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The Structure around the Nitrite Ion in Concentrated Aqueous Solutions

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The hydration structure and intra-ionic geometry of NO_2^- in a 10 mol% $NaNO_2$ solution in D_2O have been determined by the time-of-flight neutron diffraction. Measurements were made with two solutions which are identical in all respects except for the isotopic substitution of nitrogen atom. It appears that there exist 3.7±0.5 water molecules coordinated to NO_2^- with the intermolecular distance $r(N\cdots D)=2.71\pm0.02$ Å. The intramolecular bond distance r_{NO} and the root mean square amplitude l_{NO} in NO_2^- have precisely been determined.

In recent years, detailed information on the microscopic structure concerning polyatomic ions in aqueous solutions have been obtained through various diffraction experiments. For example, the structure of hexaaquo complexes containing the divalent transition metal in strong electrolyte solutions, such as $Ni(H_2O)_6^{2+}$, $Co(H_2O)_6^{2+}$, $Mn(H_2O)_6^{2+}$, etc., seems to be well established by X-ray and neutron diffraction studies.[1–7] However, information on the hydration structure of polyatomic anion available from a single diffraction measurement is limited according to the following reasons: i) The contribution by ion–water correlation in the total interference function is generally small. ii) Since the scattering power of atoms in anion (typically, O, N, or Cl) is roughly comparable to that in water molecule, it is difficult to specify the anion–water interaction by a single diffraction experiment. iii) The distribution of water molecules around a given polyatomic anion tends to be much broadened in comparison with the case of cation–water correlation because of the larger ionic size and relatively smaller negative charge of the anion. The neutron diffraction method employing the isotopic substitution is expected to overcome these difficulties.

In this paper we report the result of time-of-flight (TOF) neutron diffraction measurements on D_2O solutions of 10 mol% $NaNO_2$ including two kinds of nitrogen isotopes. We can obtain direct experimental information on both the hydration structure around NO_2^- and the intramolecular structure of this anion in the solution.

Experimental

Isotopically enriched sample $Na^{15}NO_2$ (99.0% ^{15}N) obtained from CIL Inc. and natural $NaNO_2$ (99.6% ^{14}N) of reagent grade, which were both dried in vacuo, were dissolved into D_2O (99.8% D, Merck Inc.) to prepare two 10 mol% $NaNO_2$ aqueous solutions with different isotopic compositions of nitrogen atom. The sample parameters are listed in Table 1. Respective solutions were sealed in vacuo into a cylindrical quartz cell (8 mm in inner diameter and 0.4 mm in thickness). TOF neutron diffraction measurement was carried out at 25 °C using HIT spectrometer[8] installed at a pulsed spallation neutron source (KENS) in National Laboratry for High Energy Physics, Tsukuba, Japan. Scattered neutrons were observed using detectors located at the scattering angles of 150, 91, 44, 32, 25, 14, and 8°, respectively. The data accumulation time was ca. 8 h for both samples. The measurement of scattering intensities was also made for a vanadium rod (8 mm in diameter), an empty quartz cell and a background at the same temperature.

Measured scattering data were corrected for the background intensity, the absorption of the sample and cell,[9] multiple,[10] and incoherent scatterings. The obtained count rate for the sample was converted to the absolute scale by the use of intensity data from the vanadium rod. The first-order difference functions[11] $\Delta_N(Q)$ was determined from the numerical difference in the normalized scattering cross section between two 10 mol% solutions of $Na^{14}NO_2$ and $Na^{15}NO_2$. It has frequently be pointed out for the data analysis of heavy water solutions that there is a troublesome problem for the inelasticity effect derived from the self term of deuterium atoms, which is roughly proportional to $\sin^2\theta$ (θ: the scattering angle). However, in the term of $\Delta_N(Q)$ this effect seems to be cancelled out by the subtraction of the two data sets which contain the

Table 1. The isotopic Compositions and Mean Scattering Lengths b_N of Nitrogen Atoms, Mean Scattering and Absorption Cross Sections and the Number Densities Scaled in the Stoichiometric Unit $(NaNO_2)_{0.1}(D_2O)_{0.9}$, σ_s, σ_a, and ρ_0, Respectively, for Samples Used in This Study

Samples	^{14}N/%	^{15}N/%	$b_N/10^{-12}$ cm	σ_s/barns	σ_a/barns[a)]	ρ_0/Å^{-3}
$Na^{14}NO_2$	99.6	0.4	0.936	19.862	0.243	0.0308
$Na^{15}NO_2$	1.0	99.0	0.649	19.242	0.056	

a) For the incident neutron wavelength of 1.8 Å.

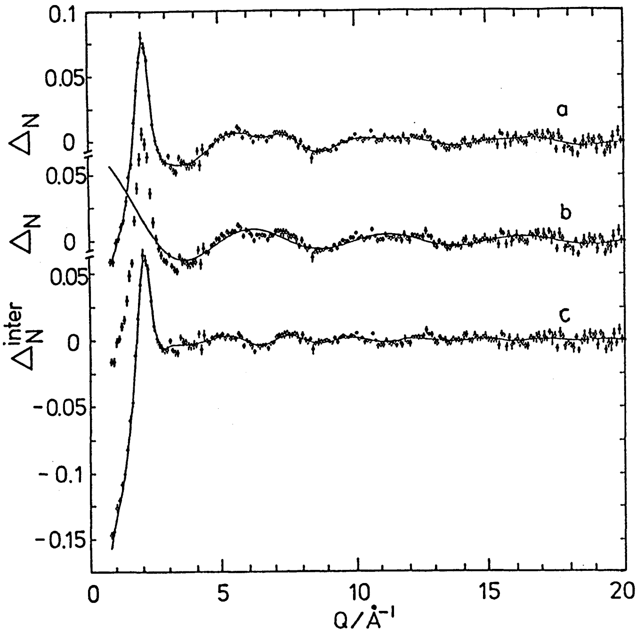

Fig. 1. a) Circles: The observed difference function, $\Delta_N(Q)$, for 10 mol% $NaNO_2$ solution in D_2O. The solid line: Smoothed $\Delta_N(Q)$ used for Fourier transform (Fig. 2a). b) Circles: The observed $\Delta_N(Q)$. The solid line: The intramolecular N–O contribution, $I^{intra}(Q)$. c) Circles: The intermolecular contribution, $\Delta_N^{inter}(Q)$. The solid line: The back Fourier transform of $\overline{G}_N^{inter}(r)$ shown in Fig. 2b.

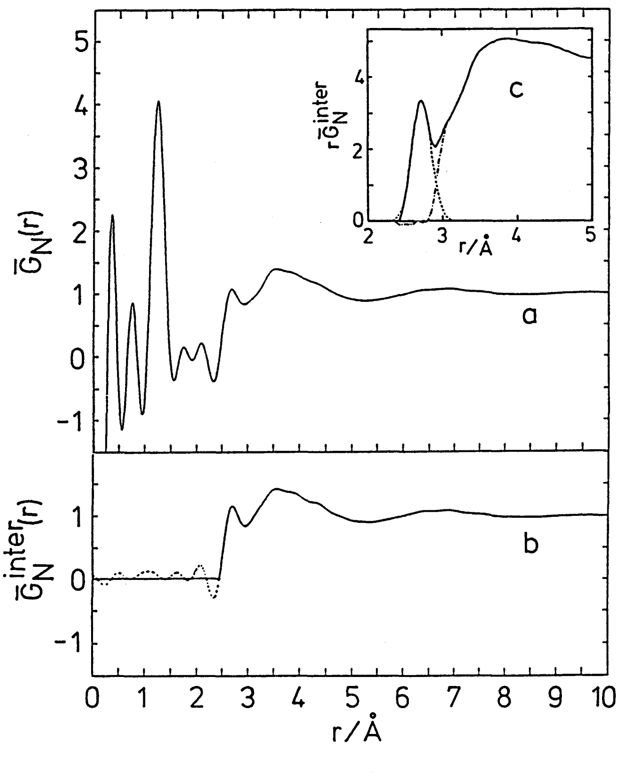

Fig. 2. a) The total and b)intermolecular distribution function around the nitrogen atom, $\overline{G}_N(r)$ and $\overline{G}_N^{inter}(r)$, truncated at Q_{max}=15.4 Å^{-1}, for 10 mol% $NaNO_2$ solution in D_2O. c) Gaussian fitting for the determination of n(N···D).

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

A/barns	B/barns	C/barns	D/barns
0.0366	0.0689	0.0021	0.0045

identical inelastic distortion. After all, the inelasticity effect is negligibly small in $\Delta_N(Q)$ even at the larger scattering angle such as 2θ=91°.[11,12] Since experimentally observed $\Delta_N(Q)$ at various scattering angles 2θ=14—91° agree well each other within the statistical errors, we have combined the data from scattering angles with the range 2θ=14—91° and then determined the whole $\Delta_N(Q)$ as in Fig. 1a.

$\Delta_N(Q)$ can be represented by the weighted sum of four partial structure factors which include contributions concerning the nitrogen atom, i.e.,

$$\Delta_N(Q)=A[a_{NO}(Q)-1]+B[a_{ND}(Q)-1]+C[a_{NNa}(Q)-1]+D[a_{NN}(Q)-1]. \quad (1)$$

Here
$$A=2c_Nc_Ob_O(b_{14N}-b_{15N})$$
$$B=2c_Nc_Db_D(b_{14N}-b_{15N})$$
$$C=2c_Nc_{Na}b_{Na}(b_{14N}-b_{15N})$$
$$D=c_N^2(b_{14N}^2-b_{15N}^2)$$

and c_i is the number of i-th atom in the stoichiometric unit $(NaNO_2)_{0.1}(D_2O)_{0.9}$. The value of weighting factors A, B, C, and D is numerically shown in Table 2.

The Fourier transform of $\Delta_N(Q)$ yields the distribution function around nitrogen $\overline{G}_N(r)$, in Fig. 2.

$$\overline{G}_N(r)=1+(A+B+C+D)^{-1}(2\pi^2\rho_0 r)^{-1}\int_0^{Q_{max}} Q\,\Delta_N(Q)\sin(Qr)\mathrm{d}Q \quad (2)$$
$$=[Ag_{NO}(r)+Bg_{ND}(r)+Cg_{NNa}(r)+Dg_{NN}(r)](A+B+C+D)^{-1}.$$

$\overline{G}_N(r)$ is dominated by $g_{NO}(r)$ and $g_{ND}(r)$terms because A and B are much larger than C and D in Table 2.

Results and Discussion

The first peak located at r=1.26 Å in $\overline{G}_N(r)$ is assigned to the intramolecular N–O interaction in NO_2^-. The position of this peak is in good agreement with the value r=1.25 Å obtained from the X-ray diffraction study of molten $NaNO_2$.[13] The oscillational feature appeared in the range within 1 Å in $\overline{G}_N(r)$ can be associated with the termination ripples, which are caused by the set-up of finite upper limit Q_{max}=15.4 Å^{-1}, on the Fourier integration. The intramolecular N–O contribution, $I^{intra}(Q)$, can be theoretically written as follows,

$$I^{intra}(Q)=2c_Nn_{NO}b_O(b_{14N}-b_{15N})\exp(-l_{NO}^2Q^2/2)\frac{\sin Qr_{NO}}{Qr_{NO}}, \quad (3)$$

where n_{NO} is the coordination number of oxygen atoms around the nitrogen atom, and l_{NO} and r_{NO} denote the root mean square amplitude and internuclear distance of N–O bonds, respectivey. The parameters, n_{NO}, l_{NO}, and r_{NO} in Eq. 3 were determined to be 2.3±0.3, 0.062±0.010 Å, 1.258±0.006 Å, respectively, from the least square fit of Eq. 3 to the observed $\Delta_N(Q)$ in the range with $8<Q<20$ Å^{-1}. The fitting was performed by using the SALS program.[14] The value of intramolecular distance r_{NO} obtained in this study is roughly equivalent to that, $r_{NO}=1.236\pm0.014$ Å, reported in the X-ray diffraction study of $NaNO_2$ single crystal.[15] The closeness of the magnitude of n_{NO} to the hypothetical value 2 proves the validity of present data analyses and data corrections. The calculated $I^{intra}(Q)$ was then subtracted from observed $\Delta_N(Q)$ (Figs. 1b, 1c) and transformed to the intermolecular distribution function, $\overline{G}_N^{inter}(r)$ (Fig. 2b), in which unphysical termination ripples below $r=2$ Å are reduced. The second peak at $r=2.7$ Å in $\overline{G}_N(r)$ remains unchanged after removing the intramolecular N–O contribution. Since it seems unreasonable from the electrostatic point of view that the oxygen atom in the nearest neighbor D_2O molecule is facing directly toward the nitrogen atom in the NO_2^- ion in the solution, the second peak can be assigned to the nearest neighbor N···D correlation. The peak position, r(N···D), and the coordination number, n(N···D), obtained from the Gaussian fit of the first peak in $r\overline{G}_N^{inter}(r)$ curve in the range of $2.50<r<2.90$ Å (Fig. 2c) were estimated to be 2.71±0.02 Å and 3.7±0.5, respectively. The nearest neighbor N···D distance, r(N···D)= 2.71 Å corresponds well to the sum of van der Waals radii of nitrogen and hydrogen atoms (1.6 Å+1.2 Å=2.8 Å), suggesting the weak hydration behavior of NO_2^- in aqueous solutions. The third peak at $r=3.5$ Å, in $\overline{G}_N(r)$ may be considered to include both intermolecular N···O and N···D contributions. However, it is impossible to decide in detail the $NO_2^-\cdots D_2O$ configuration because this peak in $\overline{G}_N(r)$ cannot uniquely be decomposed at the present time. To obtain unambiguous information on the $NO_2^-\cdots D_2O$ configuration in the solution, it is needed to determine both distribution functions, $g_{NO}(r)$ and $g_{ND}(r)$, which are given through further experiments including various H/D isotopic subtsitutions.[16–18] This will be a near-future subject.

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