

Hydration structure around the nitrogen atom of the pyridine molecule

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The coordination property of the pyridinyl nitrogen atom plays an important role in the wide fields of chemical and biological sciences, however, the experimental determination of the hydration structure of the pyridine molecule has not been reported. In the present report, we describe results of neutron diffraction measurements on the aqueous 10 mol% pyridine solutions in which $^{14}\text{N}/^{15}\text{N}$ and H/D isotopic ratios were changed.

Neutron diffraction measurements were carried out at 298 K using the ISSP diffractometer, 4G (GPTAS) installed at the JRR-5M research reactor with an incident neutron wavelength of 1.093(3) Å. Scattered neutrons were collected over the angular range of $3 < 2\theta < 118$ deg. corresponding to $0.3 < Q < 9.8$ 1/Å. Preset time was 180 s for each data point. After correction for the background, absorption and multiple scattering, the observed scattering intensities were converted to the absolute scattering cross section by the use of corrected scattering cross section from the vanadium rod.

The first-order difference function between [1] (^{14}N -pyridine- D_2O) and (^{15}N -pyridine- D_2O) was determined from the difference in the observed scattering cross sections between sample solutions with different $^{14}\text{N}/^{15}\text{N}$ compositions. The distribution function around the pyridinyl nitrogen atom was derived by the Fourier transform of the observed first-order difference function (Fig. 1a). In the present experimental condition, contributions from the N-O(water) and N-D(water) partial structure factors are dominant in the observed difference function. The calculated intramolecular contribution within the pyridine molecule was subtracted from the observed total difference function to obtain the intermolecular difference func-

tion. The intermolecular distribution function was evaluated by the Fourier transform of the intermolecular difference function (Fig. 1b).

The first peak observed in the intermolecular distribution function is assigned to the nearest neighbor N...D (water) interaction. The least squares fitting analysis of the observed intermolecular difference function revealed that, on the average, 2.4 water molecules are hydrogen-bonded in the N...D-O-D type. The nearest neighbor N...D distance is determined to be 1.93 Å.

Reference

[1] J. E. Enderby, G. W. Neilson, "Water, A Comprehensive Treatise", Plenum Press, New York (1979), Vol. 6, p. 1.

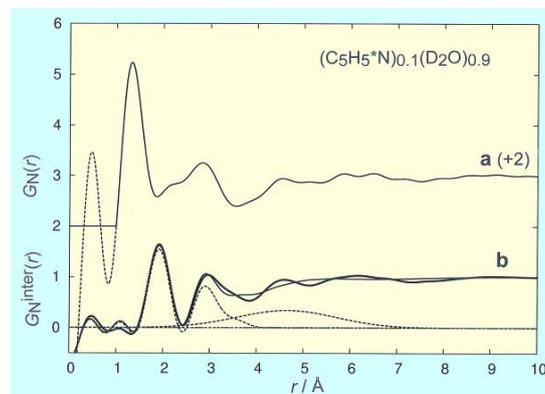


Fig. 1. Fig. 1 a) Total and b) intermolecular distribution functions around nitrogen atom of the pyridine molecule.