JASMAC
Conference of the Japan Society of Microgravity Appllication

PS05

水酸化リチウム濃厚水溶液の X 線構造解析

X-ray Structural analysis of concentrated Lithium Hydroxide Aqueous Solution

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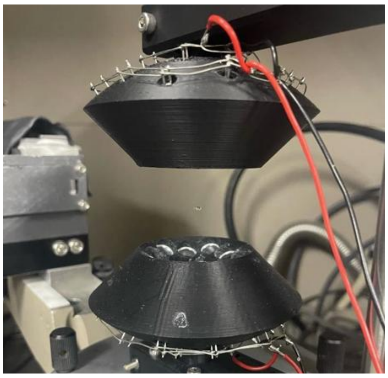


Abstract: Elucidating the local structure of high-concentration electrolyte solutions is important for understanding their physical properties and optimizing their applications. In this study, we installed a self-made acoustic levitation apparatus on the sample stage of an X-ray analysis device (RIGAKU RINT-2000) and performed X-ray structural analysis on levitated pure water and 5 mol/L lithium hydroxide (LiOH) solution. The obtained scattering intensities were corrected for polarization and absorption, and the radial distribution function (RDF) was calculated using Fourier transformation. Additionally, molecular dynamics simulations using LAMMPS were conducted to validate the experimental results. Compared to water, the first peak of the LiOH concentrated solution was observed to shift slightly to the right, and the shoulder shape tended to become smaller. The RDF of water showed peaks at approximately 2.75 Å, 4.61 Å, and 6.92 Å. From the MD results, the first peak of $g_{oo}(r)$ was approximately 2.70 Å, and the first peak of $g_{OH}(r)$ appeared further away at approximately 3.2 Å.

1. Introduction

An acoustic levitation method is a non-contact technique that levitates an object at a specific position by utilizing acoustic radiation pressure generated by standing waves. It is suitable for handling highly corrosive liquid such as Highly concentrated electrolyte because it is not affected by the container.　In this study, X-ray structural analysis was performed on water and concentrated lithium hydroxide solutions levitates using the acoustic levitation method. The radial distribution function $g(r)$was derived from the obtained scattering intensity data, and an attempt was made to evaluate the local structure of the liquid by comparing it with molecular dynamics (MD) simulation results.

2. Experimental method

The lithium hydroxide solution was adjusted to a saturated concentration (molar ratio of H_2O : LiOH = 1 :

0.05) and 3 μL was measured using a micropipette and levitated. The experiment was conducted using a homemade acoustic levitation device attached to an X-ray analysis device (RIGAKU RINT-2000). Mo-Kα rays were used for X-rays, and the diffraction angle was measured in 0.1° increments from 3° to 80°. A schematic diagram of the device used in the experiment is shown in Figure 1.

In addition, molecular dynamics (MD) simulations of water were performed. The SPC/FW-type parameters were used as the water molecule model, and 6,640 water molecules were arranged under cubic periodic boundary conditions (80 Å × 80 Å × 80 Å). Interactions were evaluated using the Lennard-Jones potential and Coulomb interaction (Eward method, accuracy 1×10-5). The time step was set to 1.0 fs, and after equilibration (15 ps) under a Nosé–Hoover NPT ensemble at 300 K and 1 atm, a 50 ps main calculation was performed. From the obtained atomic coordinates, the radial distribution functions $g(r)$ for oxygen-oxygen, oxygen-hydrogen, and hydrogen-hydrogen were calculated.

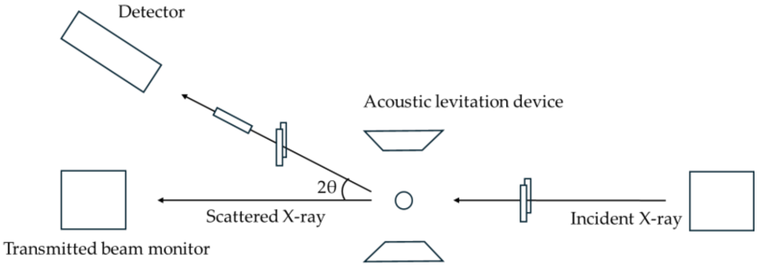


Figure 1. Schematic diagram of the experimental apparatus.

3. Results

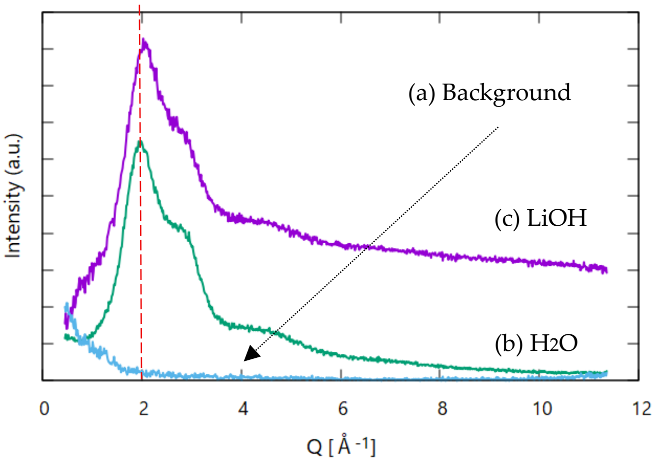
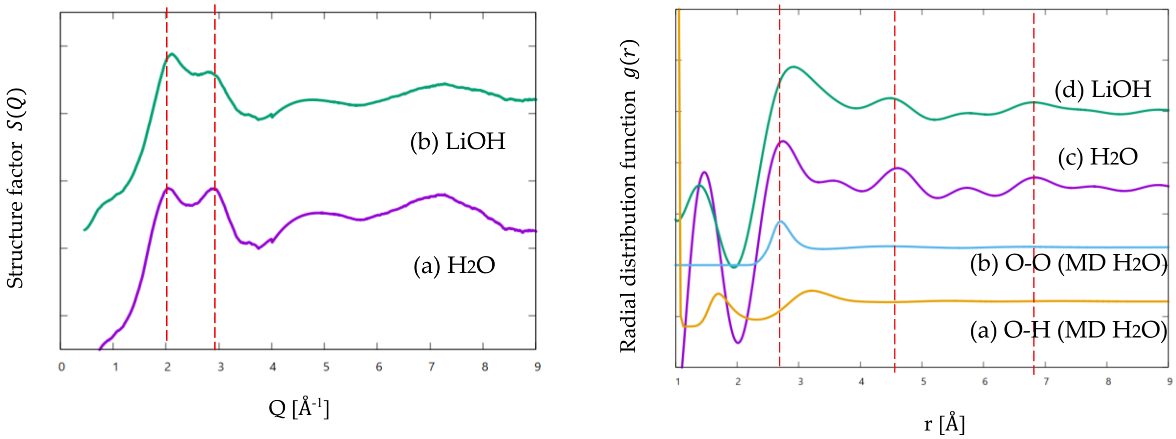


Figure2. H_2O, LiOH, background XRD measurement results (scattering intensity).

The measurement results showed that the background intensity was almost zero and remained constant except for the influence of the direct beam in the low-angle region. Since the sample was liquid, a continuous and broad peak was observed, unlike the sharp peaks seen in crystalline systems.

Highly concentrated lithium hydroxide solution shifted the first peak to the right compared to water. In addition, the shoulder seen on the high-angle side of the first peak became smaller than that of water.

4. Discussion



(a) **(b)**

Figure3. (a) Structural factor $S(Q)$, (b) Radial distribution function $g(r)$

$S(Q)$ and $g(r)$ were derived from the scattering intensity obtained from the experimental results. Since hydrogen atoms contribute little to X-ray scattering, the $g(r)$ obtained from the experiment reflects only the O-O distance. In the experimental H2O $g(r)$, the first peak appeared at approximately 2.75Å, the second peak at approximately 4.61Å, and the third peak at approximately 6.92Å.

Furthermore, MD analysis results showed that $g_{OO}(r)$ was approximately 2.7 Å, and $g_{OH}(r)$ had a peak position approximately 0.5 Å higher than that. On the other hand, the $g(r)$of water as a whole obtained from the experimental results has a first peak at approximately 2.75 Å, but since the $g(r)$ obtained from the experiment includes not only oxygen–oxygen correlations but also oxygen–hydrogen and hydrogen–hydrogen contributions, the peak position is averaged and shifts slightly toward the higher r side.

The radial distribution function of LiOH shows that the first peak is shifted to the high-r side by approximately 0.15 Å compared to water. The sample used in this study was a lithium hydroxide solution with a molar ratio of H_2O:LiOH = 1:0.05, which means that there are approximately 20 water molecules per Li^+ ion. Since the coordination number of water molecules in the local closest-packed state is approximately 8–10, it is considered that approximately 10 water molecules coordinate around the Li+ ion as the first hydration shell, with the remaining approximately 10 molecules coordinating as the second hydration shell. Therefore, the rightward shift of the first peak is thought to result from the Li+ ion strongly attracting some of the oxygen atoms in the first hydration shell, thereby increasing the distance to the oxygen atoms in the second hydration shell.

5. Conclusion

The radial distribution function of highly concentrated lithium hydroxide solution shifted the first peak to the high r side by approximately 0.15 Å compared to water. This is thought to be because the Li+ ions in the solution attracted some of the oxygen atoms they were coordinating with, causing the first peak of $g(r)$ to shift to the high r side.

1） 長倉三郎：水の構造化学.The chemical Society of Japan,11(1963)377