

Intermolecular Structure between Urea Molecule and Metal Ions in Concentrated Aqueous Solutions

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Neutron diffraction measurements were carried out for $6\text{Li}/7\text{Li}$, $35\text{Cl}/37\text{Cl}$, and $14\text{N}/15\text{N}$ isotopically substituted concentrated aqueous urea solutions involving $^*\text{LiCl}$ and Na^*Cl salts in order to obtain information concerning intermolecular structure between the urea molecule and coexisting ions in concentrated aqueous solutions.

Six sample solutions with different isotopic compositions, I. $(\text{Na}^{35}\text{Cl})_{0.05}[(14\text{ND}_2)_2\text{C}=\text{O}]_{0.1}(\text{D}_2\text{O})_{0.85}$, II. $(\text{Na}^{\text{nat}}\text{Cl})_{0.05}[(14\text{ND}_2)_2\text{C}=\text{O}]_{0.1}(\text{D}_2\text{O})_{0.85}$, III. $(\text{Na}^{\text{nat}}\text{Cl})_{0.05}[(15\text{ND}_2)_2\text{C}=\text{O}]_{0.1}(\text{D}_2\text{O})_{0.85}$, IV. $(6\text{LiCl})_{0.1}[(14\text{ND}_2)_2\text{C}=\text{O}]_{0.1}(\text{D}_2\text{O})_{0.8}$, V. $(7\text{LiCl})_{0.1}[(14\text{ND}_2)_2\text{C}=\text{O}]_{0.1}(\text{D}_2\text{O})_{0.8}$, and VI. $(7\text{LiCl})_{0.1}[(15\text{ND}_2)_2\text{C}=\text{O}]_{0.1}(\text{D}_2\text{O})_{0.8}$, were employed in the present study.

Diffraction measurements were made at 298 K using ISSP diffractometer, 4G (GP-TAS) installed at the JRR-3M research reactor with an incident neutron wavelength of 1.090 Å. Scattered intensities were collected over the angular range of $3 < 2\theta < 118$ deg. After corrections for the background, absorption, multiple and incoherent scatterings, observed scattering intensities were converted to the scattering cross sections.

The first-order-difference functions [1] were evaluated by a numerical difference between observed scattering cross sections for sample solutions with different isotopic compositions. Fourier transform of the difference function gives the distribution function around the substituted atom. For NaCl-urea solutions, two distribution functions, $G_{\text{Cl}}(r)$ (around Cl⁻) and $G_{\text{N}}(r)$ (around N atom of urea), were successfully determined as indicated in Fig. 1a. Distribution functions, $G_{\text{Li}}(r)$ (around Li⁺) and $G_{\text{N}}(r)$ (around N atom of urea), were obtained as shown in Fig. 1b.

Preliminary analysis of the observed $G_{\text{Cl}}(r)$ (Fig. 1a) indicates that there are ca. 6 nearest neighbor water molecules around the chloride ion. The value agrees well with that reported for various aqueous solutions, which implies that the first hydration shell of the chloride ion is well maintained in the presence of the urea molecule. On the other hand, relatively small second peak appearing in the distribution function around the lithium ion, $G_{\text{Li}}(r)$ (Fig. 1b) may suggest that the first hydration shell of Li⁺ is significantly affected by coexisting urea molecule.

Reference

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

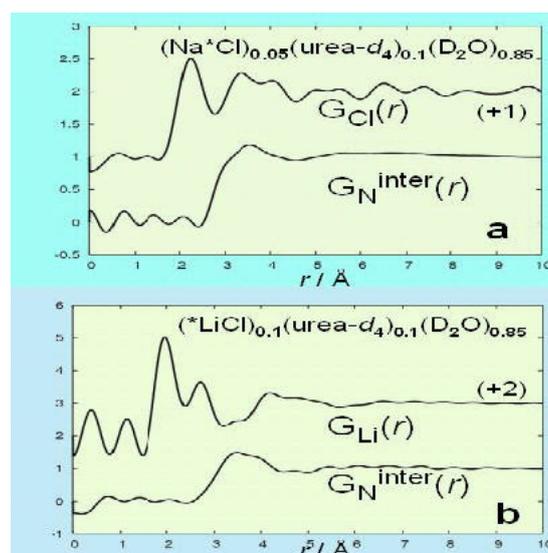


Fig. 1. Fig. 1. a) $G_{\text{Cl}}(r)$ and $G_{\text{N}}^{\text{inter}}(r)$ functions observed for NaCl-urea-D₂O solutions. b) Distribution functions, $G_{\text{Li}}(r)$ and $G_{\text{N}}^{\text{inter}}(r)$ functions observed for LiCl-urea-D₂O solutions.