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音波浮遊法を用いた濃厚電解質の X 線解析

X-ray analysis of concentrated electrolytes using the sonic levitation method

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1. Introduction

An acoustic levitation method is a non-contact method of levitating an object to a specific position by utilizing acoustic radiation pressure due to standing waves. It is suitable for handling highly corrosive liquid samples such as concentrated electrolytes because it is not affected by the container. In this study, X-ray analysis of water and concentrated electrolytes suspended by the acoustic levitation method was performed to clarify the differences in liquid structure depending on the type and concentration of cations.

2. Experimental method

Water, sodium hydroxide solution, and potassium hydroxide solution were used as samples. Sodium hydroxide solutions were prepared at molar ratios of $H_2O/NaOH$ = 1/0.2, 1/0.4, and 1/0.6, and potassium hydroxide solutions were prepared at molar ratios of H_2O/KOH = 1/0.1, 1/0.2, 1/0.3, and 1/0.4, respectively, and were suspended at 2 mm diameter via the acoustic levitator. This experiment was conducted using an X-ray diffraction facility (RIGAKU RINT-2000) with the acoustic levitator of our own design. The Mo-Kα was used as the X-ray source, and the diffraction angles were measured from 3° to 60° at intervals of 0.1°.

Corrections were made to the measured X-ray intensities for polarization and absorption factors, and normalized to account for coherent and incoherent scattering factors. The normalized intensities were Fourier transformed to derive a radial distribution function. The relationship between the absolute scattering intensity required to obtain the interference function and the absolute scattering intensity is established in Equation 1.

$$\frac{\alpha_N I^{obs}(Q)}{PA} = I_{eu}^{coh}(Q) + I_{eu}^{inc}(Q) + I_{eu}^{mul}(Q), \tag{1}$$

Where A is the absorption factor, P is the polarization factor, and α_N is the normalization constant. The interference function for the multicomponent system is shown in Equation 2.

$$i(Q) = \frac{I_{eu}/N - \langle f^2 \rangle}{\langle f \rangle^2} \tag{2}$$
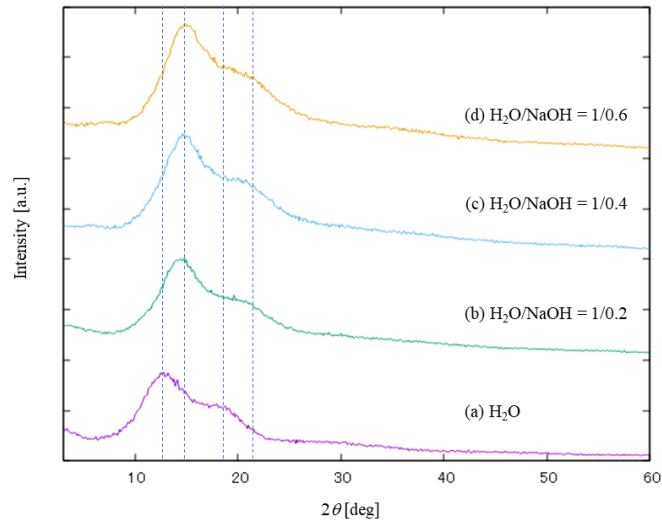
3. Results

Figure 1. X-ray diffraction patterns of water and sodium hydroxide solution.
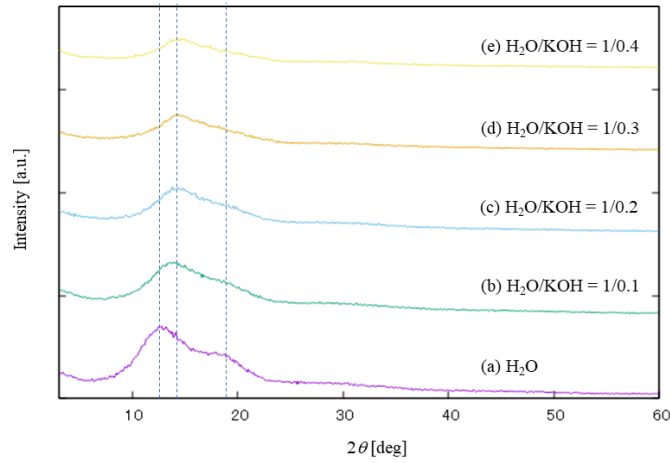

Figure 2. X-ray diffraction patterns of water and potassium hydroxide solutions.

Since the sample was a liquid, continuous and broad peaks were observed, unlike the sharp peaks observed in the crystalline system. In both water and sodium hydroxide solution, a shoulder was observed on the high angle side of the first peak. The peak position of sodium hydroxide solution was found to be shifted about 2° to the high angle side compared to that of water. The amount of change in peak position for the potassium hydroxide solution was smaller than that for the sodium hydroxide solution.
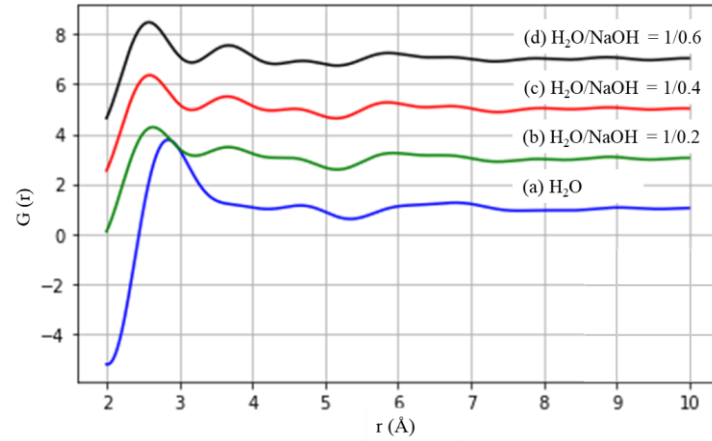
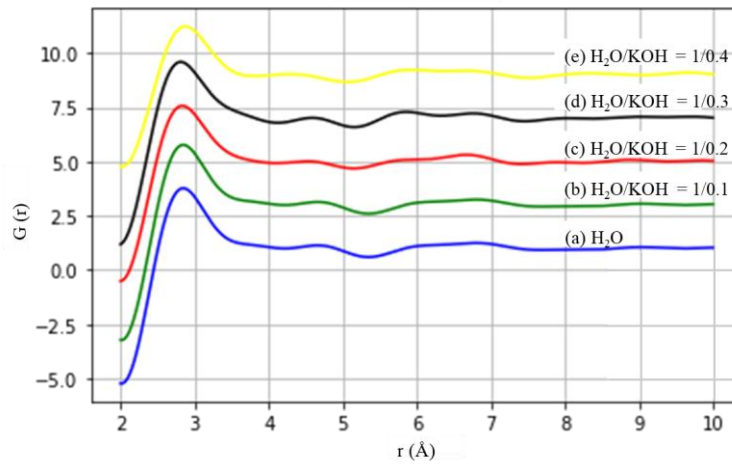**Figure 3**.   RDF of water and sodium hydroxide solution.

Figure 4.   RDF of water and potassium hydroxide solution.

The first peak appeared at 2.75 Å in the RDF of water. The first peak appeared at 2.6 Å in the RDF of sodium hydroxide solution. The peak position of potassium hydroxide solution was the same as that of water.

4. Conclusion

Hydrogen atoms have electrons only in the 1s orbital, then the diffraction pattern cannot be obtained because of the small scattering of X-rays. Therefore, the diffraction pattern of water provides only information on oxygen. In solid ice, when we focus on oxygen, it forms a tetrahedron. Similarly, for silicon with tetrahedral structure, it is known that a shoulder appears on the right side of the first peak[2]. The first peak of the radial distribution function of water is located very close to 2.76 Å[3], which is the distance between oxygen atoms in solid ice. Thus, the liquid structure of water indicates that the short-range order of solid state has remained. It can be assumed that the peak position of the sodium hydroxide solution has changed due to the coordination of the hydrated water to Na+. In the potassium hydroxide solution, the water of hydration is coordinated around K+ in the same way, but the peak position remains unchanged. This might be because the hydration bonds around K+ are weaker than those around Na+ and did not affect the o-o distance.

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2) Yoshio Waseda:THE STRUCTURE OF NON-CRYSTALLINE MATERIALS Liquids and Amorphous Solids, McGraw-Hill Inc.(1980)p258
3) Saburo Nagakura : Structural Chemistry of Water, The chemical Society of Japan,11(1963)p377