

# Neutron Diffraction Study on the Intermolecular Structure in Highly Concentrated Aqueous Urea Solutions

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Intermolecular hydrogen-bonded structure in the concentrated aqueous urea solution has been received much attention because of its importance for various fields of chemical and biological sciences. A number of neutron diffraction studies have been conducted in order to investigate the hydration structure of the urea molecule [1-6], however, direct experimental information on the structure of urea-urea interaction has not yet been obtained. In the present report, we describe results of neutron diffraction measurements on <sup>14</sup>N/<sup>15</sup>N and H/D isotopically substituted aqueous 25 mol% urea solutions in order to obtain the N(urea)-N(urea) partial structure factor and corresponding N-N partial distribution function.

Five isotopically substituted aqueous 25 mol% urea solutions were used in the present study, namely,

- I. [(<sup>14</sup>ND<sub>2</sub>)<sub>2</sub>C=O]0.25(D<sub>2</sub>O)0.75,
- II. [(<sup>15</sup>ND<sub>2</sub>)<sub>2</sub>C=O]0.25(D<sub>2</sub>O)0.75,
- III. [(<sup>14</sup>-<sup>15</sup>ND<sub>2</sub>)<sub>2</sub>C=O]0.25(D<sub>2</sub>O)0.75,
- IV. [(<sup>14</sup>NZ<sub>2</sub>)<sub>2</sub>C=O]0.25(Z<sub>2</sub>O)0.75, and
- V. [(<sup>15</sup>NZ<sub>2</sub>)<sub>2</sub>C=O]0.25(Z<sub>2</sub>O)0.75,

where <sup>14</sup>-<sup>15</sup>N is the 1:1 mixture of <sup>14</sup>N and <sup>15</sup>N, and " Z " denotes the null mixture of H and D. Sample solutions were sealed in a cylindrical quartz cell (12.0 mm in inner diameter and 1.1 mm in thickness).

Neutron diffraction measurements were carried out at 298 K using the ISSP diffractometer 4G (GPTAS) installed at the JRR-3M research reactor with an incident neutron wavelength of 1.099(4) Å. Scattered neutrons were collected over the angular range of  $3 < 2\theta < 118$  deg. corresponding to  $0.30 < Q < 9.80$  1/Å. Preset time was 230 s for each data point. Measure-

ments were made in advance for an empty cell, a vanadium rod of 10 mm in diameter, and an instrumental background. After correction for the background, absorption and multiple scattering, the observed count rates were converted to the scattering cross section by the use of corrected scattering intensities from the vanadium rod.

The intermolecular first-order difference function,  $\Delta N\text{-inter}(Q)$  [7], was derived from the difference in observed scattering cross sections between sample solutions that have different average coherent scattering length of the nitrogen atom. The observed  $\Delta N(Q)$  function can be described by a linear combination of the partial structure factors involving contribution from the nitrogen atom. Numerical values of the coefficients A - D are summarized in Table 1.

$$\Delta N(Q) = A[a_{\text{NO}}(Q)-1] + B[a_{\text{NH}}(Q)-1] + C[a_{\text{NC}}(Q)-1] + D[a_{\text{NN}}(Q)-1],$$

where,

$$\begin{aligned} A &= 4x \Delta b_{\text{N}} b_{\text{O}}, \\ B &= 8x(1+x) \Delta b_{\text{N}} b_{\text{H}}, \\ C &= 4x^2 \Delta b_{\text{N}} b_{\text{C}}, \text{ and} \\ D &= 4x^2(b_{\text{N}}^2 - b_{\text{N}}'^2). \end{aligned}$$

Table 1. Weighting factor for partial structure factors in the first- and second-order difference functions (in barns).

| Difference       | A      | B      | C      | D      |
|------------------|--------|--------|--------|--------|
| I - III          | 0.0830 | 0.2383 | 0.0238 | 0.0618 |
| III - II         | 0.0830 | 0.2383 | 0.0238 | 0.0516 |
| (I-III)-(III-II) | 0      | 0      | 0      | 0.0102 |

The N-N partial structure factor was successfully obtained from the second-order difference between two first-order difference functions, between samples I - III and III - II. Although observed intermolecular difference functions between samples I - III and III - II look very similar, the derived N-N partial structure factor clearly indicates the first diffraction peak at  $Q = 1.5 \text{ 1/\AA}$ . Difference distribution functions  $GN(r)$  between samples I - III and III - II, and the N-N partial distribution function are represented in Fig. 1. The observed intermolecular N-N partial distribution function,  $g_{NN}(r)$ , is characterized by a well-resolved first peak at  $r = 5 \text{ \AA}$ , which may imply that the stable urea cluster is present in the concentrated aqueous solution. Detailed structural information on the N-H and N-O partial structure functions can be obtained from the combination of the observed scattering cross sections for samples I - II and IV - V, respectively. Further data analysis is in progress.

#### References

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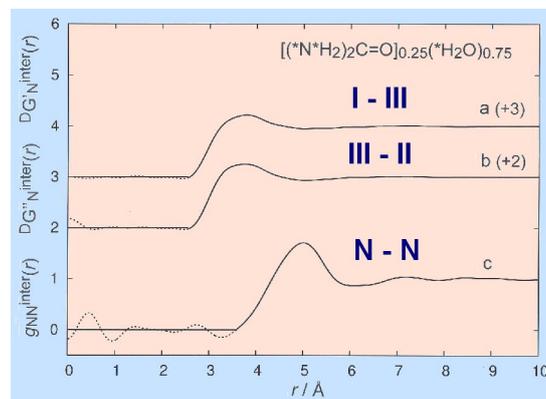


Fig. 1. a, b) Intermolecular difference distribution functions and c) N-N partial distribution function observed for aqueous 25 mol% urea solutions.