaline[20] conditions. The second hydration shell of the amino nitrogen atom within the glycine carbamate molecule is considered to be more stable compared with that of the glycine molecule. It is supposed that the hydrogen-bonded network between water molecules in the first and second hydration shells of the amino group of the glycine carbamate molecule could be more stabilized by the presence of neighboring carbamate group which forms strong hydrogen bonds with water molecules in its first hydration shell.

In conclusion, direct information concerning the intramolecular structure and the hydration structure around the amino group of glycine carbamate in aqueous solution was successfully determined from first-order difference functions obtained from the difference in observed scattering cross sections between $^{14}N/^{15}N$ isotopically substituted samples. It is of interest to investigate the hydration structure of different carbamates prepared from other amino acids or amine compounds. This could be the subject of future research.

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