# Neutron and X-ray Diffraction Studies on the Structure of Concentrated Aqueous Sodium Acetate Solutions

# Hisashi NAGANUMA, Yasuo KAMEDA, Takeshi USUKI and Osamu UEMURA

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

Time-of-Flight (TOF) neutron and X-ray diffraction measurements were carried out for aqueous 8 mol% CH<sub>3</sub>COONa solution (CD<sub>3</sub>COONa solution in D<sub>2</sub>O was employed for the neutron diffraction measurement) to obtain detailed information on the hydration structure of both Na<sup>+</sup> and CH<sub>3</sub>COO<sup>-</sup> in the concentrated aqueous solution. The intramolecular structural parameters within CD<sub>3</sub>COO<sup>-</sup> were determined to be  $r_{\rm CO} = 1.24(1)$  Å,  $r_{\rm CD} = 1.09(1)$  Å,  $r_{\rm CC} = 1.51(2)$  Å and  $\angle O$ —C—O = 126(3)°, respectively, through a least-squares fitting analysis of the observed neutron total interference term in the high-Q region ( $10 \le Q \le 32$  Å<sup>-1</sup>). Hydration parameters,  $r(Na^+ \cdots H_2O) = 2.39(1)$  Å and  $n(Na^+ \cdots H_2O) = 4.7(1)$  for Na<sup>+</sup>,  $r(O \cdots H_2O) = 2.78(1)$  Å and  $n(O \cdots H_2O) = 4.0(1)$  for CH<sub>3</sub>COO<sup>-</sup>, were respectively determined from the least-squares refinement of observed X-ray intermolecular interference term. It is revealed that the carboxyl group within the acetate ion forms hydrogen bonds with 4 water molecules in the first hydration shell. Hydrogen-bonded distances between the solvent water molecules were determined to be  $r(O \cdots D) = 1.89(1)$  Å and  $r(D \cdots D) = 2.44(1)$  Å, from the observed neutron intermolecular interference term.

KEYWORDS: neutron diffraction, X-ray diffraction, aqueous sodium acetate solution, hydration structure

#### §1. Introduction

Hydration structure of the acetate ion,  $CH_3COO^-$ , has long been a matter of interest. X-ray diffraction studies on concentrated aqueous solution of various divalent transition metal acetate by Caminiti et  $al^{(1)}$  have revealed structural properties on the metal acetate complex in aqueous solution, however, unambiguous hydration structure of the acetate ion itself has not yet been determined. In this paper, we describe results of X-ray and TOF neutron diffraction measurements on the aqueous 8 mol% sodium acetate solution. Intramolecular structural parameters of the acetate ion in the aqueous solution were determined from a least-squares fitting analysis of the observed neutron total interference term in the high-Q region. The structural information on the first hydration shell of both  $CH_3COO^-$  and  $Na^+$  in the solution, and information on the intermolecular hydrogenbonded network between solvent water molecules, were respectively obtained from the least-squares refinements for observed X-ray and neutron intermolecular interference terms.

# §2. Experimental

#### 2.1 Neutron diffraction measurement

A fully deuterated aqueous 8 mol% CD<sub>3</sub>COONa solution was prepared by dissolving the required amount of CD<sub>3</sub>COONa (99.0 % D, Aldrich Chemical Co.) into D<sub>2</sub>O (99.9 % D, Aldrich Chemical Co.). The sample solution was sealed in a cylindrical quartz sample cell (7.3 mm in inner diameter and 0.5 mm in thickness). The TOF neutron diffraction measurement was carried out at 25 °C using the HIT-II spectrometer installed

at the pulsed spallation neutron source (KENS) at the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. Scattered neutrons were detected by 104 <sup>3</sup>He detectors covering scattering angles of  $10 \leq 2\theta \leq 157^{\circ}$ . The data accumulation time was ca. 5 h. Diffraction measurements were made in advance for an empty cell, background and a vanadium rod of 8 mm in diameter. After corrections for absorption,<sup>2)</sup> multiple<sup>3)</sup> and incoherent scatterings, observed count rates were converted to the absolute scale by using corrected scattering intensities from the vanadium rod. The observed neutron total interference term,  $i_N(Q)$ , scaled at the stoichiometric unit,  $(CD_3COONa)_x(D_2O)_{1-x}$ , was derived



Fig.1. The observed neutron total interference term (dots) and the best-fit with the calculated interference term of Eq. (2.1)(solid line) for aqueous 8 mol% CD<sub>3</sub>COONa solution in D<sub>2</sub>O. The residual function (dots) is shown below.

by the same manner as described in our previous paper.<sup>4)</sup>

#### 2.2 X-ray diffraction measurement

X-ray diffraction with MoK $\alpha$  radiation ( $\lambda = 0.7107$ Å) was measured at 25  $^{\circ}$ C on an aqueous 8 mol%CH<sub>3</sub>COONa solution under the reflection geometry using a  $\theta$ - $\theta$  X-ray diffractometer manufactured by Rigaku Co. The scattered X-ray intensities from the sample were collected at an interval of  $0.2^{\circ}$  over an angular range of  $3 < 2\theta \leq 150^{\circ}$ , corresponding to the scattering vector range,  $0.5 \le Q \le 17.1 \text{ Å}^{-1} (Q = 4\pi \sin \theta / \lambda)$ , with a fixed counting time of 100 s. The whole angular range was scanned four times in order to keep good statistics for the scattering data, and to minimize any long-term instrumental drift. After correction and normalization procedures, scattering data were then converted to the observed X-ray interference term  $i_X(Q)$ . Details concerning the X-ray diffraction measurement were previously described.<sup>5</sup>)

#### 2.3 Data analysis

Intramolecular parameters for  $\text{CD}_3\text{COO}^-$  are determined from the least squares fitting analysis of the observed  $i_N(Q)$  in the high-Q region  $(10 \le Q \le 32 \text{ Å}^{-1})$ , where contributions from intermolecular interactions are expected to be negligibly small. The calculated intramolecular interference term  $i_N^{\text{intra}}(Q)$  can be evaluated by the following equation,

$$i_{\rm N}^{\rm intra}(Q) = x \cdot i_{\rm N}^{\rm intra}(Q) (\text{for } \text{CD}_3\text{COO}^-) + (1-x) \cdot i_{\rm N}^{\rm intra}(Q) (\text{for } \text{D}_2\text{O}), \quad (2.1)$$

where

$$i_{\rm N}^{\rm intra}(Q)$$
(for CD<sub>3</sub>COO<sup>-</sup>)  
=  $\sum_{i \neq j} \sum_{b_i b_j} \exp(-l_{ij}^2 Q^2/2) \sin(Qr_{ij})/(Qr_{ij}), (2.2)$ 

and

$$i_{\rm N}^{\rm intra}(Q) (\text{for } D_2 O) = 4b_{\rm O}b_{\rm D} \exp(-l_{\rm OD}^2 Q^2/2) \sin(Qr_{\rm OD})/(Qr_{\rm OD}) + 2b_{\rm D}^2 \exp(-l_{\rm DD}^2 Q^2/2) \sin(Qr_{\rm DD})/(Qr_{\rm DD}).$$
(2.3)

Parameters  $r_{ij}$  and  $l_{ij}$  denote the internuclear distance and rms amplitude for i—j atom pair, respectively.  $b_i$  is the coherent scattering length of the atom i. In evaluation of  $i_N^{intra}(Q)$  for CD<sub>3</sub>COO<sup>-</sup>, contributions from all possible i—j pair within the molecule were taken into account. Internuclear distances,  $r_{CC}$ ,  $r_{CO}$  and  $r_{CD}$ , and the bond angle,  $\angle OCO$ , within the CD<sub>3</sub>COO<sup>-</sup> were treated as independent parameters. The corresponding rms amplitudes were fixed to values calculated from the normal coordinate analysis by Derissen.<sup>6</sup> Parameters for the D<sub>2</sub>O molecule,  $r_{OD}$ ,  $r_{DD}$ ,  $l_{OD}$  and  $l_{DD}$ , were allowed to vary independently. The fit was performed in the range of  $10 \le Q \le 32$  Å<sup>-1</sup>. The observed  $i_N(Q)$  and its Fourier transform,  $g_N(r)$ , are represented in Figs. 1 and 2, respectively.

The X-ray intermolecular interference term,  $i_{\rm X}^{\rm inter}(Q)$ , was derived by subtracting intramolecular contribution

Fig.2. The neutron total distribution function,  $g_N(Q)$  (dots), and the Fourier transform of the model function,  $i_N^{intra}(Q)$  (solid line). Contributions from CD<sub>3</sub>COO<sup>-</sup> and D<sub>2</sub>O molecules are indicated by dotted and broken lines, respectively.

from the observed total  $i_X(Q)$ . The intramolecular contribution was evaluated by the use of molecular parameters determined from the present neutron data described in the next section. Intermolecular structural parameters for the nearest neighbor Na<sup>+</sup>  $\cdots$  H<sub>2</sub>O, H<sub>2</sub>O $\cdots$  H<sub>2</sub>O and CH<sub>3</sub>COO<sup>-</sup>  $\cdots$  H<sub>2</sub>O pairs as well as the second and third nearest neighbor H<sub>2</sub>O $\cdots$  H<sub>2</sub>O interactions were obtained by the least-squares fitting analysis of the observed  $i_X^{inter}(Q)$  using the model function involving the short- and long-range interactions,

$$i^{\text{model}}(Q) = \sum_{i} (2 - \delta_{ij}) f_i f_j \exp(-l_{ij}^2 Q^2/2) \\ \times \sin(Qr_{ij}) / (Qr_{ij}) \\ + 4\pi\rho \exp(-l_0^2 Q^2/2) \\ \times [Qr_0 \cos(Qr_0) - \sin(Qr_0)] Q^{-3}, (2.4)$$

where,  $f_i$  and  $\rho$  denote the atomic scattering factor of atom i and the number density, respectively. In order to describe the CH<sub>3</sub>COO<sup>-</sup>···H<sub>2</sub>O interaction, the nearest neighbor O(acetate)····H<sub>2</sub>O distance, rms amplitude and coordination number, were treated as independent parameters. In addition, the bond angle  $\angle C$ —O····H<sub>2</sub>O and the dihedral angle  $\alpha$  between the plane involving carboxyl group and the plane involving C—O····H<sub>2</sub>O atoms were determined independently. The neutron intermolecular interference term,  $i_{\rm N}^{\rm inter}(Q)$ , was derived by subtracting calculated intramolecular  $i_{\rm N}^{\rm intra}(Q)$  from the observed total  $i_{\rm N}(Q)$ . Structural parameters for intermolecular hydrogen-bonded O···D and D···D interactions were derived from the least squares fit of the observed  $i_{\rm N}^{\rm inter}(Q)$ .

#### §3. Results and Discussion

3.1 Intramolecular structure of CD<sub>3</sub>COO<sup>-</sup> and D<sub>2</sub>O molecules

Intramolecular distances and the bond angle  $\angle OCO$  within the CD<sub>3</sub>COO<sup>-</sup> determined from the analysis of the observed  $i_N(Q)$  (Fig. 1),  $r_{CC} = 1.51(2)$  Å,  $r_{CO} = 1.24(1)$  Å,  $r_{CD} = 1.09(1)$  Å and  $\angle OCO = 126(3)^{\circ}$ , are in good agreement with those found in the crystalline





Fig. 3. Observed X-ray and neutron intermolecular interference terms (circles). The best-fit of calculated interference terms of Eq. (2.4) are denoted by solid lines.



Fig. 4. Observed X-ray and neutron intermolecular distribution functions (circles). Contributions from the short- and long-range interactions are indicated by broken lines.

 $CH_3COONH_4$ ,<sup>7)</sup> indicating that the molecular structure of acetate ion remains unchanged in the concentrated aqueous solution. Present values for intramolecular parameters of D<sub>2</sub>O ( $r_{OD} = 0.983(1)$  Å,  $l_{OD} = 0.075(1)$  Å,  $r_{DD} = 1.565(3)$  Å and  $l_{DD} = 0.120(2)$  Å) agree well with those reported for pure liquid D<sub>2</sub>O.<sup>4)</sup>

## 3.2 Hydration structure of $CH_3COO^-$ and $Na^+$

Observed intermolecular interference terms  $(i_{\rm X}^{\rm inter}(Q))$ and  $i_{\rm N}^{\rm inter}(Q)$  and distribution functions  $(g_{\rm X}^{\rm inter}(r))$  and  $g_{\rm N}^{\rm inter}(r)$  are represented in Figs. 3 and 4, respectively.

Since contributions from H—X (X: O, C, Na and H) pairs are much small in the observed X-ray interference term due to small scattering power of H atom, structural parameters for the nearest neighbor Na<sup>+</sup> ···H<sub>2</sub>O, CH<sub>3</sub>COO<sup>-</sup> ···H<sub>2</sub>O and H<sub>2</sub>O···H<sub>2</sub>O interactions have been determined by a least squares fit of Eq. (2.4) to the observed  $i_{\rm X}^{\rm inter}(Q)$  in the range of  $1.0 \leq Q \leq 17.1$  Å<sup>-1</sup>. The nearest neighbor O(acetate)···H<sub>2</sub>O distance, rms amplitude and coordination number were respectively determined to be 2.78(1) Å, 0.21(1) Å and 4.0(1), implying that four H<sub>2</sub>O molecules are hydrogen-bonded to the carboxyl oxygen of the acetate ion. The bond angle,  $\angle C$ — $O \cdots H_2O$ , and the dihedral angle  $\alpha$  were obtained to be 101(1)° and 40(1)°, respectively. These values are very similar to those observed for the formate ion, HCOO<sup>-</sup> ( $\angle C$ — $O \cdots H_2O = 103(2)°$  and  $\alpha = 33(3)°^{8}$ ), suggesting the similarity in the structure of the first hydration shell around the carboxyl group. Present values for the nearest neighbor Na<sup>+</sup>  $\cdots H_2O$  interaction,  $r_{\rm Na^+} \cdots H_2O = 2.39(1)$  Å,  $l_{\rm Na^+} \cdots H_2O = 0.23(1)$  Å and  $n_{\rm Na^+} \cdots H_2O = 4.7(1)$ , are in good agreement with those observed for concentrated aqueous NaX (X: HCOO,<sup>8</sup>) Cl, Br, ClO<sub>4</sub> and NO<sub>3</sub><sup>9</sup>) solutions.

### 3.3 Intermolecular hydrogen-bonded structure

Relative weightings for O—D (38 %) and D—D (42 %) pairs are dominated in the present  $i_{N}^{inter}(Q)$ . The shortrange parameters for O—D and D—D interactions have been derived from a least squares fitting analysis of the  $i_{\rm N}^{\rm inter}(Q)$  in the range of  $1.0 \leq Q \leq 17.1$  Å<sup>-1</sup>. In the fitting procedure, contributions from  $Na^+ \cdots D_2O$ ,  $CD_3COO^- \cdots D_2O$  and  $D_2O \cdots D_2O$  pairs are involved in the model function employing structural parameters which have already been obtained from the analysis of the  $i_{\mathbf{x}}^{\text{inter}}(Q)$  as described in the former section. The nearest neighbor O···D and D···D hydrogen-bonded distances determined from the present  $i_{\rm N}^{\rm inter}(Q)$   $(r_{\rm O...D} = 1.89(1)$  Å and  $r_{\rm D...D} = 2.44(1)$  Å) agree well with those observed for pure liquid water.<sup>10,11</sup> However, the present values of  $n_{O...D}$  (= 1.1(1)) is much smaller than that for pure water  $(n_{O...D} = 2.0(2)^{11})$ , indicating that the hydrogen-bonded network structure among water molecules is significantly modified by coexisting ions in the present solution.

#### Acknowledgements

The authors would like to thank Professor Toshiharu Fukunaga (Kyoto University) and Dr. Keiji Itoh (Kyoto University) for their help during the course of the neutron diffraction measurement. All calculations were carried out with the S7/7000U computer at the Yamagata University computing service center. This work was partially supported by a Grant-in-Aid for Scientific Research No. 12640534 from the Ministry of Education, Science, Sports and Culture, Japan.

- R. Caminiti, P. Cucca, M. Monduzzi, G. Saba and G. Crisponi: J. Chem. Phys. 81 (1984) 543.
- H. H. Paalman and C. J. Pings: J. Appl. Phys. 33 (1962) 2635.
- 3) I. A. Blech and B. L. Averbach: Phys. Rev. **137** (1965) A1113.
- Y. Kameda and O. Uemura: Bull. Chem. Soc. Jpn. 65 (1992) 2021.
- Y. Kameda, R. Takahashi, T. Usuki and O. Uemura: Bull. Chem. Soc. Jpn. 67 (1994) 956.
- 6) J. L. Derissen: J. Mol. Struct. 7 (1971) 67.
- 7) I. Nahringbauer: Acta Cryst. 23 (1967) 956.
- Y. Kameda, T. Mori, T. Nishiyama, T. Usuki and O. Uemura: Bull. Chem. Soc. Jpn. 69 (1996) 1495.
- Y. Kameda, K. Sugawara, T. Usuki and O. Uemura: Bull. Chem. Soc. Jpn. **71** (1998) 2769.
- 10) A. K. Soper and M. G. Phillips: Chem. Phys. 107 (1986) 47.
- Y. Kameda, T. Usuki and O. Uemura: Bull. Chem. Soc. Jpn. 71 (1998) 1305.