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博士論文

**Spectroscopic studies on the molecular
behavior of water molecules in highly
concentrated electrolyte solutions**

高濃度電解質水溶液における
水分子の分子挙動の分光学研究

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General information

Early research on bulk water structure

Water is the most ubiquitous substance in the world and constitutes an indispensable presence across almost every field. Although the molecular structure of water is simpler than that of almost all other non-protonic solvents, its high polarity—arising from the covalent bonding of hydrogen and oxygen atoms—results in a high electron density on the oxygen atom side. Combined with the unbonded lone electron pairs on the oxygen atom, this makes water an excellent electron donor. Conversely, the low electron density on the hydrogen atom side allows water molecules to act as good electron acceptors. This dual characteristic enables water molecules to form intermolecular hydrogen bonds through dipole-dipole interactions. The presence of these hydrogen bonds is responsible for water being regarded as a liquid with a complex, highly structured arrangement¹, giving rise to its anomalous physical properties². Research into the structure of water dates back to the 19th century. As early as 1883, Thomsen and Raoult reported that the molecular weight of water was twice that of water vapor³⁻⁶. In 1884, Whiting proposed the presence of solid particles in liquid water through a theory of the coalescence of three pressures⁵⁻⁷, marking one of the earliest studies to conceptualize

liquid water as a mixture. In 1891, Vernon suggested that the maximum density of water molecules could be attributed to polymerization between water molecules^{5,6,8}. In 1892, Röntgen, the discoverer of X-rays, introduced the idea that water is a mixture of species in various states, describing it as a saturated solution of ice molecules. This theory provided a broader explanation for many anomalies of water, such as the maximum density observed at 4 °C and the decrease in water viscosity with increasing pressure. The concept of water as a mixture laid a strong foundation for subsequent theories on the molecular states of water^{5,9}. The study of water's structure advanced significantly with the application of X-ray techniques in crystallography. Debye and Scherrer utilized X-rays to investigate the structure of various liquids, including water^{10,11}. However, limitations in data extraction methods at the time hindered deeper analysis. In 1922, Bragg proposed a model of ice structure based on X-ray studies, describing each water molecule as interacting with four neighboring molecules in a tetrahedral arrangement^{6,12}. This model had a profound impact on understanding water molecule interactions. Over time, advancements in experimental techniques and computer simulations have greatly refined the study of water's structure. Current consensus holds that water molecules interact with one another through hydrogen bonding, forming an extensive hydrogen-bonding network. Each water molecule can participate in up to four hydrogen bonds. These detailed insights into the structure of water have significantly

advanced research across fields such as biology, environmental science, and medicine. Notably, water's exceptional solvent properties enable the dissociation of electrolytes, leading to electrolyte solutions with more extensive practical applications than pure water. Consequently, the influence of ions on the structure of water has become a central focus in studies of water's structural properties.

Ion-solvent interactions in electrolyte solutions

The Debye-Hückel model is one of the most classical frameworks for describing electrolyte solutions¹³. In this model, ions are assumed to be completely dissociated, and the solvent is treated as a continuous dielectric medium, with its molecular structure ignored. As a result, the model accounts only for ion-ion interactions while neglecting direct interactions between ions and solvent molecules. However, in concentrated solutions or for weak electrolytes, ions are not fully dissociated, limiting the applicability of the classical Debye-Hückel model to dilute solutions of strong electrolytes. Bjerrum later modified the model by introducing the concept of ion pairs in solution, accounting for the aggregation of ions via electrostatic interactions when the separation distance falls below a certain threshold¹⁴. On the other hand, interactions between solvent molecules and ions were first theorized in 1920 by Born, who proposed

a formula for solvation energy¹⁵. However, this formula also treated the solvent as a continuous dielectric medium, disregarding its molecular characteristics. In 1933, Bernal and Fowler provided a new perspective by considering that ions induce reorientation of the dipoles of solvent molecules in their vicinity, taking into account the specific interactions between ions and individual solvent molecules¹⁶. With the development of this understanding, efforts to quantify the strength of ion-solvent interactions have emerged. For example, Gutmann introduced the *donor number* (DN) based on the enthalpy change in organic reactions, reflecting the electron-donating ability of solvent molecules, which is widely used to evaluate cation solvation¹⁷. Similarly, the *acceptor number* (AN), based on changes in electron density of a reference substance in different solvents, measures the electron-accepting ability of solvent molecules and is commonly used to assess anion solvation¹⁸. The way ions interact with solvent molecules significantly determines the physicochemical properties of electrolyte solutions, including density, viscosity, heat capacity, conductivity, and reactivity. Hence, understanding ion-solvent interactions is of paramount importance.

Initially, the need to understand these interactions stemmed from the study of chemical reactions in aqueous solutions¹⁹. Over time, this understanding has become crucial across disciplines, especially in electrochemistry, encompassing applications such as electrochemical energy storage devices²⁰⁻²⁶, water electrolysis²⁷⁻³⁰, and

electroplating^{31–33}. Notably, electrochemical research often involves studying the structure of electrolyte solutions at solid-phase interfaces, such as electrodes and metal oxides, where interactions among ions, water molecules, and solid surfaces play a critical role.

Analyzing the hydration shell structure around ions is a common approach to evaluating their influence on water structure. Techniques like X-ray diffraction and neutron diffraction have been extensively applied. For instance, Bouazizi et al. used X-ray diffraction to investigate the microscopic structure of NaCl aqueous solutions at various concentrations. Through radial distribution functions derived from the diffraction data, they examined how atomic distances change with concentration, revealing that the addition of NaCl reduces the extent of hydrogen bonding between water molecules³⁴. Similarly, Harsányi et al. studied RbBr aqueous solutions at two concentrations using neutron and X-ray diffraction, reporting findings consistent with Bouazizi's observations³⁵. For highly concentrated solutions, Borodin et al. combined small-angle X-ray scattering (SANS) with molecular dynamics (MD) simulations to study a 21 mol kg⁻¹ lithium bis(trifluoromethanesulfonyl)amide (LiTFSA) aqueous electrolyte. Their results revealed nanoscale heterogeneity in the solution due to disproportionate Li⁺ solvation, resulting in water-rich and ion-rich regions. The stable electrochemical potential of water in the system was attributed to the water-rich regions,

where water molecules predominantly hydrated Li^+ ions³⁶. There are numerous reports on diffraction results related to dissolution structures. These diffraction results, combined with molecular dynamics (MD) simulations³⁷⁻⁴¹, can effectively construct comprehensive structural models of solutions.

On the other hand, the complex hydrogen bonding between water molecules is widely regarded as one of the primary reasons for water's classification as a structurally complex liquid. Thus, monitoring changes in the number of hydrogen bonds between water molecules serves as a reliable indicator of the interactions between ions and water molecules¹. Spectroscopic techniques are the most commonly employed methods to study variations in hydrogen bonding. Quantitative analysis is especially crucial for evaluating changes in water structure. However, traditional Raman spectroscopy, which detects scattered light resulting from the interaction of incident light with molecules, often faces challenges in achieving robust quantitative detection in practical applications. Infrared (IR) spectroscopy, while adhering to Beer-Lambert's law, is constrained by the strong absorption of infrared light by water. Transmission-based IR spectroscopy typically requires the use of cuvettes with micro-scale optical paths to capture the complete vibrational spectrum of water molecules. This short optical path reduces the sample volume, making the results highly sensitive to minor solvent evaporation and leading to significant impacts on the signal-to-noise (S/N) ratio,

thereby limiting the method's quantitative accuracy. Although attenuated total reflection (ATR) IR spectroscopy can be employed to analyze solution samples^{42,43}, the penetration depth of the evanescent wave into the solution is directly related to the wavelength of light, making it challenging to ensure a consistent optical path. This variability can lead to quantitative deviations. Moreover, ATR-IR spectroscopy measures the solution structure at the solution/prism interface. Due to interactions between the solution and the prism, the interfacial structure may differ slightly from the bulk solution structure. Nuclear magnetic resonance (NMR) can quantitatively detect changes in water molecule populations. However, the magnetic field frequencies used in NMR are lower than the exchange frequency of hydrogen atoms between water molecules. As a result, NMR only captures an averaged signal of the dynamic exchange among hydrogen nuclei in different hydrogen-bonding states, making it difficult to distinguish specific hydrogen-bonding configurations in detail. Consequently, there remains a lack of spectroscopic methods capable of rigorously quantifying the bulk solution structure. Among the numerous spectroscopic studies of water molecules⁴⁴⁻⁵², near-infrared (NIR) spectroscopy has demonstrated exceptional advantages.

Near-infrared spectroscopy

Near-infrared spectroscopy (NIR) is a molecular vibrational spectroscopic technique based on the absorption, diffuse reflection, and emission of near-infrared light within the wavelength range of 800– 2500 nm⁵³⁻⁵⁵. Although near-infrared light was discovered by British scientist Herschel around 1800 and applied by Abney and Festing in the 1880s for detecting simple organic compounds^{53,56}, its development lagged behind other molecular vibrational spectroscopies such as infrared (IR) and Raman spectroscopy. This slower development was primarily due to limitations in spectrometer technology and the complexities associated with NIR spectral data analysis⁵³⁻⁵⁵. Norris was a pioneer in the practical application of NIR spectroscopy, using it to analyze and evaluate the quality of agricultural products. Leveraging the non-destructive nature of NIR spectroscopy, he developed quantitative detection methods for parameters such as water content in agricultural products⁵⁷. In 1977, Jöbsis extended NIR spectroscopy into the medical field, applying it for non-invasive detection of oxidation states within animal tissues^{58,59}. Subsequently, with the rapid advancement of spectrometer technologies, NIR spectroscopy has found expanding applications in biology, medicine, chemistry, and other fields. The unique features of NIR spectroscopy primarily arise from the anharmonicity of molecular vibrations. Due to this anharmonicity, NIR spectra

typically exhibit spectral bands corresponding to overtones and combination modes involving $X-H$ ($X = C, N, O$) functional groups. The anharmonic nature of $X-H$ vibrations also leads to significantly stronger absorption intensities for these groups compared to others⁵³, making the corresponding bands more observable and analyzable. Since most of the observed bands in NIR are overtones or combination modes, the peak shifts induced by molecular interactions, such as hydrogen bonding changes, are often larger than those observed in IR spectroscopy⁶⁰. Furthermore, the anharmonicity allows transitions to higher vibrational energy levels, but the probability of such transitions is much lower compared to transitions to adjacent excited states. This results in much weaker absorption intensities in the NIR region compared to the mid-IR region. However, this characteristic also enables NIR spectroscopy to avoid the need for extensive sample preparation. Longer optical path lengths can be used, ensuring a high signal-to-noise (S/N) ratio, improving quantitative analysis accuracy, and facilitating non-destructive analysis. Given these advantages, NIR spectroscopy is particularly well-suited for studying hydrogen bond perturbations and intermolecular interactions caused by external factors, such as changes in ion concentrations, making it an invaluable tool in this area of research.

The motivation of this study

As discussed earlier, near-infrared spectroscopy has demonstrated excellent capabilities in assessing the quality of agricultural products. This capability has provided us with valuable insights for exploring similar applications. For example, the freshness of vegetables can be detected by monitoring the state of water in the cell fluid (an electrolyte solution) within their cells. When the cells are fresh, the water molecules are confined within the cellular structure, with some interacting with the cell wall. As vegetables spoil and the plant cell walls are damaged, the number of "restricted" water molecules that interact with the cell wall changes, which can be well-reflected in the spectrum. We hypothesize that this cellular system is similar to electrolyte solutions or solid-liquid systems.

In electrolyte solutions, water molecules interact with ions through their dipoles, forming hydration shells. According to the Bernal-Fowler model, water molecules in the first hydration shell are strongly bound to ions, moving along with them and preventing them from behaving like free water molecules^{61,62}. Stirnemann et al. pointed out that at high salt concentrations, ions slow down the dynamics of water, even though these ions increase water molecular dynamics in dilute solutions⁶³. The Bakker group used dielectric relaxation spectroscopy to study the reorientation time of water molecule

dipoles⁶⁴. They indicated that water molecules in ion pairs or clusters are arranged in an orderly fashion by the electric field of the ions, which slows down their reorientation dynamics and reduces their response to external electric fields, thus lowering the solution's capacitance as the concentration increases.

On the other hand, Maki et al. reported that using quantitative ^1H NMR and T_1 , T_2 relaxation times to measure water molecules in aqueous solutions revealed that the observed values were consistently lower than the calculated values, showing significant ion-type and concentration dependence^{65,66}. They attributed this underestimation to the reduced mobility of water molecules, making them harder to detect with NMR. Therefore, we can regard the water molecules involved in ion hydration as "restricted" water molecules confined within a few nanometers, much like those at the solid-liquid interface. Similarly, for water molecules at the solid-liquid interface, Hansen reported that there is water molecules arranged in an ordered fashion, different from bulk water, on the solid surface⁶⁷. He suggested that water molecules on hydrophilic surfaces are more tightly arranged, forming structures similar to ice, and that these molecules exhibit lower diffusion rates. Thus, these water molecules can also be considered "restricted" water molecules.

In summary, in this study, we utilize near-infrared spectroscopy to observe the molecular behavior of these "restricted" water molecules in different systems,

combining this with other physical and chemical properties of the systems to discuss the impact of these "restricted" water molecules on the system. Particularly in high-concentration aqueous solutions, where nearly all water molecules are influenced by ions and become "restricted," this leads to more direct and significant effects on the physical and chemical properties of the system due to the water molecules' response to external perturbations.

It is important to note that the same term can represent entirely different states of water molecules depending on the context, such as "free water." In electrolyte solutions, from the perspective of hydrogen bond count, water molecules in the first hydration shell of an ion are typically considered not to have hydrogen bonds, and such water molecules are often referred to as "free water molecules." However, from the solution perspective, water molecules that do not interact with ions are commonly called "free water molecules." To avoid ambiguity, we define "free water" in this study as water molecules that are involved in ion hydration but do not participate in hydrogen bonding.

The structure of the chapters is as follows:

In chapter 1, we focus on the influence of "restricted" water molecules on the spectroscopy of aqueous solutions. We emphasize a quantitative study of the interactions between water molecules and ions in electrolyte solutions using near-infrared (NIR) spectroscopy to detect the stretching vibrations of OH groups. The

experimental subjects are defined as concentrated aqueous solutions. Specifically, after confirming the excellent quantitative detection capabilities of NIR spectroscopy, we found that the detected values of water molecules in the solutions were lower than the calculated values of water molecules present in the actual solutions. We discuss the strengths of ion-dipole interactions between water molecules and various cations and anions, relating these interactions to the anomalously low detected values of water molecules, thereby providing a new perspective for quantitatively evaluating the interactions between water molecules and ions.

In chapter 2, we explore the behavior of "restricted" water molecules in competitive solvation situations within water-molten salt mixtures, specifically in $(\text{Ca}_{1-x}\text{Zn}_x)\text{Cl}_2 \cdot 6\text{H}_2\text{O}$. Building on the conclusions established in the first chapter regarding the influence of ion-water molecule interactions on the detected values of water molecules, we investigate the changes in detected values of water molecules at different mixing ratios. Using Raman spectroscopy, we assess the interactions between ions and between ions and water molecules, and in conjunction with measurements of the mixture's viscosity and conductivity, we detail how the addition of Zn^{2+} disturbs the structure of the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ solution and explains the behavior of water molecules. This further validates the quantitative evaluation method of the interactions between water molecules and ions established in the first chapter.

In chapter 3, we discuss the competitive effects of ions and solids on the mobility of water molecules in solid-liquid coexistence systems. Specifically, we investigate the impact of water molecule behavior in a water-in-salt electrolyte on the conductivity of mixed systems. In the first section, we examine the dependence of the liquid phase volume fraction on the conductivity of the TiO_2 powder/ 20.5 mol kg^{-1} LiTFSa electrolyte coexistence system. We employ diffuse reflectance NIR spectroscopy, Raman spectroscopy, and the T_2 relaxation times of H nuclei in H_2O to study the behavior of ions and water molecules in the solid-liquid mixed system, elucidating the reasons behind the anomalous changes in conductivity within the TiO_2 powder/ 20.5 mol kg^{-1} LiTFSa electrolyte coexistence system. In the second section, we investigate changes in conductivity within the mixed system by altering the surface charge of TiO_2 to adjust the strength of interactions between ions and the solid phase, discussing the surface charge dependence of conductivity in the TiO_2 powder/ 20.5 mol kg^{-1} LiTFSa electrolyte coexistence system.

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CHAPTER 1

**Anion species dependence of non-detected water
molecules along the Hofmeister series in various
lithium salts in near infrared and nuclear magnetic
resonance spectroscopy**

1. Introduction

Electrolyte solutions are widely used in industrial production, daily life and other fields. The differences in the physicochemical properties of electrolyte solutions are usually thought to be due to the differences in the ion-solvent intermolecular interactions, and ion-ion interactions contained therein. In an electrolyte solution, ions solvate with surrounding solvent molecules through ion-dipole, and ion-induced dipole interactions,¹ to form local structures that are microscopically different from those of the bulk solvent. An activity of the solvent molecules interacting with the ions is hindered to its solvation behavior, resulting in the various properties such as vaporization,² electrochemical reaction,³ and so on. These ion-solvent molecule interactions are often considered to be important in determining the properties of electrolyte solutions.

Numerous studies have been reported on the use of molecular vibrational spectroscopy to probe the solution structure of electrolyte solutions by studying in detail the solvation behavior in various viewpoints such as precise isosbestic points occur in the Raman OH-stretching spectra from liquid water,⁴ a role of mixed solvation and ion pairing in the solution structure of lithium electrolytes,⁵ and identification and properties of ion-pairs in the aqueous solutions by FT-IR measurements.⁶ However, there

is still a lack of a spectrum that can quantitatively characterize the changes in solution structure. In particular, for electrolyte aqueous solutions, the complex hydrogen bonding between water molecules is usually considered to be one of the most important reasons why water is a structured liquid.⁷ Therefore, the quantitative detection of water molecules is of great importance for studying the structural changes of solutions and quantitatively describing the interactions between ions and water molecules. Although the absorbance of intramolecular vibrations in infrared spectroscopy follows Lambert-Beer's law, quantitative measurement is difficult for molecules that absorb infrared light extremely strongly, such as water, because it is difficult to select window materials and guarantee reproducibility of optical path length in transmission method measurements. Attenuated total reflection (ATR) infrared spectroscopy can also detect the bulk solution structure as well as the solution structure at the interface,⁸ however the penetration depth of the evanescent wave in the solution is directly related to the wavelength of the light, so it is difficult to ensure a certain optical range, which can easily lead to bias in quantitative detection. Raman spectroscopy is based on the detection of the intensity of scattered light, and therefore cannot ensure the quantitative detection of the sample.

NMR spectroscopy is a possible candidate for quantitative detection of the amount of nuclides. Maki et al. reported that it is possible to study interionic, ion-water molecule interactions in solution by quantitative ¹H NMR (¹H qNMR) studies of the

variation of the number of water molecules in an aqueous solution as a function of concentration.^{9,10} However, these studies tended to understand more about the effect of different cations on the structure of aqueous solutions and neglected the effect of anions on the structure of aqueous solutions. Moreover, the frequency of the magnetic field used in ^1H NMR detection is 43.58 MHz, which is less than the exchange rate of ^1H nuclei between water molecules. A longer range of the detection time leads to an averaging of the motion of water molecules during the ^1H NMR detection, and therefore, only a single signal peak is usually observed in the ^1H NMR spectra of water molecules, which cannot be relied upon to distinguish between different states of water states such as solvated and free water molecules.

Near-infrared (NIR) spectroscopy is an absorption technique based on molecular anharmonic vibrations.¹¹ Due to the non-simple harmonic nature of molecular vibrations, NIR spectroscopy typically reveals spectral bands corresponding to octave and combinatorial modes of $X\text{-H}$ (typically $X = \text{C}, \text{N}, \text{and O}$) functional groups, and the anharmonic nature of the $X\text{-H}$ vibrations results in the absorption intensity of the relevant groups being significantly greater than that of the other groups,¹² making these spectral bands easier to observe and analyze. Since almost all of what is observed in the NIR are doubled or combined modes, this makes the magnitude of the peak shifts caused by changes in intermolecular interactions larger than in the IR spectrum.^{12,13} In

addition, since the absorption intensity of substances in the NIR region is much lower than that in the mid-infrared region, NIR spectroscopy usually does not require pretreatment of the sample and allows the use of long optical path lengths of the cell, which guarantees the S/N ratio and ensures the accuracy of quantitative analysis. In view of the above advantages, NIR spectroscopy is valuable in observing hydrogen bonding perturbations between water molecules caused by external factors (e.g., changes in ion concentration), and intermolecular interactions.¹⁴

In this study, we first demonstrated the superior quantitative detection capability of near-infrared spectroscopy by detecting solvent molecules in solid-liquid coexisting systems in a physically heterogeneous mixture. Similar to the quantitative NMR measurement, the intensity of the solvent volume in the near-infrared measurement shows non-detectable intensity with increasing electrolyte solution concentration. We investigated the cause of this non-detect intensity and examined the correlation between the solvent-ion interaction, and compared it with the non-detect phenomenon in the NMR measurement.

2. Experimental

2.1 Preparation of solid-liquid coexistence

To confirm the quantitative accuracy of the transmission spectrum measurements, NIR spectra was measured on samples in which SiO₂ powder and various kinds of the liquid compounds for electrolyte solvents were physically mixed.

Fumed silica (Nippon Aerosil Co., Ltd., AEROSIL 200F) was prepared as the solid phase. The fumed silica was dried in a muffle furnace at 800 °C and brought down to room temperature in a desiccator in vacuum. The dried fumed silica was stored in a glove box in Ar atmosphere. The particle size of the dried silica was characterized by Field Emission Scanning Electron Microscope (FE-SEM, JEM-6335F, JEOL Ltd.), and the density of the particles was measured by Archimedes method using a pycnometer. The SEM and particle size distribution of the dried SiO₂ are shown in Fig. 1 and Table

1. The specific equation is as follows:

$$\rho = \frac{m_b - m_a}{m_b - m_a - m_c + m_d} \times \rho_s \quad (1)$$

where: m_a : the mass of the empty pycnometer; m_b : the total weight of the sample to be measured and the pycnometer; m_c : the total weight of the sample to be measured

and the pycnometer and the liquid; m_d : the total weight of the empty pycnometer and the liquid; ρ_s : the density of the liquid.

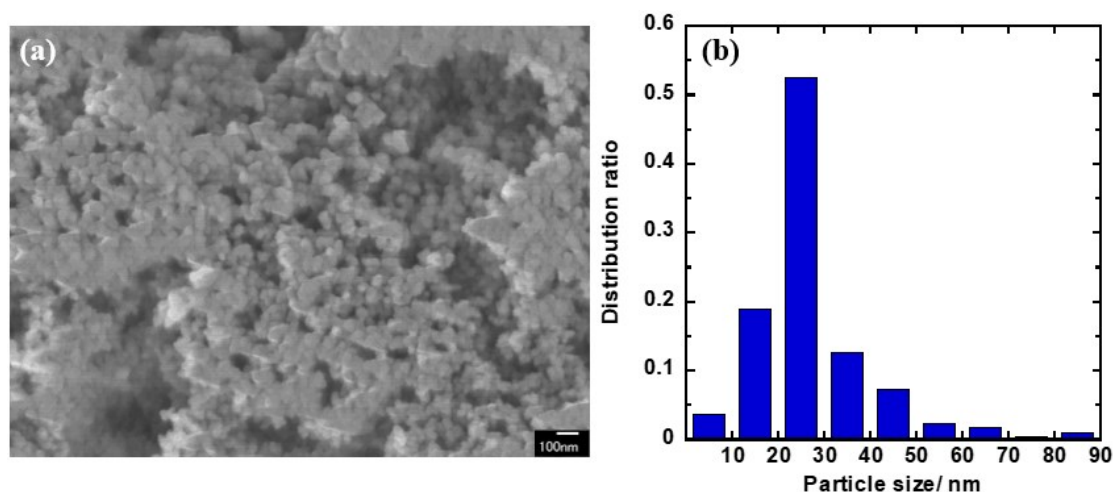


Figure 1. Characterization of fumed SiO₂. (a) SEM image of SiO₂ after drying at 800 °C and (b) particle size distribution ratio after drying at 800 °C.

Table 1. Physical properties of fumed SiO₂ as solid phase after drying.

Particle size	34 nm
Density	2.2 g cm ⁻³
Specific surface area	192.6 m ² g ⁻¹

For liquid phase, deionized distilled water (conductivity < 0.055 $\mu\text{S cm}^{-1}$) was obtained by purification of Advantec RFD240RA. Propylene carbonate (PC) (Nacalai Tesque Inc.), 1, 2-Dimethoxyethane (DME) (Nacalai Tesque Inc.) were added with molecular sieve (Nacalai Tesque Inc.) to remove the water, and after the water content was tested by Karl Fischer (Mitsubishi Chemical, CA-310) at no more than 15 ppm, PC

and DME were used for mixing with the solid phase. In this work, the volume fraction of the SiO₂ solid phase in the mixed system ranges from 0 to 20 vol%. Solid-liquid coexisting samples were made by mixing water homogeneously with dried silica solids in an alumina mortar by volume fraction of liquid phase as following equation:

$$\text{Volume fraction of liquid phase} = \frac{W_{\text{liquid}} / \rho_{\text{liquid}}}{W_{\text{liquid}} / \rho_{\text{liquid}} + W_{\text{solid}} / \rho_{\text{solid}}} \quad (2)$$

where W_{liquid} , W_{solid} , ρ_{liquid} , ρ_{solid} represent the weight of the liquid, the weight of the solid, the density of the liquid, and the density of the solid, respectively. The schematic drawing about solid-liquid mixtures is shown in Fig. 2.

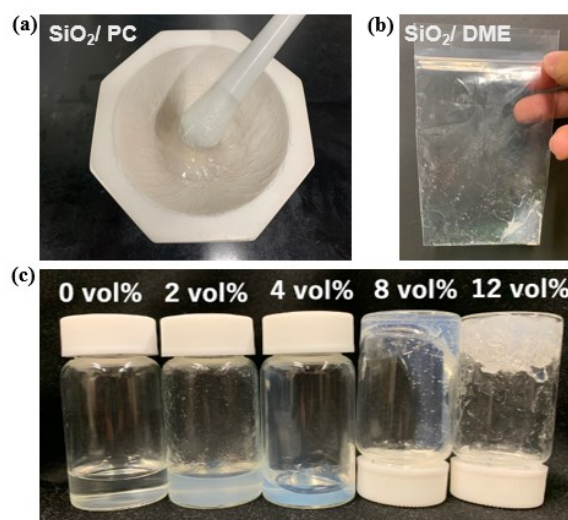


Figure 2. Images about solid-liquid mixtures. (a) Homogeneous mixing of PC and fumed SiO₂ using a mortar and pestle; (b) Homogeneously mix DME and SiO₂ in a sealed transparent bag to prevent the evaporation of DME; (c) The states of samples obtained at different mixing ratios in the H₂O/ SiO₂ system and the white text in the figure indicates the volumetric fraction of the solid phase in the mixture. All procedures were conducted in an argon-filled glove box when using organic solvents as the liquid phase.

The average apparent thickness of the liquid phase was calculated as follows. At first, the liquid phase was assumed to be uniformly distributed around the Fumed SiO₂ particles, and the thickness of this distributed liquid phase is referred to as the average apparent thickness in this study. Therefore, the solid-liquid coexistence system under this solid/liquid mixing ratio was considered as a face-centered cubic structure, as illustrated in Fig. 3a. using Eq. 3:

$$d = \left(\frac{1}{16\sqrt{2}} V \right)^{\frac{1}{3}} - r = \left[\left(\frac{\pi}{3\sqrt{2}x} \right)^{\frac{1}{3}} - 1 \right] r \quad (3)$$

where d is the average thickness of the liquid phase on the surface of the solid particle (nm); V is the unit lattice volume; r is the average radius of the solid particle, derived from Fig. 1d; and x is the volume fraction of the solid phase. The calculated results are shown in Fig. 3b.

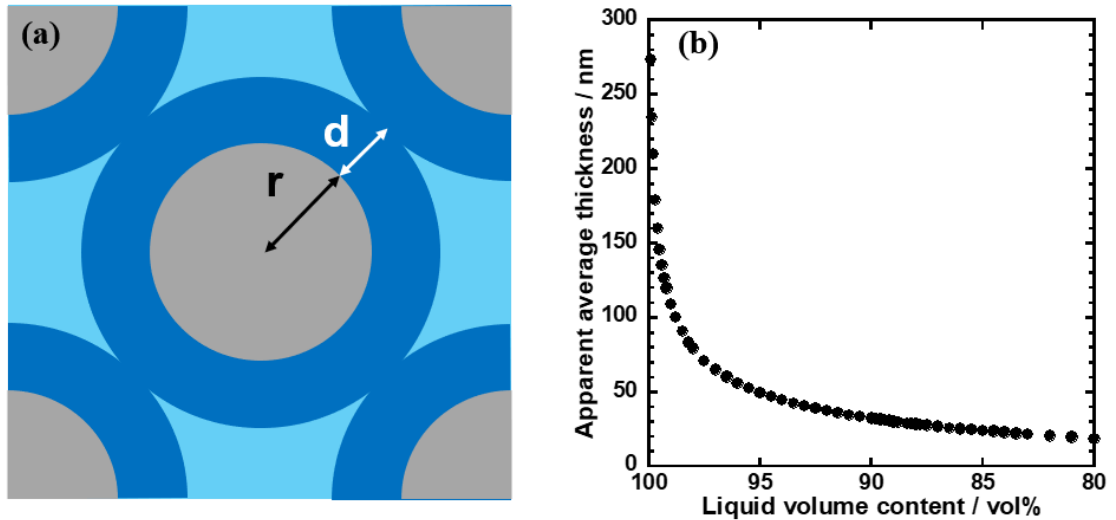


Figure 3. (a) Ideal model for solid-liquid coexistence system. r : radius of SiO₂ particles, d : average liquid phase thickness on the particle surface; (b) Relationship between average thickness of liquid phase and volume fraction of liquid phase.

2.2 Preparation of electrolyte solutions

LiCl (Nacalai Tesque Inc., Guaranteed Reagent (GR)), LiNO₃ (Kishida Chemical Co., Ltd), LiClO₄ (Kishida Chemical Co., Ltd), Li₂SO₄ (Nacalai Tesque Inc., GR), Lithium bis(trifluoromethanesulfonyl)imide (LiTFSA) (Kanto Chemical Co., Inc), NaCl (Nacalai Tesque Inc., Extra Pure Reagent (EP)), NaNO₃ (Nacalai Tesque Inc., GR), NaClO₄ (FIJIFILM Wako Pure Chemical Co., Ltd, 1st Grade), Na₂SO₄ (Nacalai Tesque Inc., GR), KCl (Nacalai Tesque Inc., GR), KBr (Nacalai Tesque Inc., EP), KNO₃ (Nacalai Tesque Inc., GR), K₂SO₄ (Nacalai Tesque Inc., GR) were dissolved in deionized distilled water (conductivity < 0.055 $\mu\text{S cm}^{-1}$) to make the mother solutions, and the concentration of the mother solutions was determined by weight method and plasma atomic emission spectroscopy (ICP-AES; Horiba Ltd., ULTIMA 2000). By adding different masses of deionized water to the same weight of stock solution, dilute to different concentrations of electrolyte solutions. The densities of all solutions were measured using a U-shaped vibrating-tube density meter (Anton Paar, model DMA 5000M) which was calibrated by air and water. The concentration and density data for all solutions are provided in Table 2-4.

Table 2. Various concentration indications and density for aqueous solutions of all Li salts.

LiTFSA		LiCl		LiNO ₃		LiClO ₄		Li ₂ SO ₄	
mol L ⁻¹	g cm ⁻³	mol L ⁻¹	g cm ⁻³	mol L ⁻¹	g cm ⁻³	mol L ⁻¹	g cm ⁻³	mol L ⁻¹	g cm ⁻³
0.10	1.013	0.50	1.009	0.42	1.015	0.20	1.010	0.08	1.005
0.32	1.045	1.00	1.021	1.09	1.043	0.42	1.024	0.19	1.015
0.55	1.078	1.51	1.033	1.58	1.062	0.61	1.035	0.34	1.028
0.87	1.126	2.00	1.044	2.12	1.083	0.82	1.049	0.42	1.036
1.31	1.189	2.25	1.049	2.61	1.103	1.03	1.062	0.55	1.048
1.33	1.193	2.75	1.060	3.05	1.120	1.25	1.075	0.79	1.068
1.64	1.237	3.00	1.066	3.54	1.140	1.39	1.083	1.01	1.087
1.94	1.281	3.25	1.071	4.27	1.168	1.60	1.096	1.25	1.107
2.30	1.333	3.50	1.076	4.38	1.172	1.79	1.108	1.43	1.122
2.73	1.393	4.00	1.087	4.94	1.194	1.96	1.118	1.63	1.138
3.08	1.443	4.50	1.098	5.58	1.219	2.19	1.132	1.78	1.150
3.47	1.496	5.00	1.108	6.33	1.248	2.39	1.144	2.09	1.174
3.96	1.565	5.49	1.118	6.82	1.264	2.52	1.152	2.23	1.186
4.60	1.652	5.99	1.129	7.41	1.289	2.56	1.155	2.35	1.195
5.13	1.722	6.49	1.139	7.68	1.299	2.74	1.166	2.51	1.207
		6.99	1.150	7.92	1.309	3.17	1.191	2.81	1.230
		7.49	1.160	8.84	1.343	3.37	1.204		
		7.99	1.171	9.08	1.352	3.64	1.220		
		8.49	1.181	9.52	1.369	3.87	1.234		
		8.99	1.191	9.71	1.376	3.97	1.240		
		9.50	1.202			4.10	1.248		
		9.92	1.211			4.40	1.266		

Table 3. Various concentration indications and density for aqueous solutions of all Na salts.

NaCl		NaNO ₃		NaClO ₄		Na ₂ SO ₄	
mol L ⁻¹	g cm ⁻³	mol L ⁻¹	g cm ⁻³	mol L ⁻¹	g cm ⁻³	mol L ⁻¹	g cm ⁻³
0.10	1.001	0.22	1.010	0.44	1.031	0.17	1.018
0.25	1.007	0.51	1.026	0.64	1.046	0.35	1.038
0.40	1.014	1.15	1.062	1.12	1.083	0.53	1.057
0.50	1.017	1.69	1.090	1.28	1.095	0.69	1.075
0.60	1.022	2.14	1.114	1.63	1.121	0.86	1.094
0.81	1.029	2.42	1.129	2.14	1.159	1.10	1.119
1.01	1.037	3.25	1.172	2.66	1.197	1.23	1.133
1.22	1.045	3.96	1.208	2.85	1.211	1.46	1.156
1.41	1.053	4.17	1.219	3.31	1.245	1.66	1.176
1.51	1.057	4.42	1.231	3.87	1.285	1.97	1.207
1.61	1.060	5.20	1.270	4.22	1.311	2.18	1.227
1.81	1.068	5.64	1.292	4.75	1.349	2.48	1.256
2.01	1.076	6.06	1.312	5.35	1.391		
2.20	1.083	6.82	1.349	6.05	1.442		
2.41	1.091	7.10	1.363	6.64	1.483		
2.51	1.094	7.81	1.396	7.16	1.520		
2.61	1.098			7.93	1.574		
2.81	1.105			8.51	1.615		
3.03	1.113			9.60	1.692		
3.21	1.120						
3.51	1.131						
3.80	1.141						
4.03	1.149						

Table 4. Various concentration indications and density for aqueous solutions of all K salts.

KCl		KNO ₃		KBr		K ₂ SO ₄	
mol L ⁻¹	g cm ⁻³	mol L ⁻¹	g cm ⁻³	mol L ⁻¹	g cm ⁻³	mol L ⁻¹	g cm ⁻³
0.20	1.007	0.22	1.011	0.15	1.010	0.05	1.003
0.40	1.016	0.36	1.020	0.29	1.022	0.09	1.010
0.60	1.025	0.51	1.029	0.43	1.034	0.13	1.015
0.80	1.034	0.69	1.039	0.60	1.047	0.19	1.023
1.00	1.043	0.88	1.051	0.75	1.060	0.24	1.029
1.20	1.052	1.06	1.062	0.92	1.074	0.28	1.035
1.40	1.061	1.26	1.074	1.08	1.087	0.33	1.041
1.60	1.069	1.44	1.084	1.24	1.100	0.38	1.048
1.80	1.078	1.66	1.097	1.40	1.113	0.41	1.052
2.01	1.087	1.82	1.107	1.60	1.129	0.48	1.061
2.21	1.096	2.01	1.118	1.77	1.143	0.53	1.067
2.33	1.099	2.26	1.132	1.91	1.154	0.58	1.074
2.52	1.112	2.42	1.141	2.14	1.173	0.61	1.078
2.72	1.117	2.70	1.158	2.34	1.189	0.67	1.085
3.00	1.130	2.96	1.172	2.50	1.202		
3.10	1.134	3.19	1.185	2.75	1.222		
3.20	1.138			2.97	1.239		
3.30	1.142			3.16	1.255		
3.49	1.150			3.41	1.275		
3.69	1.158			3.64	1.293		
4.04	1.173			3.85	1.309		
				4.10	1.329		
				4.34	1.348		
				4.71	1.377		

2.3 ^1H NMR measurement

A bench-top magnetic resonance instrument with a permanent magnet (Spinsolve-43, Magritec Inc.) was used for the qNMR measurements in this study. The temperature was set at 28.0 °C, the measurement parameters were frequency 43.56 MHz, receiver gained 28 dB, data acquisition time 16 s, and number of integrations 4 times. The pulse width was adjusted for each solution concentration, and the value with the largest peak area was used. Data processing after ^1H qNMR observation was performed using the NMR analysis software “Mestre Nova” and the area intensity of the NMR signal was obtained by the section quadrature method with an integration width of 2 ppm. The ^1H chemical shift was measured under the same conditions as for the ^1H qNMR measurement, but since the measurements in this experiment were performed over a very narrow concentration interval, it was found that simply reading the peak that appeared and using its position as the chemical shift would result in some variation. Therefore, to obtain a more accurate chemical shift value, dimethyl sulfoxide (DMSO), which has a known ^1H chemical shift of 2.490 ppm, was inserted as an internal reference material using a duplex tube, and the ^1H chemical shift, δ of the solution was calibrated from the deviation of the ^1H chemical shift of DMSO as in Eq. 4:

$$\delta_{\text{H}} = \delta_{\text{H}}(\text{sample}) + (2.490 - \delta_{\text{H}}(\text{DMSO})) \quad (4)$$

The system used for this ^1H relaxation time measurement was Acorn Area (Xigo Nanotools), which is an FT-NMR system dedicated to ^1H relaxation time measurements of permanent magnets. All measurements are performed at a temperature of 25.0 °C, and the parameters were set to a magnetic field strength of 0.3 T, an observation frequency of 13.06 MHz, a time of integrations of 4 times, and a receiver gain of 15 dB. The Carr-Purcell-Meiboom-Gill (CPMG) method for the spin-spin relaxation time (T_2) measurement. The CPMG method is a method of obtaining T_2 from the decrease in transverse magnetization during repeated spin echoes with successive 180° pulses at regular intervals, and by inverting pulses at short intervals, the effect of resonance frequency deviation can be eliminated.

2.4 Near-infrared spectra measurement and spectral processing

The NIR spectra of all samples were measured using UV-Vis-NIR (JASCO-V7200) at room temperature using the transmission method. A cell with an optical path length of 10 mm (made by Nippon Sheet Glass Company or Tosoh Quartz Corporation) was used. For aqueous solution measurements, a 9 mm quartz block was placed inside the cell and the optical path length was set to 1 mm. The light source is a tungsten halogen lamp, and the detector was a cooled PbS photoconductive element with a capture time

of 0.2 s for the NIR signal and a data detection of 1 nm. The detection range was 1200-2500 nm for water, 1580-2015 nm for PC and 1000-2240 nm for DME. All measured spectra were converted from wavelength (nm) converted to wavenumber (cm^{-1}). The converted spectrum is then processed at equal intervals, and the entire spectrum has 2000 data points. The spectral baseline is determined, and the area of the part consisting of the spectrum and the baseline is integrated as the absorbance.

As an example, the near-infrared spectrum of water was baseline corrected for the near-infrared absorption peaks of water as shown in Fig. 4. The baseline is the line between the start and end wave numbers of the absorption peaks. The peak area of the portion comprising the baseline and the spectrum is integrated to be the absorbance A of the water:

$$A = \int_{\nu_0}^{\nu_1} \Delta I d\nu \quad (5)$$

where ν_0 is the starting wavenumber of the baseline and ν_1 is the ending wave number of the baseline, correspond to the start and end wavenumbers of the near-infrared absorption peaks at the combination band of the OH symmetric and asymmetric stretching vibrations of water molecules, respectively. ΔI is the difference in absorbance between the absorbance of the spectrum at the same wave number and the baseline. All areas of the NIR spectra were integrated by Origin lab software to obtain peak areas.

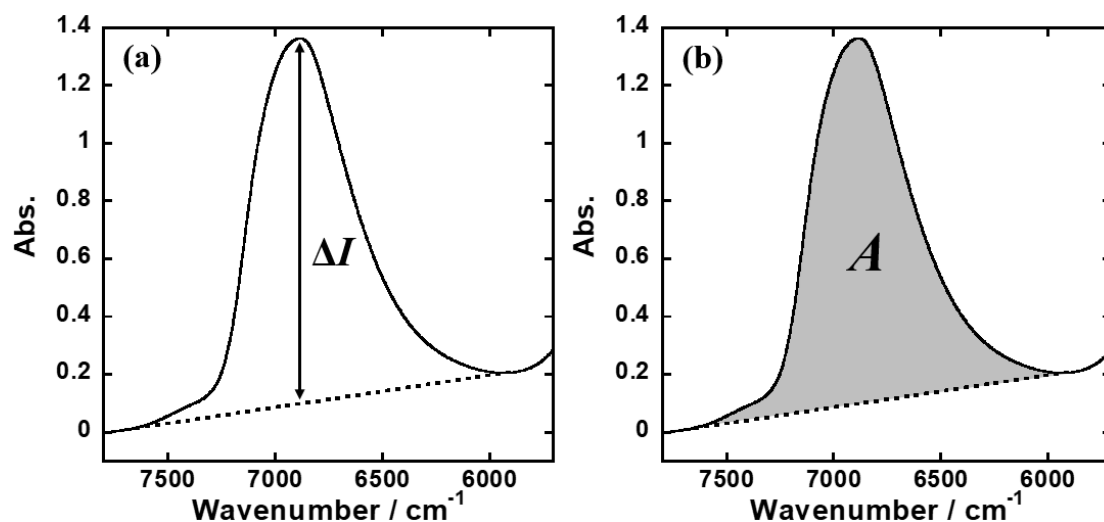


Figure 4. The starting and ending wave numbers of the near-infrared absorption peaks of water are used to determine the baseline, as shown by the dashed line in the figure. The difference in absorbance between the baseline and the absorption peak at the same wave number is ΔI , as shown in Figure a. The area of the component between the baseline and the absorption peak is integrated by Eq. 5, and the resulting peak area is used as the absorbance A of water over the entire wavelength range.

3. Results and discussion

3.1 Results of ¹H qNMR

Figure 5a and b presents the ¹H NMR spectra of aqueous solutions of LiCl and LiTfSA. Across the entire detection range, only a single signal peak corresponding to the proton in water molecules was observed. Notably, the chemical shift of the peak shifted towards higher fields as the solution concentration increased. This observation suggests an increase in the electron density around the protons of water molecules with

increasing solution concentration, likely due to the weakening or disruption of hydrogen bonding between water molecules caused by ion-water interactions. Figure 5c further illustrates the variation in the chemical shift of water protons as a function of Li^+ concentration in aqueous solutions of five different anionic Li salts. The results reveal that at the same Li^+ concentration, the weakening of hydrogen bonding between water molecules and strengthen the ion-solvent interaction follows the order:

$$\text{TFSA}^- < \text{ClO}_4^- < \text{Cl}^- < \text{NO}_3^- < \text{SO}_4^{2-} \quad (6)$$

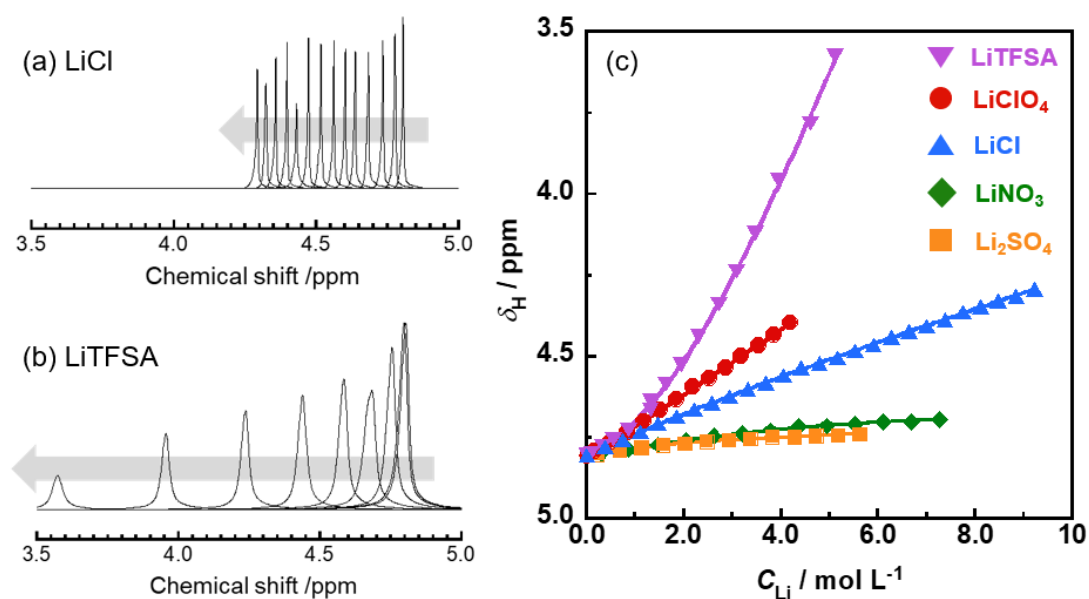


Figure 5. ^1H qNMR spectra of aqueous solutions of Li salts at different concentrations. (a) LiCl aqueous solution, (b) LiTFSA aqueous solution. From right to left, the concentration of aqueous solution gradually increases. (c) the variation of chemical shifts with concentration for five aqueous solutions of Li salts.

In ^1H qNMR, the intensity of the H signal peak is typically considered proportional to the number of protons in the solution, corresponding to the number of water

molecules. By integrating the signal peaks of the H nuclei, we obtained the peak areas, which were then used to calculate the detected concentration of water molecules in the solution by normalizing against the peak area and concentration of bulk water. The results are shown in Fig. 6. The vertical axis represents the amount of detected water molecule measured by ^1H qNMR to the water molecule concentration in pure water.

To facilitate a unified comparison of the detection value variations among the five kinds of Li electrolyte solutions, the horizontal axis is expressed the amount of water substance per unit volume.

It is worth noting that normally, c is considered to be the concentration of the solute in the solution as mentioned above. Whereas in this study the NMR signal of water and absorption of NIR light by water was observed, therefore, c represents “the concentration of water molecules” i. e., the amount of water substances in unit volume in the solution of each “concentration (the amount of solute)”, and its value was calculated by the following equation:

$$c_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{V_{\text{sol}}} = \frac{m_{\text{H}_2\text{O}}}{V_{\text{sol}}M_{\text{H}_2\text{O}}} = \frac{m_{\text{sol}} - m_{\text{electrolyte}}}{V_{\text{sol}}M_{\text{H}_2\text{O}}} = \frac{\rho_{\text{sol}} - c_{\text{sol}}M_{\text{electrolyte}}}{M_{\text{H}_2\text{O}}} \quad (7)$$

where m , V_{sol} , M , ρ_{sol} , and c_{sol} are the mass, the volume of the electrolyte solution, the molar mass of the substance, the density of the electrolyte solutions, and the concentration of the solute in the solution, respectively.

It can be observed that the amount of water molecules detected by ^1H qNMR are con-

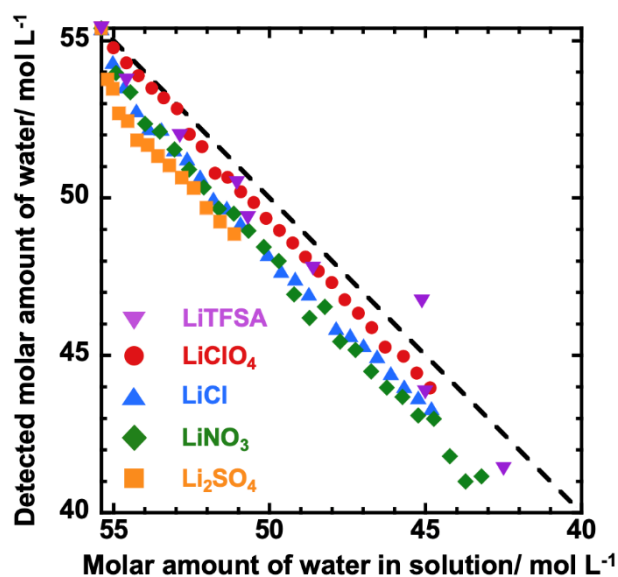


Figure 6. The relationship between the detected molar amount of water and the molar amount of water in Li electrolyte solutions detected by ^1H qNMR. The black dashed line in the figure indicates the correlations between identical values.

-sistently lower than the prepared amount, a phenomenon previously reported by Maki et al.^{9,10} Grunberg et al. demonstrated that in SiO_2 /water mixed systems, the signal peaks of water molecules broadened as the solid phase increased, and no ^1H NMR signal from water could be detected when the water volume fraction was below 3%. They attributed this to interactions between water molecules and the SiO_2 surface, which significantly reduced the mobility of water molecules near the surface, resulting in a dramatic shortening of the relaxation time and broadening of the peaks, thereby rendering the signals undetectable.¹⁵ Further studies by the Maki group have reported similar observations in solid-liquid mixed systems of gas-phase metal oxides/ LiClO_4 -PC solutions¹⁶ and in high-concentration aqueous solutions.^{9,10} Synthesizing these

results, the phenomenon was attributed to significant reductions in the mobility or activity coefficients of solvent molecules due to interactions between the ions or solid phase and the solvent molecules. These solvent molecules, with drastically restricted mobility, exhibited significantly shortened relaxation times and thus could not be detected by ^1H NMR.¹⁰

On the other hand, it is noteworthy that the non-detected amount of water molecules in different aqueous solutions displayed a pronounced anion dependence, following the order:

$$\text{TFSA}^- < \text{ClO}_4^- < \text{Cl}^- < \text{NO}_3^- < \text{SO}_4^{2-} \quad (6')$$

Based on prior studies, we associate the detected water molecule concentrations in different anionic solutions, as measured by ^1H qNMR, with the strength of ion-water interactions. Specifically, stronger ion-water interactions impose greater restrictions on water molecule mobility. To validate our hypothesis, the Spin-spin relaxation time T_2 of water molecules in each solution were measured. T_2 is a highly useful parameter for reflecting molecular mobility. The T_2 of protons is related to molecular dynamics and is highly sensitive to changes in interactions surrounding the ^1H nuclei. Figure 7 illustrates the variation in T_2 of protons with concentration for the different Li salt solutions. As ion-water interactions strengthened, T_2 progressively decreased. Except for LiTFSA, the trends observed in the other four electrolytes were highly consistent

with the quantitative detection results. Differences in ion-water interaction strengths between anions lead to varying degrees of restriction on water molecule mobility. The significantly lower T_2 values observed for LiTFSA compared to other aqueous solutions may be attributed to the presence of nanostructural heterogeneities in LiTFSA,¹⁷ which result in reduced average mobility of all water molecules and consequently shorter T_2 . Thus, it can be shown that the order of the strength of the interaction between ions and water molecules is consistent with the order of the non-detectable quantities shown above as the difference between the detected quantities.

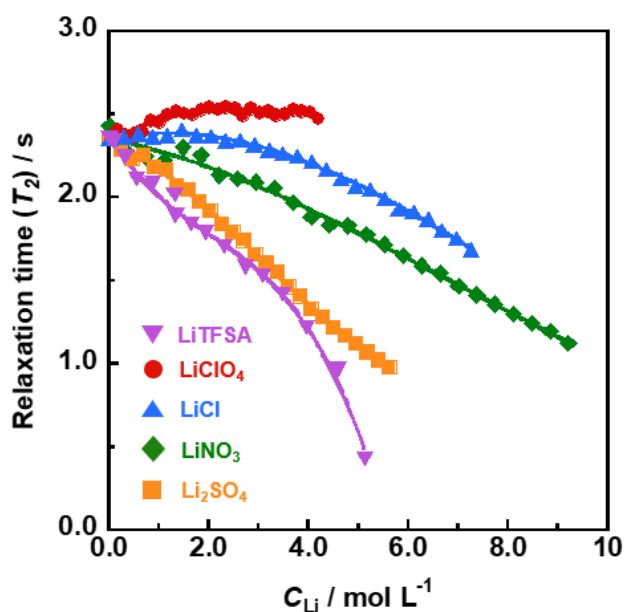


Figure 7. Concentration dependence of solvent-derived ^1H relaxation time (T_2) Li salt aqueous electrolyte solutions.

3.2 Validation of the quantitative detection capability of near-infrared spectroscopic methods

The NIR spectra of the samples of H₂O, PC, and DME homogeneously mixed with dried fumed SiO₂ are shown in Fig. 8, where the combination bands of OH symmetric stretching vibration (ν_1) and asymmetric stretching vibration (ν_3) of water are shown in Fig. 8a. The NIR spectra of PC and DME in Fig. 8(b, c) cannot be accurately distinguished from the individual absorbance attributions due to the lack of relevant literature reports. Therefore, the entire spectral range was integrated in the calculation of absorbance. The absorbance values of solvent molecules measured at each liquid volume fraction were divided by the absorbance of the pure liquid phase to obtain the detected liquid phase volume fraction. As shown in Fig. 8(d-f). In the ideal result, the detected liquid phase volume fraction decreases proportionally with the reduction in the liquid phase volume fraction in the mixture. Although at liquid phase volume fractions above 98 vol%, the experimental values slightly exceed the ideal values due to sedimentation of the solid phase, the overall results demonstrate that the experimental results remain highly consistent with the ideal results. This consistency is observed regardless of whether the solvent is water, an organic solvent such as PC, or the highly volatile DME. These findings indicate that NIR spectroscopy exhibits excellent

quantitative detection capability and is applicable to a variety of systems, irrespective of the solvent type.

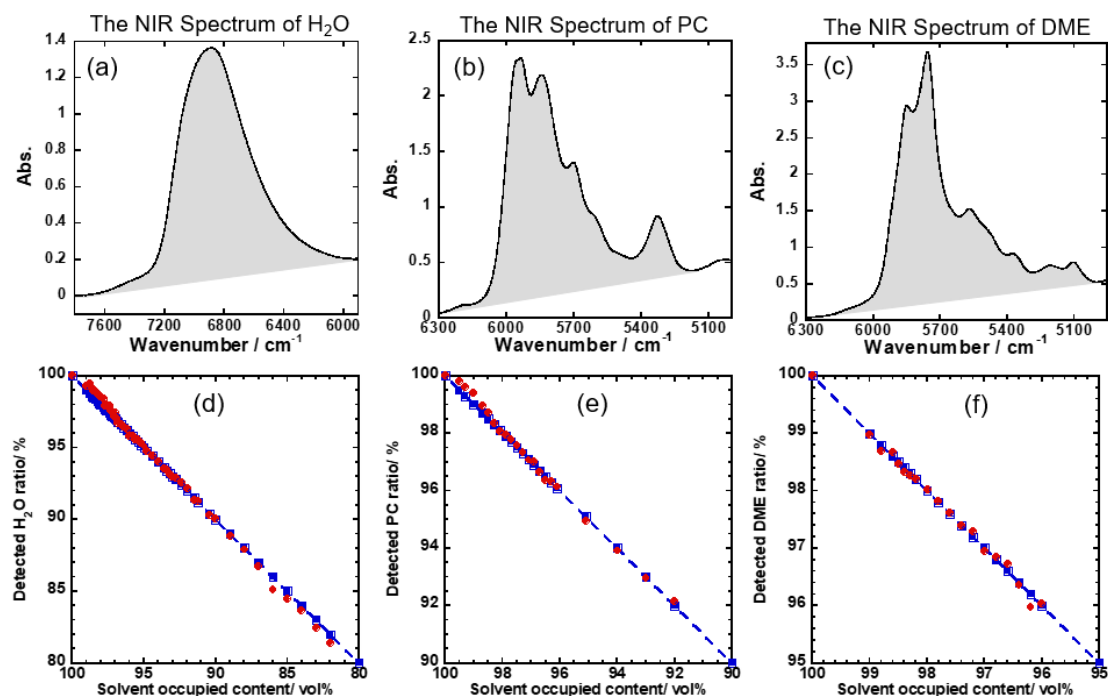


Figure 8. The near-infrared absorption spectra of solvent molecules in a mixed system composed of different solvents and fumed SiO₂ powder, mixed at varying volumetric ratios. a) SiO₂ powder/ H₂O coexisting system; b) SiO₂ powder/ PC coexisting system; c) SiO₂ powder/ DME coexisting system. By integrating the area of each absorption spectrum (the shaded gray region) to determine the absorbance of the solvent molecules and using the peak area of the pure solvent as a reference, we estimated the concentration of solvent molecules in the solid-liquid mixed system based on the ratio of the absorption peak areas, as shown in Figures. d) SiO₂ powder/ H₂O coexisting system, e) SiO₂ powder/ PC coexisting system, and f) SiO₂ powder/ DME coexisting system. In this context, the x-axis represents the actual volumetric fraction of the liquid in the solid-liquid mixed system, while the y-axis indicates the estimated concentration of solvent molecules in the solid-liquid mixture based on calculations. The squares represent ideal results, and the circles represent experimental results.

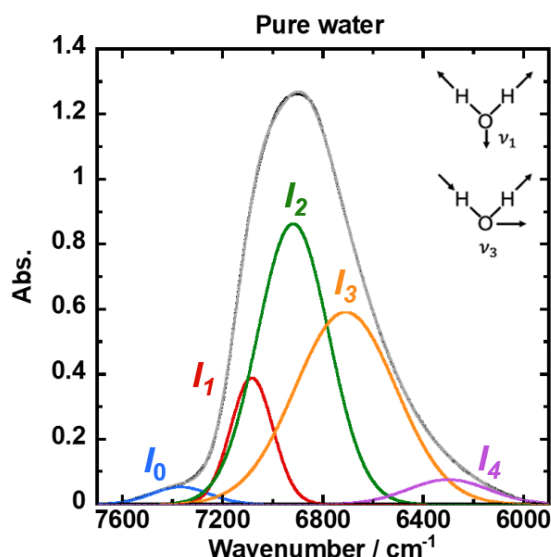


Figure 9. Deconvolution results of the near-infrared spectra of water at 6800 cm^{-1} : Combination bands of OH symmetric vibration (ν_1) and asymmetric vibration (ν_3). The details of five Gaussian bands after deconvolution are shown Table 1.

Table. 5 The five Gaussian components obtained from the deconvolution of the near-infrared absorption spectrum of water molecules represent five distinct hydrogen-bonding states of water molecules within the system.

Gaussian components of NIR combination bands/ cm^{-1}	Assignments
7369 (I_0)	Free OH stretch vibration
7084 (I_1)	OH stretch vibration of singly H-bonded water
6919 (I_2)	OH stretch vibration of H-bonded water with two or three H-bonds
6700 (I_3)	OH stretch vibration of H-bonded water molecule with a distorted icelike structure
6301 (I_4)	OH stretch vibration of H-bonded water molecule with icelike structure
For the attribution of peaks are referred to the ref. 18	

To investigate the information on the effect of SiO₂ on the water structure, the absorption peaks of water were deconvoluted. The total absorption peak of water at 6900 cm⁻¹ was subdivided into five Gaussian bands by fitting a Gaussian function using IGOR PRO software, as shown in Fig. 9 and Table 5. This result was also reported by Dagade et al.¹⁸

We assigned the I_0 band at 7369 cm⁻¹ (I_0) to free water molecules without hydrogen bonds and 7084 cm⁻¹ (I_1) to water molecules with only a single hydrogen bond OH vibration. The band at 6919 cm⁻¹ (I_2) is water molecules with two or three hydrogen bonds. The strips at 6700 cm⁻¹ (I_3) and 6301 cm⁻¹ (I_4) are water molecules with saturated hydrogen bonds, where 6700 cm⁻¹ are ice-like structures, while 6301 cm⁻¹ are water molecules with the same structure as the water molecules in ice. The variation of the relative area ratio of each band with the volume fraction of the liquid phase after deconvolution is shown in Fig. 10. It can be found that the relative ratios of water molecules in all states do not vary with the liquid phase volume fraction, and the increase in the solid phase does not seem to have a significant effect on the original structure of water. The calculated results for the average apparent thickness of the liquid phase on the solid surface are presented in Fig. 3. When the liquid phase volume fraction in the solid-liquid coexistence system reaches 80 vol%, the average apparent thickness of the liquid phase on the surface of an individual SiO₂ particle is approximately 20 nm.

Based on the deconvolution results, it can be concluded that the average apparent thickness of water molecules influenced by the solid phase is significantly less than 20 nm.

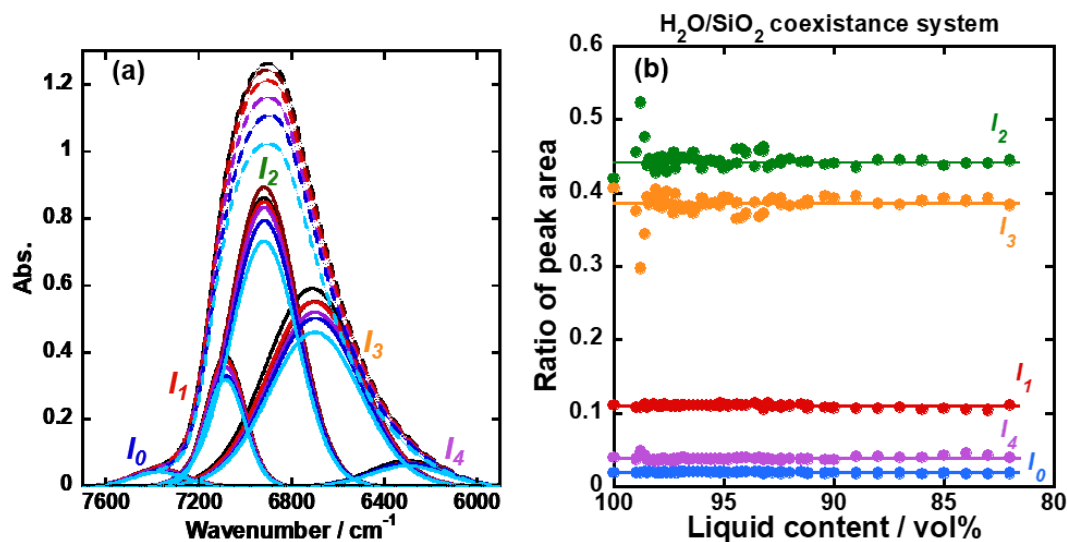


Figure 10. Deconvolution results of the near-infrared absorption spectra of water molecules in SiO₂ powder/ H₂O coexisting system with different mixing ratios. The spectrum colors transition from red to blue, indicating a decreasing volumetric fraction of water in the mixed system. a) NIR spectra of H₂O at different liquid content from 100 vol% (black) to 82 vol% (light blue); b) Variation of the relative area ratio of each Gaussian bands with the volume fraction of the liquid phase in SiO₂ powder/ H₂O coexisting system.

3.3 Results of NIR spectroscopy in aqueous solutions

Since NIR spectroscopy is based on the vibrational spectra of OH binding, cations are generally considered to have a much smaller influence on the spectra than anions, since water molecules are hydrated with cations through lone electron pairs,^{19,20}

whereas anions interact directly with OH. According to Lambert-Beer law:

$$A = \alpha dc \quad (8)$$

where A is the absorbance, α is the absorbance coefficient, d is the optical path length, and c is the concentration of the substance. The absorbance of a substance is related to the optical path length, as well as the concentration of the absorbing substance, and since all the aqueous samples in this study had an optical path length of 1 mm, only the change in absorbance due to concentration was considered.

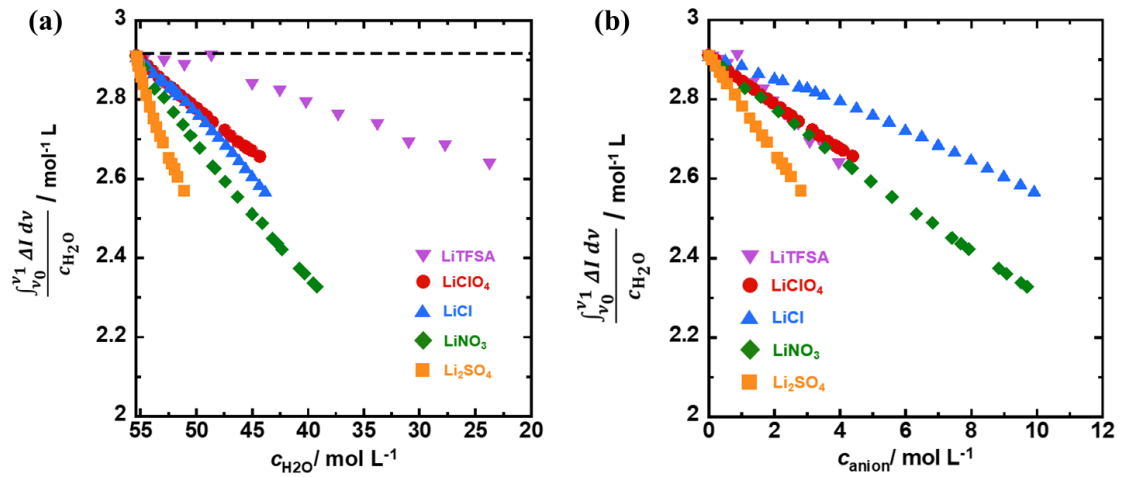


Figure 11. Relationship between the coefficient in Beer's law and (a) the concentration of water in aqueous solution, (b) the concentration of electrolyte in aqueous solution. The dotted line in the figure indicates that ideally, the ratio of absorbance to the concentration of the absorbing substance is a constant value according to Beer's law.

According to Beer's law, concentration and absorbance usually show a linear relationship for a certain optical path length, i.e., the coefficient of absorbance/concentration is a constant value. Figure 11 shows the coefficients of absorbance/ water

concentration for aqueous solutions of different Li salts versus the concentration of water, where the absorbance is calculated from Eq. 5. It can be noticed that the results for all the aqueous solutions detected deviate from Beer's law. The coefficient of absorbance/water concentration decreases with decreasing water concentration and showed a clear dependence on the anion.

To further explore the reasons for this deviation, we examined the variation of the actual detected values of water molecules with water concentration. Assuming the molar absorptivity of water molecules remains constant, the actual detected values of water molecules were calculated, based on the ratio of the absorbance of water in each solution to that of pure water obtained via Eq. 5, following Lambert-Beer law. The horizontal axis still uses the same apparent volume occupancy of water in each solution as mentioned in Section 3.1 to facilitate the harmonization of theoretical values for different Li saline solutions. The results are shown in Fig. 12. Based on the validated quantitative detection capability of the NIR spectrometry in Section 3.2, it can be assumed that in the ideal result, the detection value of water molecules in solution should be the same as the apparent volume fraction of water as shown by the black dashed line in Fig. 12. However, similar to the detection results of ^1H qNMR spectroscopy, the actual obtained detection rates of water molecules in each solution were lower than the theoretical results. In addition, the difference between the

theoretical and experimental values increased with increasing concentration and again showed a clear anionic dependence in the identical order with the results in ^1H qNMR measurement as shown in Eq.6.

$$\text{TFSA}^- < \text{ClO}_4^- < \text{Cl}^- < \text{NO}_3^- < \text{SO}_4^{2-} \quad (6'')$$

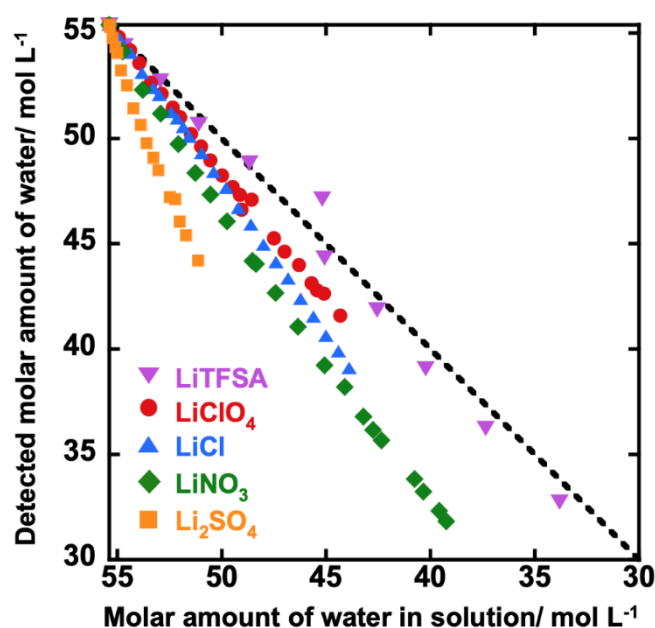


Figure 12. The relationship between the detected molar amount of water and the molar amount of water in Li electrolyte solution by NIR spectra.

We first considered the refractive index of the solution as a potential reason for the detected water concentration being lower than the theoretical value. As the electrolyte concentration in the aqueous solution increases, the solution density rises, leading to an increase in the refractive index n and a corresponding reduction in the apparent optical path length. Therefore, we measured the refractive indices of the five solutions at different concentrations. It should be noted that, due to experimental limitations, the re-

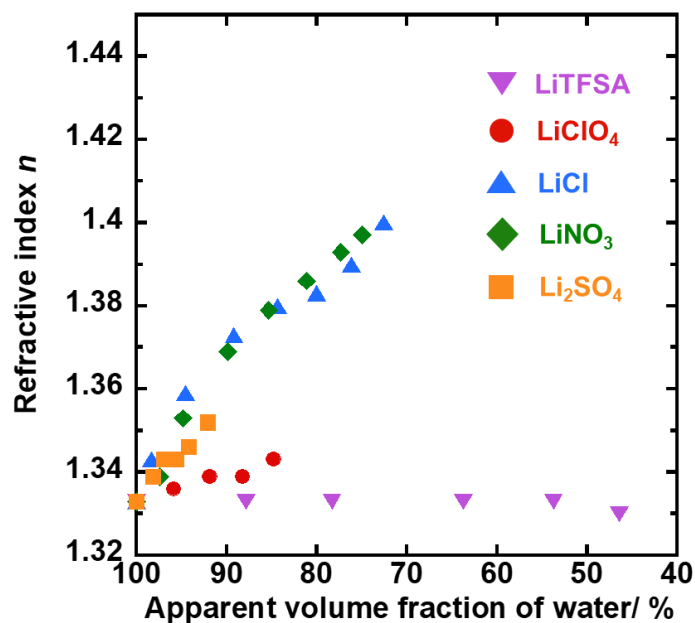


Figure 13. The refractive index of aqueous solutions of five Li salts. Considering the refractive index of bulk water as 1.333.

Table 6. Concentration and refractive index n of each aqueous solution.

LiTFSA		LiClO ₄		LiCl		LiNO ₃		Li ₂ SO ₄	
mol L ⁻¹	n	mol L ⁻¹	n	mol L ⁻¹	n	mol L ⁻¹	n	mol L ⁻¹	n
0	1.333	0	1.333	0	1.333	0	1.333	0	1.333
0.88	1.333	0.97	1.336	0.98	1.343	0.97	1.339	0.98	1.339
1.54	1.333	1.85	1.339	2.83	1.359	1.89	1.353	1.45	1.343
2.54	1.333	2.65	1.343	5.34	1.373	3.58	1.369	1.91	1.343
3.22	1.333	3.39	1.346	7.57	1.380	5.10	1.379	2.35	1.346
3.71	1.330			9.58	1.383	6.47	1.386	2.84	1.352
				11.39	1.390	7.71	1.393		
				13.03	1.400	8.46	1.397		

-fractive indices were measured in the visible light range, whereas our discussion primarily focuses on the near-infrared range. However, based on the report by Palmer et al.,²¹ the refractive index of water in the near-infrared to visible range varies only slightly, from 1.325 at 8000 cm⁻¹ to 1.333 at 18000 cm⁻¹, and the values of the refractive index between the two wave numbers show only a monotonic increase. Thus, we consider the refractive index measurements in the visible light range to be applicable to the near-infrared range. Figure 13 and Table 6 present the measured refractive index n of the solutions. With increasing concentration, all solutions except the LiTFSA aqueous solution exhibited an increase in refractive index. In contrast, the LiTFSA solution showed no significant change in refractive index. We calculated the correction factor f in each concentration solution to correct for the decrease in absorbance due to the shortening of the optical path length caused by the change in refractive index:

$$f = n/n_0 \quad (9)$$

where n is the measured refractive index of each solution, n_0 is the refractive index in vacuum. And, furthermore, we corrected the detected values of water molecules obtained by NIR spectroscopy by a correction factor f to evaluate the effect of the change in refractive index on the absorbance. The results of the corrected water molecule detection values are shown in Fig. 14. It can be found that the detected values of the water molecules detected are still lower than the ideal values even after taking

into account the effect of the refractive index on the absorbance, so we believe that there are still other reasons for the decrease in the absorption of near-infrared light by water molecules in the aqueous solution.

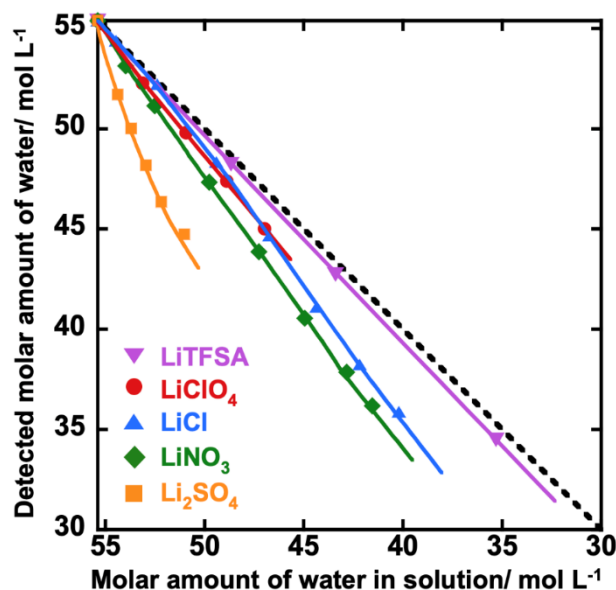


Figure 14. Detected molar amount of water molecules calculated by Eqs. 8 and 9 after considering the refractive index of each solution on the absorbance of water.

3.4 Correlation of the Hofmeister series with the detection value of water molecules

The Hofmeister series is derived from Hofmeister's report on the effects of aqueous solutions of different electrolytes on protein precipitation.²²⁻²⁴ Hofmeister hypothesized that the effects of different ions on proteins derive from the ions' effects on the water molecules surrounding the proteins, and thus the ions are broadly categorized as strongly hydrated ions and weakly hydrated ions.^{24,25} Strongly hydrated ions exhibit

pronounced hydrophilicity, have strong interactions with water molecules, tend to attract water molecules around proteins used to stabilize the protein structure, and cause the water molecules to order around themselves, thus leading to coalescence between proteins and exhibiting salting out behavior, and this type of ions is known as kosmotrope ions. On the other hand, weakly hydrated ions exhibit weak interactions with water molecules and exhibit increased solubility of proteins and these ions are called chaotrope ions.^{23,26,27} Therefore it can thus be assumed that the Hofmeister sequence is a reflection of the strength of the ion-water molecule interactions, of which the sequence for the anion relevant to this experiment is²³:

$$\text{ClO}_4^- < \text{NO}_3^- < \text{Cl}^- < \text{SO}_4^{2-} \quad (10)$$

It can be noticed that such an ordering is very similar to the conclusions obtained by ¹H NMR (Eq. 6 and 6') and NIR spectroscopy (Eq. 6''), in the order of TFSA⁻ < ClO₄⁻ < Cl⁻ < NO₃⁻ < SO₄²⁻ especially for some oxoanions. This suggests a strong correlation between the decrease of water molecule detection values in NIR spectroscopy and the strength of the interaction between ions and water molecules.

It can be found that such an ordering is resemble with the ordering of the non-detected values of water molecules obtained by ¹H qNMR and NIR measurements, indicating a strong correlation between the decrease of the water molecule detectors and the strength of the interactions between ions and water molecules. Observation of

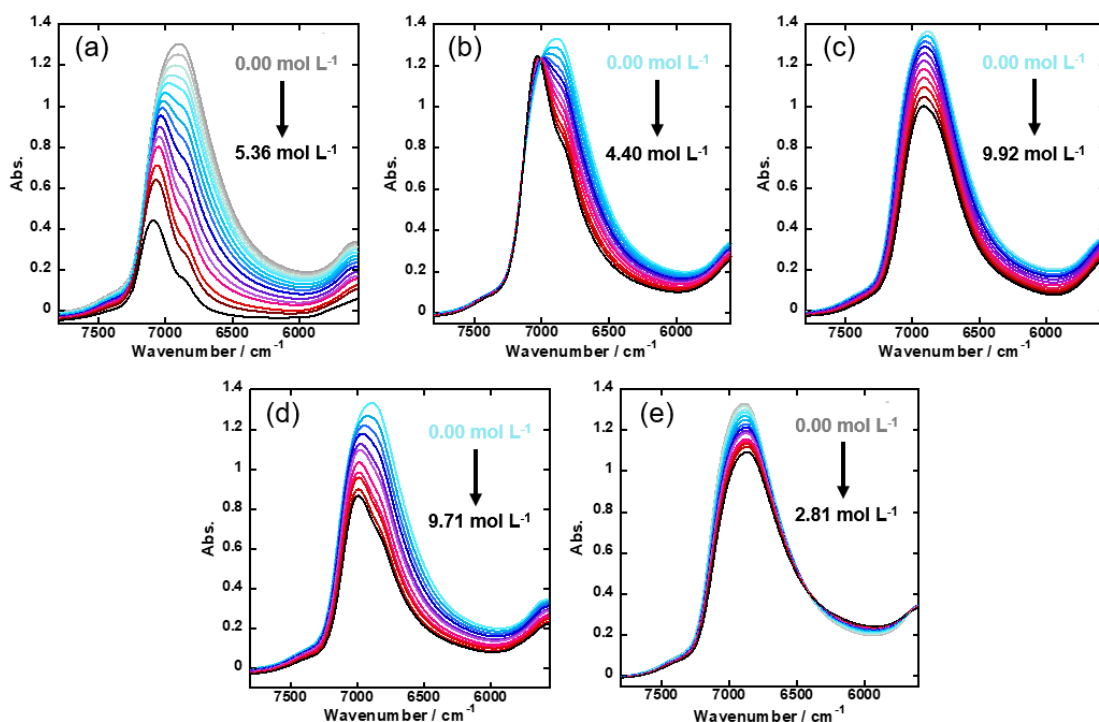


Figure 15. The near-infrared absorption spectra of water molecules in solutions of different Li salt electrolytes, corresponding to the combined frequencies of symmetric and asymmetric stretching vibrations of the OH bonds. Depending on the type of electrolyte and the concentration, the absorption spectra of water molecules exhibit distinct variations. (a) LiTfSA, (b) LiClO₄, (c) LiCl, (d) LiNO₃, (e) Li₂SO₄.

the NIR spectra of water molecules in the solutions of each concentration in Fig. 15 reveals that the aqueous solutions of LiCl, LiClO₄, LiNO₃, and LiTfSA show a significant decrease in the absorption intensity at the low wavelength side, whereas at the high wavelength side, the weakening of this intensity is relatively weak. This indicates that in LiCl, LiClO₄, LiNO₃, LiTfSA aqueous solutions, the OH stretching vibration frequency of most water molecules increases, and the hydrogen bonding between water molecules in solution decreases. On the other hand, no significant intensity decrease was observed in Li₂SO₄ aqueous solution; on the contrary, an

increase in absorbance with concentration could be observed in the low wavenumber measurements near about 6000 cm^{-1} , indicating a decrease in the OH stretching vibration frequency of water molecules and an enhancement of hydrogen bonding of water molecules. In order to quantify the effect of different anions on the structure of water molecules, the NIR spectra of water molecules in aqueous solutions of various types of Li salts were deconvoluted according to the deconvolution method shown in Fig. 9. In order to facilitate the evaluation of ion-water molecule interactions, here, we further categorized the five hydrogen-bonded states of the fractionated water molecules into two main groups, i.e., I_0+I_1 were categorized as water molecules in which the aqueous solution had weak or no hydrogen bonds. $I_2+I_3+I_4$ were categorized as water molecules in which the aqueous solution had strong hydrogen bonds or formed multiple hydrogen bonds, as shown in Fig. 16a. The results of deconvolution are shown in Fig. 16. In LiTfSA, LiClO₄, LiCl, and LiNO₃ aqueous solutions, the number of strongly hydrogen-bonded water molecules decreases dramatically, and although the overall number of water molecules decreases, a significant increase in the number of less hydrogen-bonded water molecules can still be observed. On the other hand, the overall change in Li₂SO₄ aqueous solution is relatively small. In order to evaluate the structural changes of water more intuitively, the overall decrease in the number of water molecules was considered, and the relative changes of the two types of water molecules

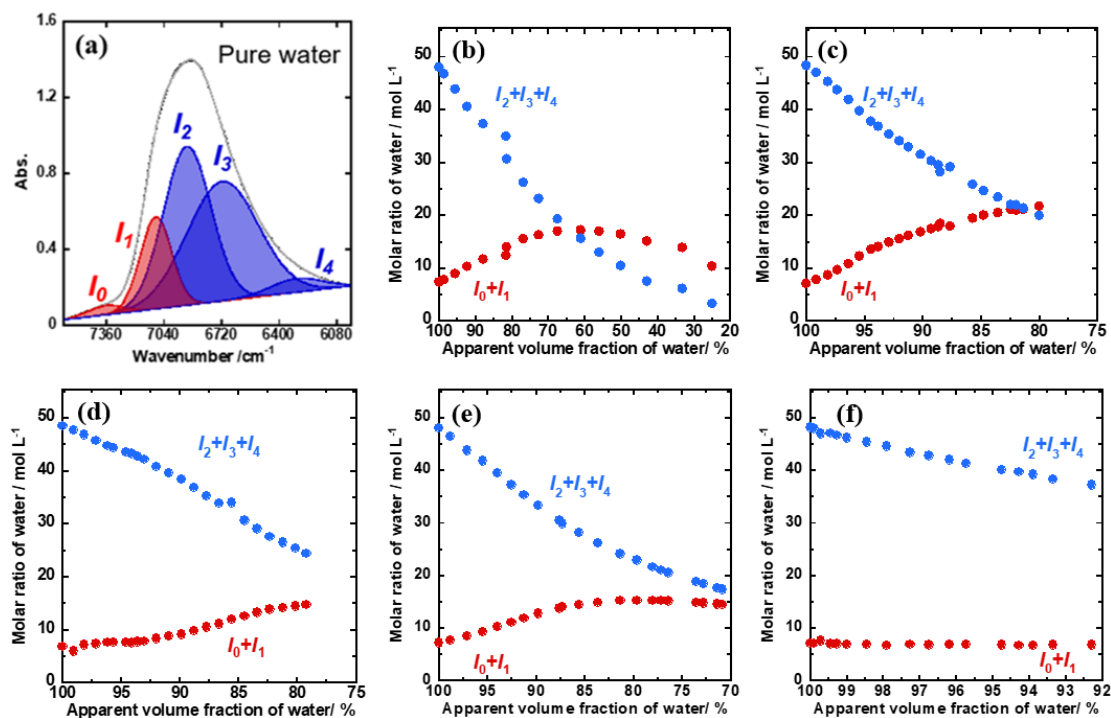


Figure 16. The deconvolution results in aqueous solutions of each Li salt. The five Gaussian components are further categorized into two main groups: I_0+I_1 are water molecules with weak or no hydrogen bonding, while $I_2+I_3+I_4$ are regarded as water molecules with strong hydrogen bonding or forming multiple hydrogen bonds. Variation of the actual number of the two types of water molecules as a function of the apparent volume fraction of water in solution, calculated from the deconvolution results. (b) LiTFSA, (c) LiClO₄, (d) LiCl, (e) LiNO₃, (f) Li₂SO₄.

are given in Fig. 17. Both Fig. 16 and Fig. 17 exhibit the fact that LiTFSA, LiClO₄, LiCl, and LiNO₃ show more pronounced spectral changes, especially for LiTFSA, while the changes in the aqueous solution spectra of Li₂SO₄ are relatively insignificant. This seems to form a paradoxical result, where the aqueous solution of LiTFSA with the strongest spectral variation has the highest detection value of water molecules, while the aqueous solution of Li₂SO₄ with the least pronounced spectral variation has a drastically lower detection value of water molecules. Based on this result, we propose

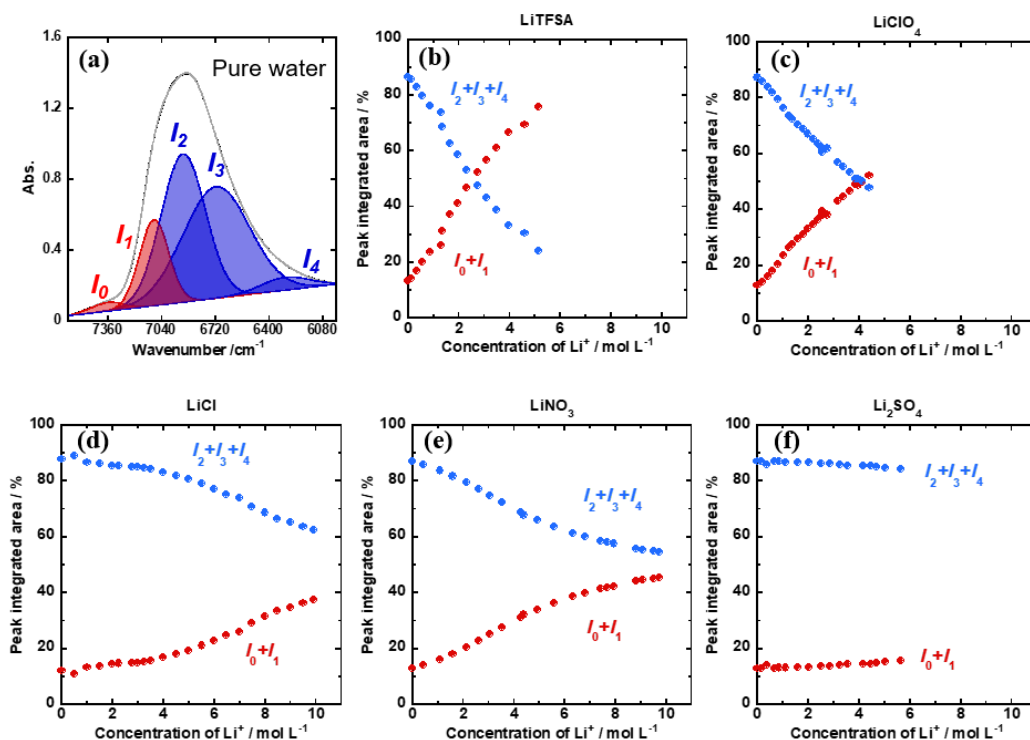


Figure 17. The deconvolution results in aqueous solutions of each Li salt. The five Gaussian components are further categorized into two main groups: I_0+I_1 are water molecules with weak or no hydrogen bonding, while $I_2+I_3+I_4$ are regarded as water molecules with strong hydrogen bonding or forming multiple hydrogen bonds. Changes in the relative occupancy of the two types of water molecules with Li^+ concentration. (b) LiTfSA, (c) LiClO_4 , (d) LiCl, (e) LiNO_3 , (f) Li_2SO_4 .

a plausible explanation that since the number of water molecules is calculated from the combination tone of OH symmetric stretching vibrations and OH asymmetric stretching vibrations of water molecules in the NIR spectra, it can be assumed that the strong anion-water molecule interaction inhibits the generation of the binding frequencies of the water molecules, which leads to the inability of these water molecules to be detected by the NIR spectra, resulting in the significant decrease of the absorbance. In other words, what is reflected in the spectra is the resultant change in the water molecules

that are not subjected to anion interactions.

In particular, although TFSA^- is not included in the Hofmeister series, it is usually recognized as a strong chaotropes anion,²⁸⁻³⁰ which, due to its low charge density, interacts with water molecules much less than water intermolecular hydrogen bonding. Therefore, the massive addition of TFSA^- only spatially destroys the hydrogen bonds between water molecules, and the formation of heterogeneous structures in aqueous solutions of LiTFSA at high concentrations is also one of the reasons for the massive destruction of hydrogen bonds between water molecules.³¹ In conclusion, the weak interaction between TFSA^- and water molecules leads to the detection of almost all water molecules by NIR light. ClO_4^- is considered to form a hydrogen bonding structure with H_2O without directional hydrogen bonding,^{19,32} whereas NO_3^- and Cl^- form weak hydrogen bonding with water molecules (as compared to intermolecular hydrogen bonding of water molecules),²⁰ and therefore, it is considered that it is due to the incorporation of the ions that the intermolecular hydrogen bonds between water molecules are disrupted. However, ClO_4^- has a higher charge density compared to TFSA^- , so it is reasonable to consider that the interaction between ClO_4^- and water molecules is stronger than TFSA^- . Further, compared to the Cl-O single bond of ClO_4^- , NO_3^- can be more favorable to form stronger hydrogen bonds with water molecules due to the nature of its NO binding with a double bond.³³ Therefore, it can be assumed that

NO_3^- interacts with water molecules more strongly than ClO_4^- . In contrast, the SO_4^{2-} ion is widely recognized as a strong kosmotropes anion with strong hydrophilic properties.^{34,35} According to other studies, SO_4^{2-} can form hydrogen bonds with eight water molecules through four O atoms and the strength of the hydrogen bond formed between SO_4^{2-} - H_2O does not exhibit significantly weaker than the strength of the hydrogen bond between water molecules in bulk water,^{36,37} the high charge density also allows more water molecules to be attracted to the water molecule, which may result in the water molecules in its first water and layer being polarized by the electric field of the ions and form uniform local vibrational modes.²⁰ Therefore, both from the strength of the ion-water molecule hydrogen bonding interactions and the charge density of the ions, we can assume that the interaction between SO_4^{2-} and water molecules is stronger than that of TFSA^- , ClO_4^- , Cl^- , and NO_3^- , which results in more water molecules not being detected through the combination tone in the NIR spectra. The water molecules detected in the spectra that did not interact with SO_4^{2-} , on the other hand, exhibited slight structural changes, which were most likely due to Li^+ . In summary, the order of the strength of the ion-water molecule interactions is $\text{SO}_4^{2-} > \text{NO}_3^- > \text{ClO}_4^- > \text{TFSA}^-$, which well validates our conclusion about the decrease in the detection value of water molecules in the NIR spectra. In addition, similar ordering of water molecule detections as that of Li salt can be observed in the NIR results of water molecules from aqueous

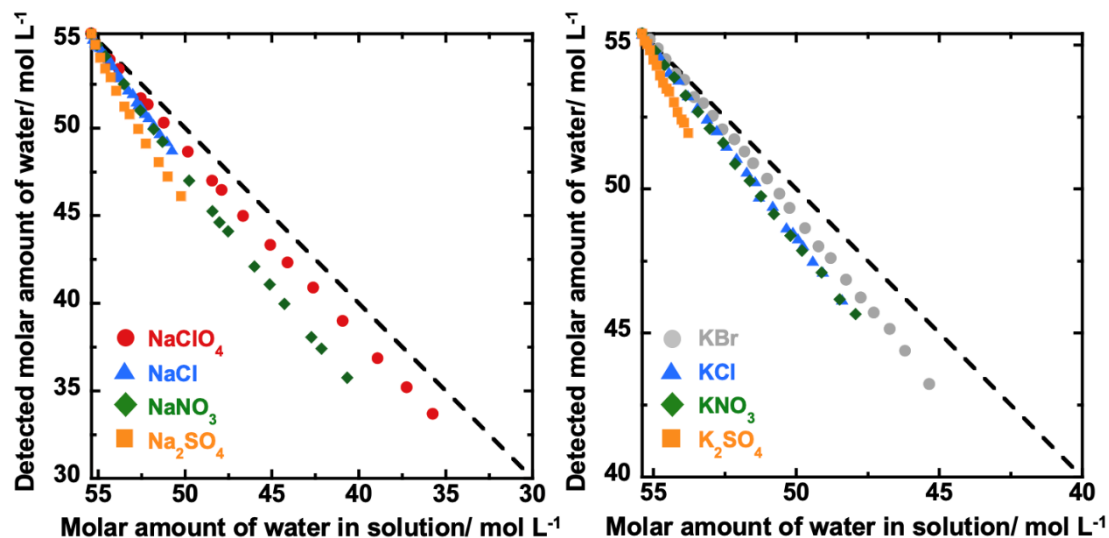


Figure 18. The relationship between the near-infrared detection values of water molecules in alkali metal electrolyte solutions and the actual theoretical values. (a) Water molecule detection rate of Na salts in relation to theoretical values; (b) Water molecule detection rate of K salts in relation to theoretical values. The x-axis represents the ratio of the volume of water to the total volume of the electrolyte solution at different concentrations, while the y-axis indicates the ratio of the number of water molecules detected via near-infrared spectroscopy to the number of water molecules in pure water. The black dashed line in the figure illustrates the ideal scenario in which the number of water molecules measured by near-infrared spectroscopy aligns with the actual number of water molecules present in the solution.

solutions of Na and K salts with different anions in Fig. 18, which is in accordance with the order of the strength of ion-water molecule interactions, and the cations have a very small effect on the vibrational spectra of OH of water molecules.

We found that while oxoanions agree relatively well with the Hofmeister series, Cl⁻ shows specificity. In the Hofmeister series, Cl⁻ serves as the reference ion, and its ordering is located between SO₄²⁻ and NO₃⁻. However, both ¹H qNMR spectroscopy results and NIR spectroscopy results exhibited lower detection values in LiNO₃ aqueous

solution than in LiCl aqueous solution, i.e., $\text{NO}_3^- > \text{Cl}^-$. Moreover, as shown in Fig. 14, after the detection values of NIR spectra were corrected by refractive index, the detection values of LiCl aqueous solution were almost the same as those of LiClO_4 . Comparing the results of Cl^- and NO_3^- in Li, Na, and K salts, we can find that the detection values of water molecules in Cl^- and NO_3^- solutions are gradually close to each other as the radius of the cation increases. We believe that this is related to the formation of ion pairs between anions and cations. Since the charge density of Cl^- is higher than that of NO_3^- and there is charge separation in NO_3^- , Cl^- prefers to form ion pairs with Li^+ , which has a high charge density, through electrostatic interactions. This leads to a decrease in the interaction between Cl^- and water molecules, and more water molecules are detected in LiCl aqueous solutions. As the cation charge density increases, the formation of ion pairs becomes more difficult and the anion interacts more with water molecules, making the difference in the ability to form ion pairs between Cl^- and NO_3^- less pronounced and leading to close values for the two anions.

4. Conclusion

The efficacy of NIR in discussing the quantitative classification of solvent molecules in concentrated solutions from their hydrogen bonding states is discussed.

The quantitative performance of NIR spectroscopy was confirmed by using the SiO₂ powder/liquid phase coexistence system, which is a physical heterophase mixture system.

The detectable amount of water molecules obtained by ¹H NMR and NIR spectroscopy in aqueous electrolyte solutions is lower than the theoretical value. Even in the values corrected for the refractive index of the solution in NIR spectroscopy, a reduction from the theoretical values was observed.

Furthermore, the effect of different electrolytes on the non-detected amount of water molecules varies in the following order: TFSA⁻ < ClO₄⁻ < Cl⁻ < NO₃⁻ < SO₄²⁻, which is similar to the order of the Hofmeister series except for Cl⁻.

The decrease in the detection values in NMR is believed to be due to a significant decrease in mobility and activity coefficients of some or all of the water molecules that were hydrated with the ions, resulting in these water molecules not being detected by ¹H NMR. On the other hand, the detection of NIR signals does not depend on the dynamics of water molecules which is the cause of non-detection in NMR but is interpreted to be exclusively due to combination tone based on intramolecular vibrations. The absence of intramolecular vibrations may be due to the fact that the activity of intramolecular vibrations is suppressed by solvent-ion interactions. Thus, it is interesting to note that both dissolved species dynamics and intramolecular vibrations,

which are different molecular properties, can quantitatively indicate the effects of ions on solvent molecules. We believe that the results of lower than theoretical water molecule detections observed in NIR spectroscopy may provide a new perspective for quantitatively evaluating the strength of ion-water molecule interactions.

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CHAPTER 2

Quantitative study on the behavior of water in CaCl₂-ZnCl₂ binary hydrate melt

1. Introduction

In high-concentration aqueous solutions and molten salt hydrates, the ratio of water molecules to solutes decreases significantly compared to dilute aqueous solutions. This reduction leads to changes in the hydrogen-bonding network formed between water molecules and a lack of sufficient water molecules to create hydration shells around cations. Consequently, the ion-ion and ion-water interactions in high-concentration aqueous solutions and molten salt hydrates become highly complex.¹⁻⁴ These intricate interactions result in physical and chemical properties of molten salt hydrates that differ markedly from those of dilute solutions, including variations in electrical conductivity and water molecule decomposition potentials. Therefore, a detailed understanding of the interactions between ions and water molecules in high-concentration aqueous solutions and molten salt hydrates is crucial for fields such as electrochemistry, materials chemistry, and chemical engineering. Mixing molten salt hydrates with different cations is an effective method to observe changes in solution structure. Due to the differing interactions among various cations, anions, and water molecules, changing the mixing ratio of the two ions allows for easier observation of the preferential interactions between ions or between ions and water molecules. This, in turn, effectively clarifies the impact of the two ions on the solution structure.

Extensive research has been conducted on solution structures using various analytical techniques, including infrared spectroscopy,^{5, 6} Raman spectroscopy,⁷⁻⁹ magnetic resonance spectroscopy (NMR),¹⁰⁻¹² neutron scattering spectrum,¹³⁻¹⁵ and X-ray absorption and scattering spectroscopy.¹⁶⁻¹⁸ Additionally, two-dimensional (2D) infrared spectroscopy¹⁹⁻²¹ and molecular dynamics simulations^{22,23} is widely employed to study ion transport mechanisms in solutions. However, there remains a lack of a method with robust quantitative capabilities for accurately quantifying the structure of aqueous solutions. While infrared spectroscopy does offer quantitative detection capabilities, the strong absorption of infrared light by water often leads to significant measurement errors. Furthermore, the absorption intensity in attenuated total reflectance (ATR) method is also influenced by the wavelength of the light, which can compromise precision in quantification.

Near-infrared (NIR) spectroscopy is an absorption technique based on molecular anharmonic vibrations. Due to the anharmonic nature of molecular vibrations, NIR spectroscopy typically reveals spectral bands corresponding to overtones and combination modes of $X-H$ ($X = C, N, O$) functional groups. The anharmonicity of $X-H$ ($X = C, N, O$) vibrations lead to significant absorption intensities, making these bands more readily observable and analyzable. The observed absorption peaks in NIR spectra primarily correspond to the overtones and combination modes of fundamental $X-H$ (X

= C, N, O) vibrations. This characteristic allows for the detection of peak shifts induced by changes in intermolecular interactions. Furthermore, because the absorption intensity of materials in the near-infrared region is much lower than that in the mid-infrared region, NIR spectroscopy often does not require extensive sample pretreatment, thus ensuring high precision in quantitative analysis.²⁴ Given the aforementioned advantages, near-infrared spectroscopy offers a valuable advantage for observing the perturbations of hydrogen bonds between water molecules caused by external factors, such as variations in concentration of ion. However, in our previous studies, it was observed that the quantity of water molecules in aqueous solutions, as determined by near-infrared (NIR) spectroscopy, was lower than the calculated amount of water present in the actual solution. Moreover, this discrepancy was found to be closely related to the solution concentration and the types of ions present. Therefore, In this study, we employed near-infrared spectroscopy to quantitatively detect and analyze changes in the water structure within a mixed molten salt hydrate system composed of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$. Additionally, Raman spectroscopy and ^1H NMR were utilized, along with measurements of conductivity and viscosity, to gain a comprehensive understanding of the interactions between Ca^{2+} , Zn^{2+} , Cl^- and water molecules, including the transformations of coordination complexes.

2. Experimental

2.1 Materials and sample preparation

Milli-Q water was used to dissolve reagent-grade $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Nacalai Tesque Inc.) and ZnCl_2 (KISHIDA CHEMICAL CO., LTD), resulting in the preparation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$ solutions. These solutions were then mixed in varying molar ratios to prepare a series of $(\text{Ca}_{1-x}\text{Zn}_x)\text{Cl}_2 \cdot n\text{H}_2\text{O}$ ($0 \leq x \leq 1$) mixed solutions. The density of all obtained solutions was measured using a digital density meter (Anton Paar, DMA 5000 M). The specific concentrations are presented in Table 1.

Table 1. The concentrations of ZnCl_2 , CaCl_2 , and water in the mixed electrolyte solution of $(\text{Ca}_{1-x}\text{Zn}_x)\text{Cl}_2 \cdot n\text{H}_2\text{O}$ at different molar mixing ratios

x	$c_{\text{ZnCl}_2} / \text{mol L}^{-1}$	$c_{\text{CaCl}_2} / \text{mol L}^{-1}$	$c_{\text{H}_2\text{O}} / \text{mol L}^{-1}$	n
0.0	0.00	6.88	41.25	6.00
0.1	0.68	6.16	41.08	6.00
0.2	1.36	5.45	40.91	6.00
0.3	2.03	4.74	40.62	6.00
0.4	2.69	4.03	40.37	6.01
0.5	3.34	3.33	40.07	6.01
0.6	3.98	2.65	39.85	6.01
0.7	4.65	1.99	39.91	6.01
0.8	5.33	1.33	40.04	6.01
0.9	6.01	0.67	40.16	6.01
1.0	6.70	0.00	40.28	6.01

2.2 Electrical conductivity

The conductivity of all solutions was measured using a PRECISION LCR METER (HP 4284A) with a two-electrode AC impedance method. A specified volume of the solution was placed into a U-shaped cell, and a pair of platinum electrodes was inserted to ensure complete contact between the solution and the electrodes. The measurements were conducted in a constant-temperature water bath set at 30 °C. By applying an AC voltage of 0.6 V with a frequency ranging from 20 Hz to 1 MHz, the AC impedance of the solution was obtained. The conductivity of the solution was then calculated using the following formula:

$$K_{cell} = \kappa_{std} \cdot R_{std} \quad (1)$$

$$\kappa = K_{cell} \cdot R^{-1} \quad (2)$$

where K_{cell} is the cell constant, which was determined by measuring the resistance of the reference material. κ_{std} is the known electrical conductivity of the reference material, R_{std} is the resistance of the reference material, κ is the electrical conductivity of the solution, and R is the solution resistance. In this study, the 0.1 mol kg⁻¹ KCl aqueous solution was used as reference material.

2.3 Viscosity

The viscosity of all solutions was measured using an Ostwald viscometer. The experiments were conducted in a thermostatic water bath at 30 °C. The viscosity of the solutions was calculated by measuring the flow time of the test solution between the marked lines and using the flow time and viscosity of pure water as the standard, according to the following formula:

$$\eta_r = \frac{\eta}{\eta_0} = \frac{\rho \Delta t}{\rho_0 \Delta t_0} \quad (3)$$

where η_r is the specific viscosity, η , ρ , and Δt are the solution viscosity, density, and falling time, and η_0 , ρ_0 and Δt_0 are the pure water viscosity, density, and falling time.

2.4 pH measurement

The pH of all solutions was measured using a pH/ ion meter F-53 (HORIBA, Ltd.). After calibrating the meter with a three-point calibration method, the glass electrode was immersed in the solution, and the stable reading was recorded as the pH of the solution.

2.5 Spectroscopy measurement

^1H NMR spectroscopy and chemical shift analysis were performed on all solutions using the Spinsolve-43 (Magritec Inc.) to determine the quantity of water molecules in each solution. The experiment was conducted at a temperature of 30 °C, with measurement parameters set to a frequency of 43.58 MHz, a sweep width of 500.0 Hz (11.47 ppm), a data acquisition time of 16 seconds, and 16 scans. The pulse width was adjusted for each solution to ensure the maximum peak area was obtained. The peak areas were determined by integrating the intensity of the ^1H NMR signal within a range of ± 1.5 ppm around the peak center, with the peak area of pure water serving as the standard for calculating the number of detected water molecules in each solution.

The conditions for measuring the ^1H chemical shift was identical to those used for quantitative ^1H NMR measurements. The duplex tube method was employed, where an inner tube containing the internal reference material- dimethyl sulfoxide (DMSO) was inserted into an outer tube containing the solution to be analyzed. The ^1H chemical shift of each solution was calibrated based on the chemical shift deviation of DMSO as in Eq. 4:

$$\delta_{\text{H}} = \delta_{\text{H}}(\text{sample}) + (2.490 - \delta_{\text{H}}(\text{DMSO})) \quad (4)$$

The H self-diffusion coefficient D of water was measured using pulsed-field gradient

NMR (PFG-NMR) with a Spinsolve-43. The measurements were conducted at a temperature of 30 °C, and a Shigemi duplex tube (BMS-005B) was used to suppress convection effects. The detection conditions were set with a gradient pulse duration (δ) of 2 ms, a diffusion time (Δ) of 70 ms, max gradient (G) of 75 % and 4 scans.

The NIR spectra of all samples were measured using UV-Vis-NIR (JASCO-V7200) at room temperature using the transmission method. A cell with an optical path length of 10 mm (made by Nippon Sheet Glass Company or Tosoh Quartz Corporation) was used. For aqueous solution measurements, a 9 mm quartz block was placed inside the cell and the optical path length was set to 1 mm. The light source is a tungsten halogen lamp, and the detector was a cooled PbS photoconductive element with a capture time of 0.2 s for the NIR signal and a data detection of 1 nm. The detection range was 1200-2500 nm for water. All measured spectra were converted from wavelength (nm) converted to wavenumber (cm^{-1}). The converted spectrum is then processed at equal intervals, and the entire spectrum has 2000 data points. The spectral baseline is determined, and the area of the part consisting of the spectrum and the baseline is integrated as the absorbance.

As an example, the near-infrared spectrum of water was baseline corrected for the near-infrared absorption peaks of water as shown in Fig. 1. The baseline is the line between the start and end wave numbers of the absorption peaks. The peak area of the

portion comprising the baseline and the spectrum is integrated to be the absorbance A of the water:

$$A = \int_{\nu_0}^{\nu_1} \Delta I \, d\nu \quad (5)$$

where ν_0 is the starting wavenumber of the baseline and ν_1 is the ending wave number of the baseline, correspond to the start and end wavenumbers of the near-infrared absorption peaks at the combination band of the OH symmetric and asymmetric stretching vibrations of water molecules, respectively. ΔI is the difference in absorbance between the absorbance of the spectrum at the same wave number and the baseline. All areas of the NIR spectra were integrated by Origin lab software to obtain peak areas.

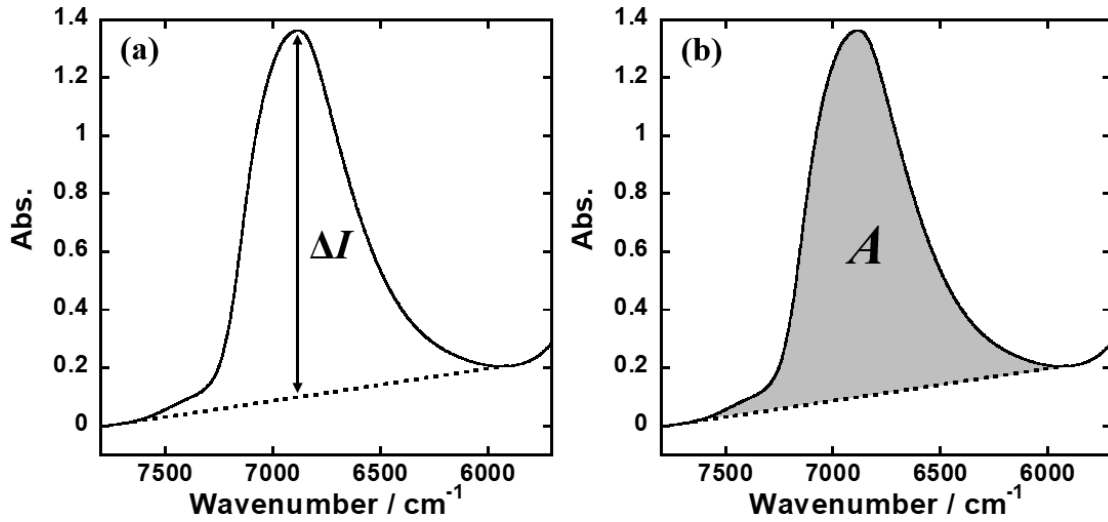


Figure 1. The starting and ending wave numbers of the near-infrared absorption peaks of water are used to determine the baseline, as shown by the dashed line in the figure. The difference in absorbance between the baseline and the absorption peak at the same wave number is ΔI , as shown in (a). The area of the component between the baseline and the absorption peak is integrated by Eq. 5, and the resulting peak area is used as the absorbance A of water over the entire wavelength range.

Raman spectra were recorded using a T-64000 Raman spectrometer (HORIBA, Ltd.) equipped with a Nb: YVO₄ laser and a charge-coupled device cooled using liquid nitrogen as a detector. The 532 nm line was used for excitation. The solution samples were loaded into glass tubes and spectra were recorded in the back-scattering geometry. The monochromator was calibrated using the CCl₄ peak at 459 cm⁻¹. All experiments were performed at room temperature. The measurement range is between 100-550 cm⁻¹ for ZnCl₄²⁻ and [Zn(H₂O)₆]²⁺, and 2500-4000 cm⁻¹ for water molecular.

3. Results and discussion

3.1 Quantitative ¹H NMR detection and chemical shifts of H atoms

To modify the cationic composition in mixed molten salt hydrates, ZnCl₂ 6H₂O was added to CaCl₂ 6H₂O. The resulting ¹H NMR spectrum is depicted in Fig. 2a. Only signals from H atoms in the H₂O molecules were observed throughout the measurement range. It is evident that the chemical shift of these signals is strongly dependent on the ratio of the mixed cations. The results of the chemical shifts are shown in Fig. 2b. When a small amount of Zn²⁺ is added, the chemical shift of H moves towards a higher magnetic field, indicating an increase in the electron density around the H atoms. As

the $x > 0.5$, the chemical shift of H begins to move towards a lower magnetic field, indicating a decrease in the electron density around the H atoms.²⁵ Changes in the electron density of H atoms in aqueous solutions reflect variations in hydrogen bonding between water molecules. An increase in the electron density of H atoms generally suggests the weakening (or breaking) of hydrogen bonds between H₂O molecules, whereas a decrease in electron density is typically associated with the strengthening (or formation) of hydrogen bonds between H₂O molecules.

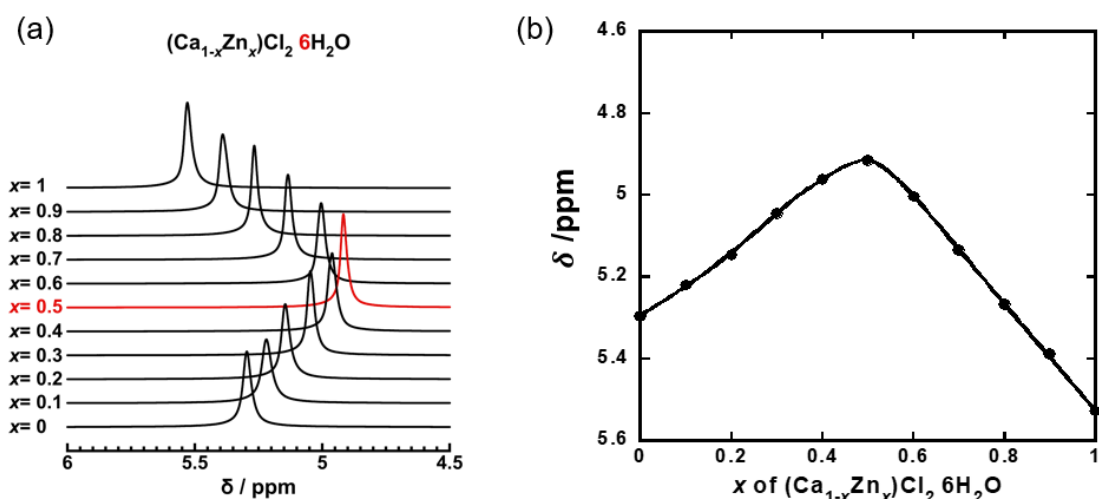


Figure 2. (a) ¹H NMR spectra at different CaCl₂-ZnCl₂·6H₂O mixing ratios; (b) Chemical shift of H with different mixing ratios.

On the other hand, the peak intensity of the ¹H nuclei in quantitative ¹H NMR is usually considered to correspond to the number of H nuclei, i.e., the number of water molecules, in solution. Therefore, we integrated the signal peaks of the ¹H nuclei to obtain the peak area and calculated the detection value of water molecules in solutions

by the ratio of the peak area to the concentration of water molecules at bulk water. The results are shown in Fig. 3, where the vertical axis represents the ratio of the concentration of water molecules obtained by quantitative ^1H NMR detection to the concentration of water molecules in pure water as the actual detected molar amount of water molecules:

$$\text{Detected molar amount of water} = \frac{A_{\text{water in electrolyte solution}}}{A_{\text{bulk water}}} \times c_{\text{bulk water}} \quad (6)$$

where A denotes the value of the peak area obtained by integrating the peaks of water molecules in the ^1H NMR spectra, and c denotes the concentration of water molecules in each solution, and it is worth noting that $c_{\text{water in electrolyte solution}}$ in this equation denotes the concentration of water molecules measured by ^1H NMR spectroscopy. The theoretical values in the graphs are calculated from the density, concentration of the mixed solutions according to the following equation:

$$c_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{V_{\text{sol.}}} = \frac{m_{\text{sol.}} - m_{\text{ZnCl}_2} - m_{\text{CaCl}_2}}{V_{\text{sol.}} M_{\text{H}_2\text{O}}} = \frac{\rho_{\text{sol.}} - M_{\text{ZnCl}_2} c_{\text{ZnCl}_2} - M_{\text{CaCl}_2} c_{\text{CaCl}_2}}{M_{\text{H}_2\text{O}}} \quad (7)$$

where c represents the concentration of each component in the mixed molten salt hydrate, m represents the mass, $V_{\text{sol.}}$ represents the volume of the mixed molten salt hydrate, $\rho_{\text{sol.}}$ represents the density of the mixed molten salt hydrate, and M represents the molar mass of the substance.

It can be found that the detected values of water in all mixed solutions are lower than the theoretical values of water in solutions obtained by density and concentration calcul-

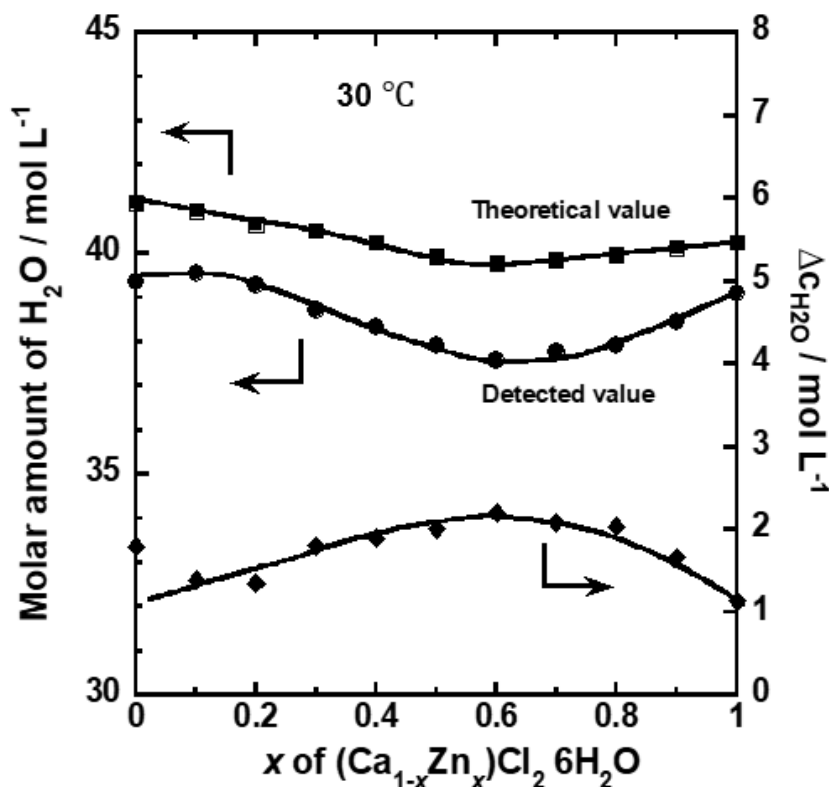


Figure 3. Comparison between the number of water molecules detected by quantitative ^1H NMR spectroscopy in the mixture and the number of water molecules calculated. $\Delta c_{\text{H}_2\text{O}}$ represents the difference between the calculated and detected values. The square points in the figure represent the concentration of water molecules in the mixture, calculated based on density and concentration. The circular points represent the concentration of water molecules derived from the signal peaks obtained through quantitative ^1H NMR measurements. The diamond shapes represent the difference between the theoretical values and the measured values.

-ations. This phenomenon is very similar to the results reported by Maki et al..^{26,27}

Grünberg et al. reported that in a mixed system of SiO_2 and water, the signal peaks of the water molecules broadened as the solid phase increased, and the ^1H NMR signal originating from water could not be detected when the volume fraction of water was less than 3%. They attributed this to the interaction of water molecules adsorbed on the

surface of SiO₂ with SiO₂, which resulted in a decrease in the mobility of water molecules near the surface, a substantial decrease in the relaxation time, and a broadening of the peak width thus leading to non-detectability.²⁸ Therefore, we suggest that water molecules hydrated with ions have substantially reduced motility due to strong interactions with the ions, corresponding to substantially larger peaks in the ¹H NMR spectra, leading to difficulties in being observed in the actual spectra. Therefore, in combination with the results of quantitative ¹H NMR spectroscopy, it can be seen that in mixed molten salt hydrates, when the concentration of Zn²⁺ is relatively low, increasing the concentration of Zn²⁺ increases leading to more water molecules interacting with the ions, even though the total concentration of the ions in the mixed system remains constant. Whereas, when Zn²⁺ dominates the mixed system, continuing to increase Zn²⁺ makes the ion-water molecule interactions weaker. The results of this quantitative assay also showed very good agreement with the results of the chemical shift of H, i.e., at lower concentrations of Zn²⁺, increasing Zn²⁺ led to increased ion-water molecule interactions, resulting in weakening (or breaking) of hydrogen bonds between otherwise water molecules, and more water molecules took part in the water-sum of the ions. When Zn²⁺ is present in large amounts, ion-water molecule interactions weaken and more hydrogen bonds form between water molecules.

3.2 Near-infrared spectroscopy of water molecules in mixed molten salt hydrates

Although ^1H NMR can quantitatively detect the quantity of water molecules, the frequency of the magnetic field used in NMR is lower than the exchange rate of hydrogen atoms between water molecules. Since NIR spectroscopy is based on vibrational spectroscopy of OH binding, it is usually assumed that cations affect the spectra to a much lesser extent than anions because, while water molecules are hydrated with cations through lone-electron pairs^{9,29}, anions interact directly with OH. As a result, the motion of water is averaged out, and the NMR spectrum of water only reveals a single signal peak. To better investigate the impact of changes in the ion mixing ratio on hydrogen bonding in molten salt hydrates, we employed near-infrared (NIR) spectroscopy to analyze water. The results are shown in Fig. 4a. An asymmetric broad peak corresponding to the combined modes ($\nu_1+\nu_3$) of the OH symmetric stretching vibration (ν_1) and the OH antisymmetric stretching vibration (ν_3) of water molecules is observed in the range of approximately 6000–8000 cm^{-1} .³⁰ Similar to quantitative ^1H NMR, the number of water molecules in each mixed hydrate was estimated by integrating the area under the absorption peaks. However, consistent with previous studies, the measured quantity of water molecules is lower than the theoretical value calculated from density and concentration, as shown in Fig. 4b, furthermore, the measu-

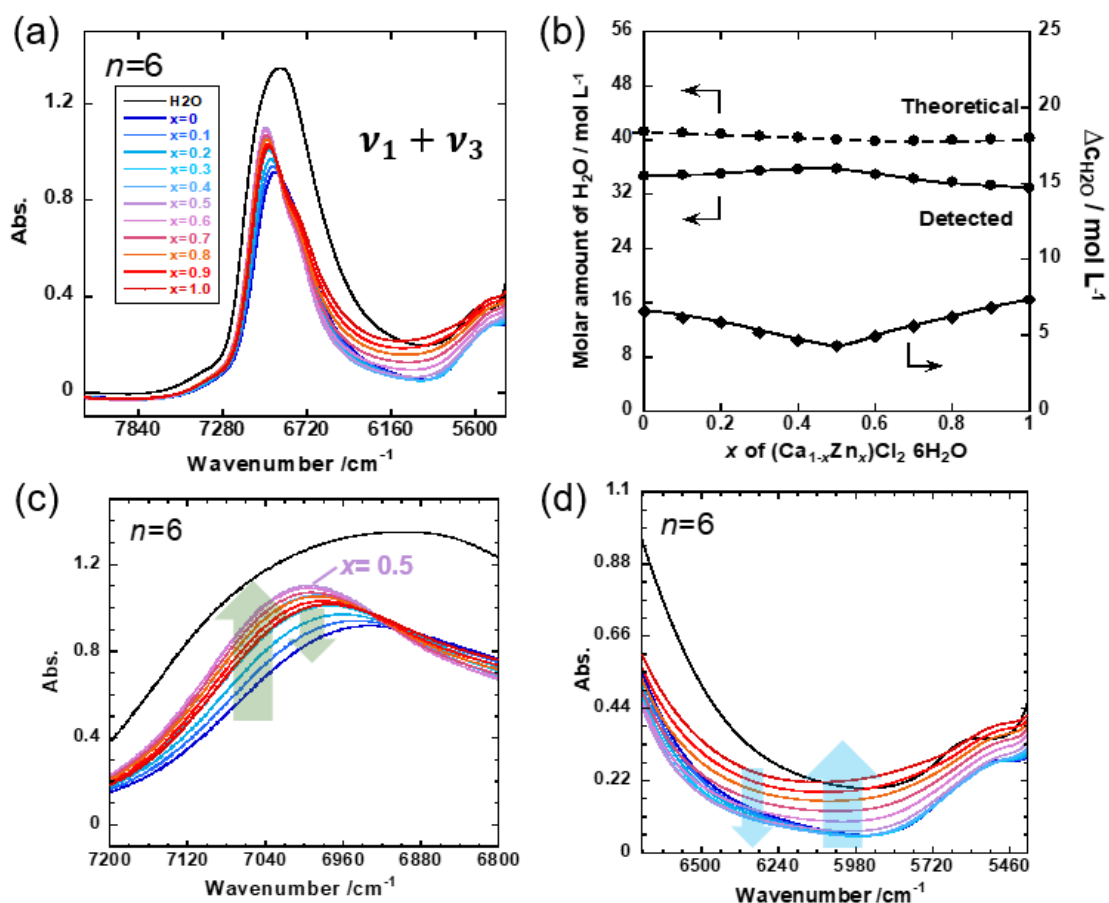


Figure 4. (a) Near-infrared spectra of H₂O at different CaCl₂-ZnCl₂ 6H₂O mixing ratios, showing the combination modes of symmetric and asymmetric stretching vibrations of O-H; (b) Comparison of the number of water molecules obtained by quantitative analysis of the near-infrared spectra of water with the number of water molecules calculated. (left y-axis) Δ_{CH_2O} represents the difference between the calculated and measured values. (right y-axis); (c) Magnified near-infrared spectrum of water around 7000 cm⁻¹; (d) Magnified near-infrared spectrum of water around 6000 cm⁻¹.

-red values of water molecules also exhibit a significant dependence on concentration of Zn²⁺. In a previous study, we proposed that the decrease in absorbance of water molecules in NIR spectra was due to the interaction of ions with water molecules inhibiting the generation of the combined modes ($\nu_1 + \nu_3$) of the OH symmetric stretching vibration (ν_1) and the OH antisymmetric stretching vibration (ν_3), which led

to a decrease in the peak area. To further validate this idea, the near-infrared spectrum of water needs to be further analyzed.

Compared to the absorption peaks of pure water, the absorption peaks of water molecules in molten salt hydrates exhibit a significant decrease in intensity, which is attributed to the substantial reduction in the number of water molecules within the molten salt hydrates. The decrease in absorption intensity is less pronounced on the high-wavenumber side (around 7280 cm^{-1}) but shows a marked reduction on the low-wavenumber side (around $6800\text{--}5800\text{ cm}^{-1}$). The NIR spectrum of water is generally considered to be composed of contributions from water molecules in various hydrogen bonding states. The high-wavenumber region typically represents water molecules with few or no hydrogen bonds, such as those in the vapor phase, while the low-wavenumber region corresponds to water molecules significantly influenced by hydrogen bonding, such as those in the ice phase.^{31,32} The variation in absorption intensity around 7280 cm^{-1} is consistently opposite to the changes observed around 6000 cm^{-1} . Notably, the absorption intensity does not simply increase or decrease but exhibits more complex behavior. Overall, with the gradual increase of Zn^{2+} , hydrogen bonds between water molecules in the mixed hydrates are initially disrupted and then progressively form new hydrogen bonds. This phenomenon is highly consistent with the results observed through NMR. This non-monotonic variation suggests a competitive interaction within

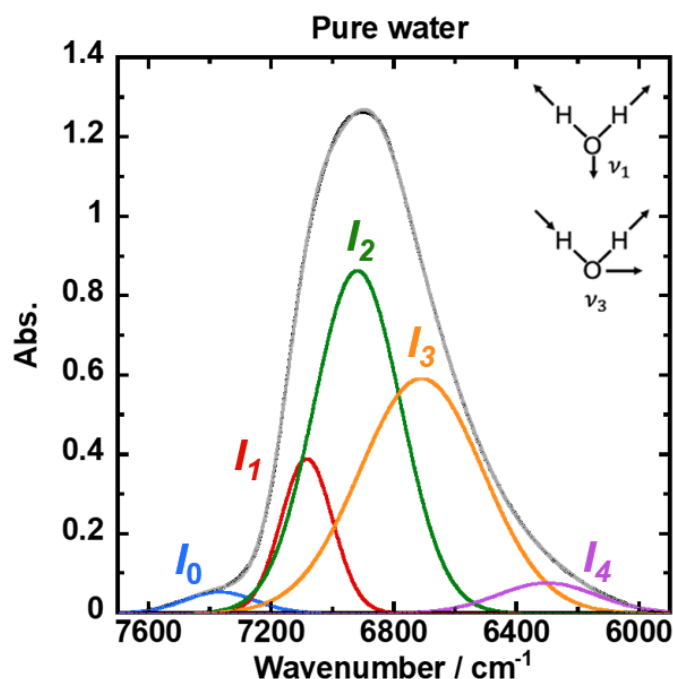


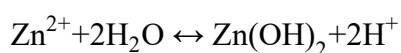
Figure 5. Deconvolution results of the near-infrared spectra of water at 6800 cm^{-1} : Combination bands of OH symmetric vibration (ν_1) and asymmetric vibration (ν_3). The details of five Gaussian bands after deconvolution are shown Table 1.

Table. 2 The five Gaussian components obtained from the deconvolution of the near-infrared absorption spectrum of water molecules represent five distinct hydrogen-bonding states of water molecules within the system.

Gaussian components of NIR combination bands/ cm^{-1}	Assignments
7369 (I_0)	Free OH stretch vibration
7084 (I_1)	OH stretch vibration of singly H-bonded water
6919 (I_2)	OH stretch vibration of H-bonded water with two or three H-bonds
6700 (I_3)	OH stretch vibration of H-bonded water molecule with a distorted icelike structure
6301 (I_4)	OH stretch vibration of H-bonded water molecule with icelike structure
For the attribution of peaks are referred to the ref. 33	

the mixed system, where water molecules and Cl^- tend to preferentially interact with either Ca^{2+} or Zn^{2+} , while the other ion forms more ion pairs with Cl^- .

By deconvoluting the water absorption peaks using Gaussian functions, we identified five distinct absorption peaks corresponding to different hydrogen bonding states, as shown in Table 2 and Fig. 5.³³ Based on spectral intensity changes, we classified the five types of water molecules into two categories: I_0 (7368 cm^{-1}) and I_1 (7084 cm^{-1}) are attributed to water molecules involved in ion hydration, while I_2 (6919 cm^{-1}), I_3 (6710 cm^{-1}), and I_4 (6301 cm^{-1}) are attributed to water molecules not significantly affected by ions, similar to bulk water. The detection results for the two types of water molecules shown in Fig. 6a further corroborate the observations regarding spectral absorption intensity. When the $x < 0.5$, the number of water molecules involved in ion hydration increases, leading to a weakening or breaking of hydrogen bonds between water molecules. Conversely, when $x > 0.5$, the hydrogen bonding between water molecules is either strengthened or increased. Zn^{2+} forms partial covalent bonds with oxygen atoms, resulting in the appearance of OH stretching vibrations at lower frequencies.²⁹ On the other hand, due to the significant decrease in pH observed in Fig. 7, we hypothesize that when Zn^{2+} predominates in the mixed solution, it triggers a hydrolysis reaction:



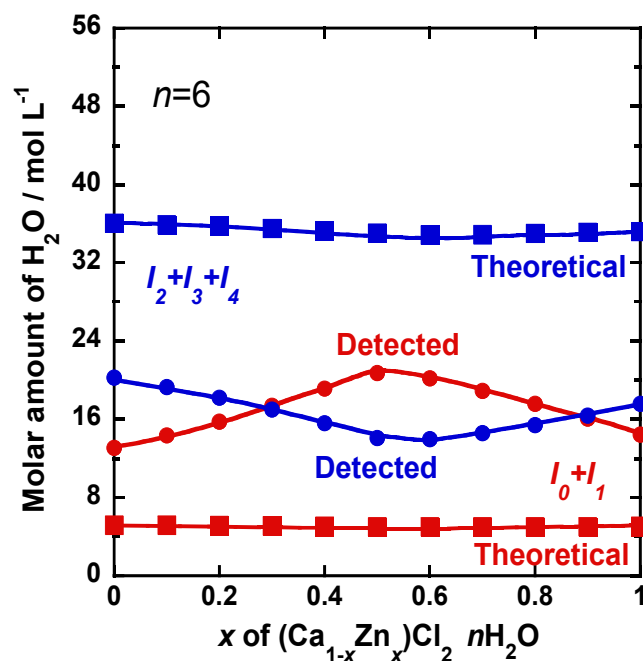


Figure 6. Variation in the area of water molecules interacting with ions (I_1+I_2 , red) and water molecules affected by ions ($I_3+I_4+I_5$, blue) as a function of the CaCl_2 - ZnCl_2 mixing ratio, after deconvolution using Gaussian functions. In the figure, the square points represent the theoretical values calculated from the number of water molecules in the solution and the deconvolution results of pure water, while the circular points indicate the experimentally measured results obtained from the deconvolution of the near-infrared absorption spectrum of the mixed solution.

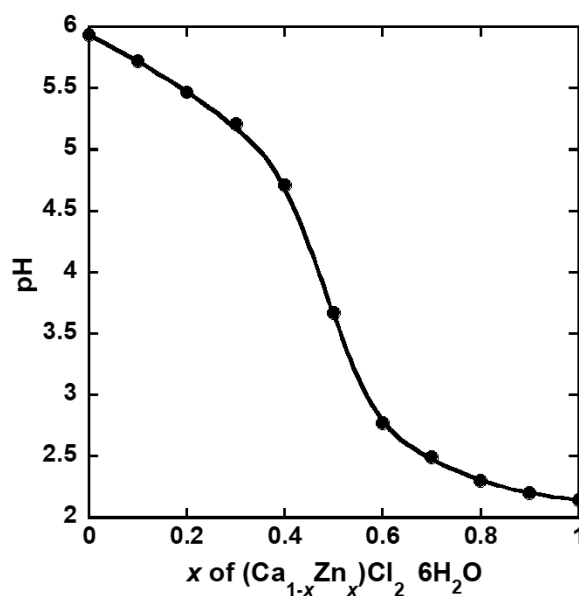


Figure 7. pH of $(\text{Ca}_{1-x}\text{Zn}_x)\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ mixed solutions as a function of Zn^{2+} concentration.

resulting in the formation of H^+ clusters in the form of $H^+(H_2O)_n$, which leads to the formation of new hydrogen bonds.³⁴⁻³⁶ This process leads to the formation of new hydrogen bonds. It is noteworthy that the trend in the number of water molecules not interacting with ions ($I_3+I_4+I_5$), as measured by near-infrared spectroscopy, shows a high degree of consistency with the quantitative NMR detection results shown in Fig. 3. This result supports the perspective of Maki et al., who suggested that water molecules involved in ion hydration have their motion restricted and thus cannot be detected by NMR.^{26,27}

3.3 Competitive Interactions Between Ions and Water Molecules in $(Ca_{1-x}Zn_x)Cl_2 \cdot 6H_2O$

To elucidate the variations in interactions between ions and between ions and water molecules with changes in mixing ratios, Raman spectra of all mixed systems were recorded, as shown in Fig. 8a. The peak observed near 280 cm^{-1} is attributed to the Zn-Cl vibrational mode in $[ZnCl_4]^{2-}$.³⁷ The peak around 390 cm^{-1} is assigned to the Zn-O vibrations in $[ZnCl_x(H_2O)_{4-x}]^{(2-x)+}$ complexes, as the formation of $[Zn(H_2O)_6]^{2+}$ is considered minimal in high concentration solutions.³⁸ As the concentration of Zn^{2+} increases, the peak corresponding to $[ZnCl_4]^{2-}$ gradually exhibits a red shift. This red

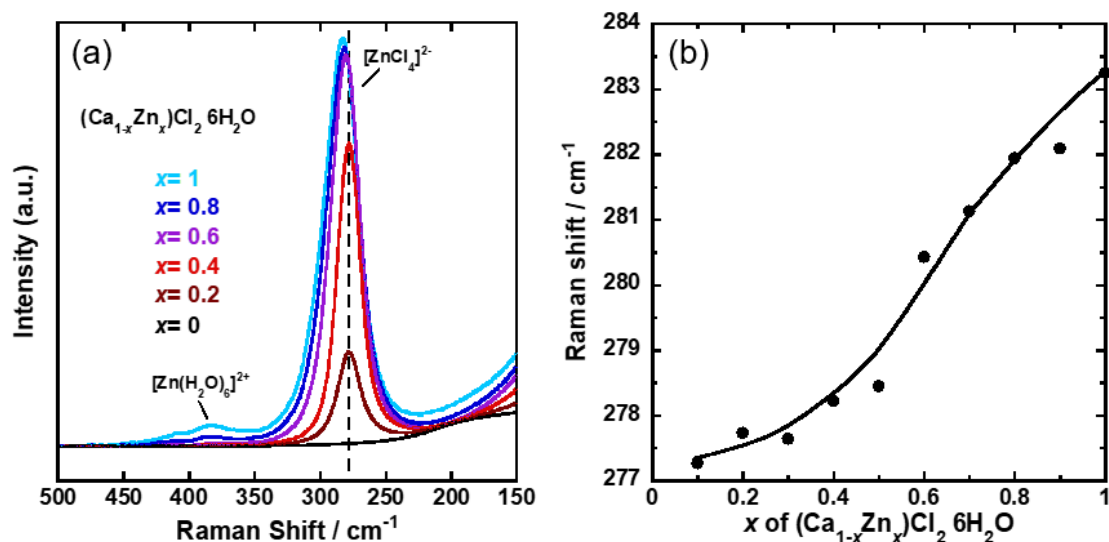


Figure 8. (a) Raman spectra of $[\text{ZnCl}_4]^{2-}$ and $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ at different CaCl_2 - $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$ mixing ratios. The signal peak at 280 cm^{-1} is attributed to $[\text{ZnCl}_4]^{2-}$, while the peak at 390 cm^{-1} is associated with the Zn-O vibrations in the $[\text{ZnCl}_x(\text{H}_2\text{O})_{4-x}]^{2-}$ complex. (b) Shift in the Raman peak position of $[\text{ZnCl}_4]^{2-}$ as a function of Zn^{2+} concentration.

shift is due to enhanced ion interactions between Zn^{2+} and Cl^- , indicating that with increasing Zn^{2+} , $[\text{ZnCl}_4]^{2-}$ complexes are continuously forming. Notably, a distinct Zn-Cl vibration peak is still observable even when $x = 0.1$. In contrast, the peak for Zn-O shows only a weak intensity even when $x = 0.6$. To account for baseline effects, the intensity of the Zn-O peak was normalized using the intensity of the $[\text{ZnCl}_4]^{2-}$ peak at 280 cm^{-1} as a reference. The normalized results are shown in Fig. 9. For $x < 0.5$, there is no significant change in the intensity of the Zn-O peak, indicating that at lower concentrations of Zn^{2+} , Zn^{2+} preferentially interacts with Cl^- to form complexes.³⁸ This interpretation is supported by the results shown in Fig. 10, which include viscosity, conductivity, and the self-diffusion coefficient of H.

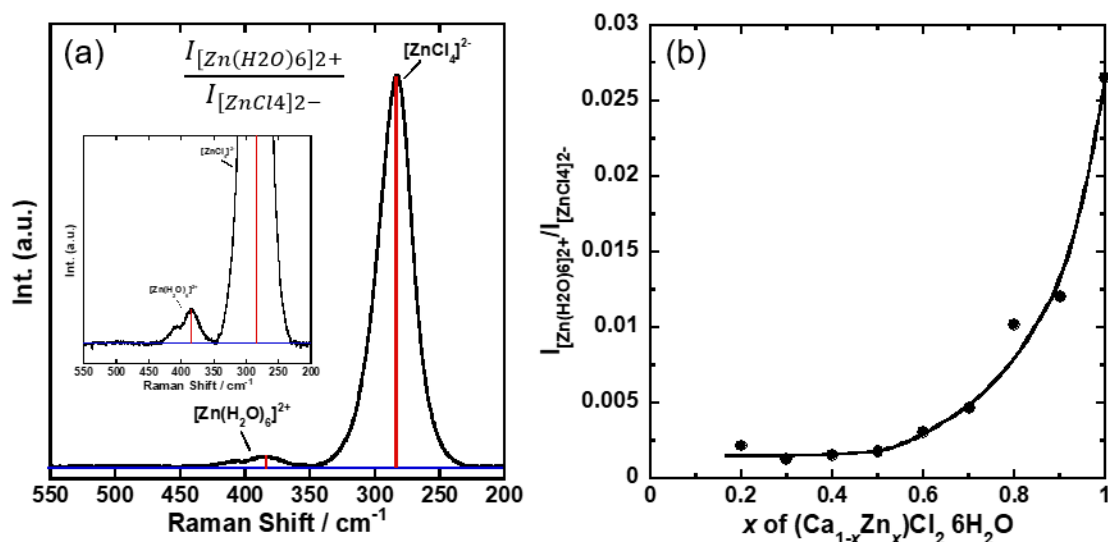


Figure 9. (a) Normalized intensity of the $[Zn(H_2O)_6]^{2+}$ peak with $[ZnCl_4]^{2-}$ peak intensity as the reference; (b) Plot of the normalized intensity of the $[Zn(H_2O)_6]^{2+}$ peak as a function of Zn^{2+} concentration.

In comparison to dilute solutions, the reduction in the number of water molecules in $CaCl_2 \cdot 6H_2O$ leads to a Cl^- entering the first solvation shell of Ca^{2+} ,³⁹ thereby forming a contact ion pair (CIP). This phenomenon results in increased viscosity and reduces electrical conductivity of the solution. Given that Zn^{2+} has a lower charge density than Ca^{2+} , the introduction of Zn^{2+} causes Cl^- to preferentially interact with Zn^{2+} . On the other hand, in high-concentration $CaCl_2$ solutions, the high activity of Cl^- facilitates the formation of chloride complexes.^{40,41} As a result, Cl^- moves away from the first solvation shell of Ca^{2+} , allowing more water molecules to enter the solvation shell of Ca^{2+} . Consequently, a significant decrease in the viscosity and an increase in conductivity of the mixed system are observed, which, as shown in Fig. 6, correlates with the further disruption of hydrogen bonding between water molecules at $x < 0.5$ in

near-infrared and NMR spectra. Kajinami et al. also obtained similar results through X-ray diffraction measurements, where no Zn-O peaks were observed in the range of $x < 0.5$.⁴² On the other hand, when $x > 0.5$, although it is generally accepted that cations cause much less direct effect on OH vibrations than anions, however, unlike general metal ions such as Ca^{2+} , Na^+ , K^+ , the strong binding of Zn-O can also lead to an effect on OH vibrations. Therefore, it can be suggested that the substantial increase in Zn^{2+} leads to the rapid formation of Zn-O bonds in the $[\text{ZnCl}_x(\text{H}_2\text{O})_{4-x}]^{(2-x)+}$ complex, causing the OH stretching vibrations to shift towards lower frequencies. Simultaneously, the hydrolysis reaction also intensifies, leading to the formation of new hydrogen bonds. This results in a slight increase in the viscosity of the mixed system, a reduction in the self-diffusion coefficient of H_2O , and a decrease in conductivity, as in Fig. 10.

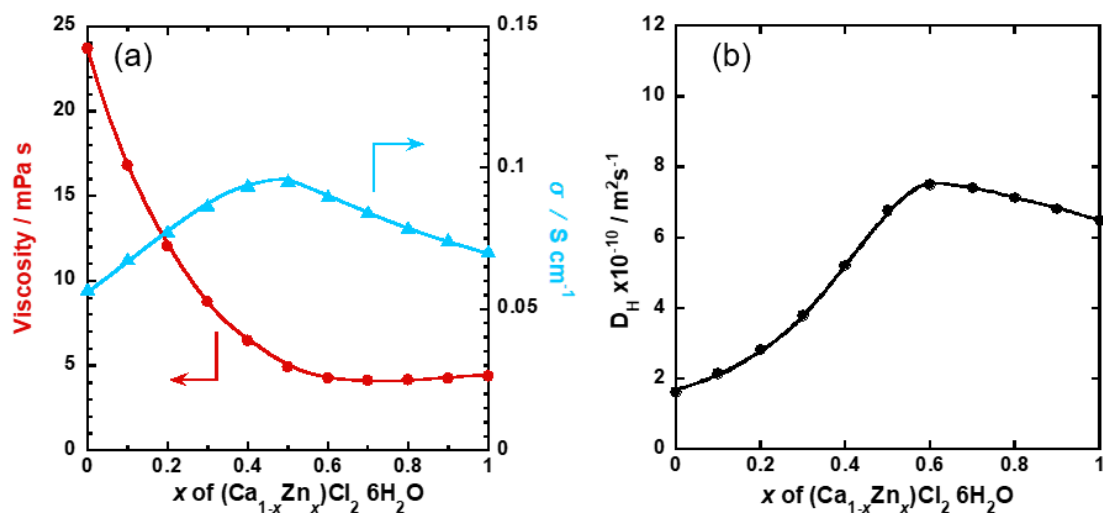


Figure 10. (a) Viscosity (red) and conductivity (blue) of $(\text{Ca}_{1-x}\text{Zn}_x)\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ mixed solutions as a function of Zn^{2+} concentration. (b) Self-diffusion coefficient of H as a function of Zn^{2+} concentration.

As mentioned earlier, in our previously reported quantitative NIR spectroscopic studies on aqueous solutions of Li salts with different anions, we suggested that the low number of water molecules in the aqueous solution of the electrolyte detected by NIR spectroscopy allowed the suppression of the generation of the combined modes ($\nu_1+\nu_3$) of the OH symmetric stretching vibration (ν_1) and the OH antisymmetric stretching vibration (ν_3) due to the interactions between the anions and the water molecules. (ref)

In $(\text{Ca}_{1-x}\text{Zn}_x)\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ mixed system, when $x < 0.5$, according to the previous results, Cl^- in the solvation shell of Ca^{2+} is attracted by Zn^{2+} leading to more water molecules into the solvation shell of Ca^{2+} and the strong interaction of $\text{Zn}^{2+}-\text{Cl}^-$ is also considered to lead to the weakening of the strength of the interactions between Cl^- and water molecules, so the number of water molecules affected by the anion is reduced, so although a weakening of the hydrogen bonding strength of water can be observed in the spectra of Fig. 4a, the detection value of water molecules appeared to rebound, as in Fig. 4b. when $x > 0.5$, OH coordinates with Zn^{2+} to form a strong Zn-O bond, and this interaction resulted in the vibration of OH being affected. Moreover, the strong Zn-O interaction leads to the dissociation of O-H, which exacerbates the water addition decomposition reaction and leads to a decrease in the OH binding number, which can be observed from the spectra that the absorbance of the water molecule decreases again.

4. Conclusions

In this study, the solution structure of the $(\text{Ca}_{1-x}\text{Zn}_x)\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ mixed system as a function of the mixing ratio was clarified using quantitative ^1H NMR and near-infrared spectroscopy, in conjunction with Raman spectroscopy. When $x < 0.5$, the added Zn^{2+} tends to interact more with Cl^- , resulting in an increased number of water molecules in the Ca^{2+} solvation shell and weakened interactions between water molecules. When $x > 0.5$, the rapid formation of Zn-O bonds in the $[\text{ZnCl}_x(\text{H}_2\text{O})_{4-x}]^{(2-x)+}$ complex and the intensified hydrolysis reaction lead to a decrease in the pH of the mixed solution. Concurrently, the generated H^+ primarily exists as $\text{H}^+(\text{H}_2\text{O})_n$ clusters, which results in the formation of new hydrogen bonds between water molecules. The consistency between the quantitative ^1H NMR results and the near-infrared spectroscopy analysis of the trends in non-interacting water molecules also confirms that the reason for the water molecule count detected by quantitative ^1H NMR being lower than theoretical values is due to the restricted movement of water molecules interacting with ions, making them difficult to detect. Moreover, the result further validates our idea that the anomalously low number of water molecules detected in NIR spectroscopy is related to the strength and number of anion-water molecule interactions. When the ion-water molecule interactions have a direct effect on the OH stretching vibration, the generation

of the combined modes ($\nu_1+\nu_3$) of the OH symmetric stretching vibration (ν_1) and the OH antisymmetric stretching vibration (ν_3) is suppressed. This provides a new perspective for future quantitative studies on the structure of aqueous solutions.

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CHAPTER 3

Effect of Coexisting TiO₂ Powder on Ionic Conduction of Highly Concentrated LiTFSA Aqueous Electrolyte (20.5 mol kg⁻¹)

1. Introduction

Much research has been studied on the diversification of aqueous energy storage devices due to their safety and ease of handling, which is not the case with conventional energy storage devices using flammable solvents.¹⁻⁴ For example, overcoming the water decomposition voltage of 1.23 V is expected to be feasible through research using highly concentrated aqueous electrolyte solutions.⁵ Especially, battery systems using highly concentrated aqueous electrolyte solutions are expected to have features not found in conventional aqueous electrolytes, such as increased output voltage by taking advantage of the low activity of water as solvent and increased current capacity due to increased ionic concentration.

In particular, aqueous lithium bis(trifluoromethanesulfonyl)amide (LiTFSA; $\text{LiN}(\text{SO}_2\text{CF}_3)_2$) with concentrations exceeding 20 mol kg⁻¹ have a heterogeneous ionic distribution, with water-rich regions consisting of hydrated cation such as $\text{Li}(\text{H}_2\text{O})_4^+$ and anion-rich regions consisting of $\text{Li}(\text{TFSA})_x^{(x-1)-}$ ionic aggregates, despite being 1:1 electrolytes simply consisting of cations, anions, and solvents. This has led to the term “water-in-salt” electrolyte, which has attracted much attention.⁶⁻⁹

In general, in highly concentrated aqueous solutions, it is difficult to achieve the stable hydration structure and independent migration of ions observed due to the

formation of ion pairs. For example, since the ratio of Li:H₂O is ca. 1:3 in the 20 mol kg⁻¹ LiTFSA system, complete hydration of Li⁺ ion is not expected. However, the ionic interaction between Li⁺ and TFSA⁻ is certainly enhanced between Li⁺ and O in TFSA⁻, which causes some Li⁺ ions to release water molecules. Therefore, it is suggested that coexisting Li⁺ ions that are not interacting with TFSA⁻ can hydrate with water molecules beyond their existence ratio, forming relatively stable hydrated ions.^{1,10,11} Consequently, aggregated hydrophobic Li(TFSA)_x^{(x-1)-} domains form disproportionate structures due to the presence of hydrophilic Li-rich domains in the gaps between them. Hydrated Li⁺ ions avoid interaction with TFSA⁻ ions and maintain a high conductivity of 10 mS cm⁻¹ despite high concentration and viscosity.⁹

We are interested in whether the enhanced conductive path of Li⁺ ions is maintained in various composite materials in electrochemical devices, because many electrolytes coexist with and are supported by separators or active materials made of various powders and gels resulting in the formation of numerous solid/liquid interfaces. The structural characteristics of these interfaces can significantly impact the performance of electrochemical devices. For example, Bhattacharyya et al. found that the addition of metal oxide powders to non-aqueous solutions enhances electrolyte dissociation due to the interactions between the solid and counterions (with charges opposite to those on the solid surface).¹²⁻¹⁴ They referred to such composites as “soggy sand” electrolyte.

These results in an increased conductivity of the space charge region, leading to an overall conductivity increase by an order of magnitude. Suzuki et al. reported the heterogeneous distribution of a binary solvent solution of propylene carbonate-1,2-dimethoxyethane containing LiClO₄ on SiO₂ surfaces, indicating that such distributions can affect the conductivity within solid-liquid mixed systems.¹⁵ Moreover the structural changes of LiTFSa aqueous electrolyte with different concentration at solid-phase interfaces have been extensively studied using atomic force microscopy (AFM), surface force apparatus (SFA), and molecular dynamics simulations (MD).¹⁶⁻²⁰ However, the impact of these structural changes on the electrical conductivity has yet to be discussed, and there is a lack of experimental data exploring the influence of solids on the structure of 20.5 mol kg⁻¹ LiTFSa electrolyte.

In this study, we investigated the electrical conductivity and its activation energy in solid/liquid mixed systems by mixing the 20.5 mol kg⁻¹ LiTFSa electrolyte with anatase TiO₂ metal oxide powder. To explain the relationship between electrical conductivity and ionic interaction for the effect of solid phase of TiO₂ powder, Raman spectra was measured in order to observe the state of the hydration structure by Raman spectroscopy.

However, the volume fraction of water is extremely low in the presence of a large portion of ionic species and in coexistence with solids, and little amount exceeding the limit of sensitivity of Raman spectra made the difficulty of the measurement. Therefore,

we employed near-infrared (NIR) spectroscopy to detect the behavior changes in water molecules. Additionally, we turned our attention to the near-infrared (NIR) spectroscopy of water molecules. Due to the anharmonicity of molecular vibrations, vibrational spectra can be observed in the NIR range. Moreover, due to the significant anharmonicity of heterodiatomic OH bond in water solvent, these groups exhibit absorption peaks in the NIR region that are much stronger than those of other functional groups, giving NIR spectroscopy a natural advantage in detecting water molecules. Furthermore, because of the anharmonicity of the spectra, the NIR spectra of water molecules are highly sensitive to changes in hydrogen bonding environments. This makes it frequently used in studies related to changes in water structure. For instance, Dagade et al. conducted a detailed analysis of the NIR spectra of water molecules in aqueous solutions, subdividing the absorption peaks by the number of hydrogen bonds and studying the disturbance of water structure by ions.²¹ In this study, we employed diffuse reflectance NIR spectroscopy to investigate in detail the effects of TiO₂ solids on water molecules in high-concentration aqueous solutions by analyzing the changes in the distribution of water molecules with different hydrogen-bonding states as a function of solid-liquid mixing ratios. Additionally, because the nuclear spin-spin relaxation time (T_2) is highly sensitive to interactions surrounding the nuclei, we examined the behavior changes of water molecules in the presence of TiO₂ in water-in-

salt electrolytes by measuring the T_2 of water molecules.

2. Experimental

2.1 Preparation of samples

For the material of solid phase, anatase TiO_2 (FUJIFILM Wako Pure Chemical Corporation, 1st Grade) was dried in a vacuum oven at 180 °C for 20 hours. After drying, it was stored in a glove box filled with Ar atmosphere. The specific surface area of the dried TiO_2 was determined by BET analysis to be $9.39 \text{ m}^2 \text{ g}^{-1}$, with a true density of 3.9 g cm^{-3} . LiCl (Nacalai Tesque Inc., GR) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSA) (KANTO CHEMICAL CO., INC SP) can be used without further purification. LiCl and LiTFSA are stored in a glove box filled with Ar atmosphere, and the required mass is weighed out. The substances are dissolved in the corresponding mass of deionized water (conductivity $< 0.055 \text{ } \mu\text{S cm}^{-1}$) to prepare solutions of concentrations from 1.0 mol kg^{-1} to 20.5 mol kg^{-1} . Typically, studies on water-in-salt electrolyte focus on electrolyte solutions with a concentration of 21 mol kg^{-1} .⁶⁻⁸ According to the phase diagram obtained by Ding et al.,²² the electrolyte solution of 21 mol kg^{-1} precipitates LiTFSA monohydrate ($\text{LiTFSA H}_2\text{O}$) crystals from the saturated

solution, causing phase separation below 25 °C on the liquidus line. This crystallization causes problems of handling sample preparation and storage. If the solution solidifies below the temperature at which crystal precipitation occurs, it can be easily and uniformly redissolved by heating in a system consisting only of liquid, allowing easy experimental operation even just below saturated solution concentration, i. e., 21 mol kg⁻¹ at 25 °C.

In performing experimental operations with a sample of concentrated solution mixed with the solid phase, it is expected that the liquid phase will separate within the solid-phase gap, resulting in a non-uniform distribution. Coagulation during experimental operation must be avoided as much as possible, because once heterogeneously separated, the hydrate does not return to its original homogeneous phase even if it is redissolved after heating among the solid particles. We confirmed that by using a LiTFSA electrolyte of 20.5 mol kg⁻¹, the solidification on the liquid phase line decreases from 25 °C to about 22.5 °C, thus enabling us to obtain results on temperature dependence with good reproducibility.

From a solution structure perspective, the [H₂O]/[Li⁺] ratio in a 21 mol kg⁻¹ LiTFSA aqueous solution is 2.65, whereas it is 2.71 at 20.5 mol kg⁻¹. This slight difference does not influence with the formation of nanometer-scale heterogeneity in the LiTFSA solution, as this nanostructure is still observable at 15 mol kg⁻¹,⁸ although with

potentially slight effects on the nanometer dimensions of water-rich domains. Thus, it can be assumed that this minor difference in water content between 21 to 20.5 mol kg⁻¹ does not influence the structural behavior of the LiTFSA aqueous electrolyte in the presence of a solid phase very much.

Densities of electrolyte aqueous solutions are measured at room temperature using a densitometer (Anton Paar, DMA 5000 M) for all electrolyte samples. All solutions were stored at 30°C to avoid the solidification of the concentrate solution. The concentration and relevant information for the prepared solutions are shown in Table 1.

Table 1. Various concentration indications and density for LiTFSA and LiCl aqueous solutions.

Solution	Concentration			Density
	/ mol kg ⁻¹	/mol L ⁻¹	[H ₂ O]/[Li ⁺]	/g cm ⁻³
LiCl	1	0.98	55.6	1.021
	20.5	14.27	2.7	1.301
LiTFSA	1	0.88	55.6	1.126
	5	2.91	11.1	1.417
	10	4.08	5.5	1.578
	15	4.71	3.7	1.665
	20.5	5.13	2.7	1.722

2.2 pH adjustment of electrolytes

Prepare pH adjustment solutions by adding solid HTFSA (KANTO CHEMICAL CO., INC SP) to 1 mol kg⁻¹ and 20.5 mol kg⁻¹ LiTFSA aqueous electrolytes to achieve a concentration of 1 wt% HTFSA. The pH adjustment solution was added to a specified mass of bulk LiTFSA electrolyte, ensuring that the final mass of the LiTFSA aqueous electrolyte remained 5 g. Thus, it can be perceived that different masses of HTFSA were added to 5 g of LiTFSA aqueous electrolyte. The adjustment of alkaline solutions was only conducted for the 1 mol kg⁻¹ LiTFSA solution, as the addition of LiOH to the 20.5 mol kg⁻¹ LiTFSA-H₂O resulted in significant precipitation. Detailed information about the resulting solutions is provided in Tables 2 and 3. The density of all electrolyte solutions was measured using a density meter (Anton Paar, DMA 5000 M) at room temperature (25 °C).

Table 2: By adding different amounts of HTFSA, the pH of 1.0 mol kg⁻¹ LiTFSA aqueous electrolyte can be adjusted.

-log[HTFSA]	4.591	4.097	3.591	3.096	2.591	2.097	1.593	1.105
pH	5.46	4.33	3.69	3.19	2.57	2.09	1.58	1.10

Table 3: By adding different amounts of HTFSA, the pH of 20.5 mol kg⁻¹ LiTFSA-H₂O can be adjusted.

-log[HTFSA]	4.912	3.911	3.407	2.904	2.379	1.913	1.409	0.920
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2.3 Preparation of solid-liquid coexistence

TiO₂ powder and the aqueous electrolyte were mixed in a volume ratio, with the liquid phase volume fraction ranging from 5 vol% to 50 vol% in an alumina mortar. After thorough mixing, the mixture was poured into a circular mold and compressed into cylindrical samples with a diameter of 10 mm by applying a pressure of 5 MPa for 30 minutes, as shown in Fig. 1.

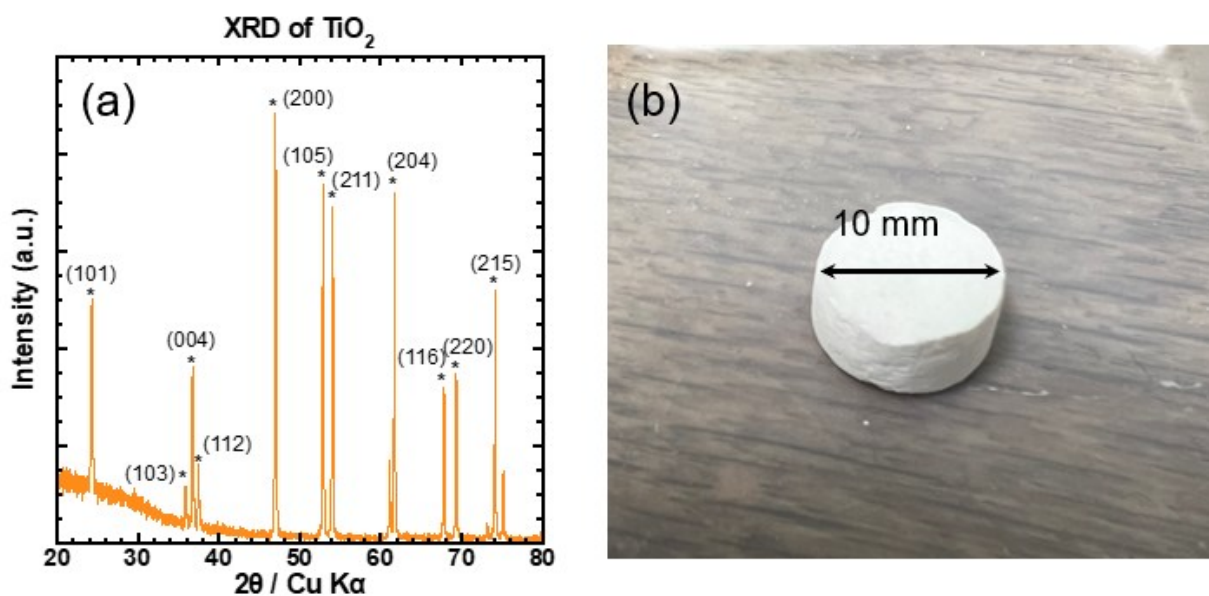


Figure 1. (a) XRD results of anatase TiO₂; (b) Schematic diagram of the sample obtained by compressing a homogeneous mixture of TiO₂ powder and liquid phase in a mold at 5 MPa for 30 minutes, with a sample diameter of 10 mm.

2.4 Electrical conductivity measurement and calculation of the activation energy

We measured the AC impedance for obtaining the electrical conductivity of the solid/liquid systems containing TiO₂ powder/ highly concentrated electrolyte. The prepared tablet samples were placed into a cell, as illustrated in Fig. 2, and AC impedance tests were conducted using a pair of platinum electrodes with a precision LCR meter (HP 4284A). An AC voltage of 0.6 V was applied, with a frequency range of 1 MHz to 25 Hz. To obtain the activation energy for ion transport, ΔE_a , the temperature inside the cell was controlled between 30 °C and 50 °C, with measurements taken every 2.5 °C. The activation energy for ionic conductivity, ΔE_a , was calculated by examining the dependency of conductivity on temperature. For cases where a linear relationship between these two variables was observed, the value of ΔE_a was determined by calculating the slope of the linear relationship between $\log \sigma$ and $1/T$ following the Arrhenius equation, as shown below:

$$\log \sigma = \frac{-\Delta E_a}{2.303RT} + \log A \quad (1)$$

where R and A are the gas constant and a constant, respectively.

In the case that non-linear temperature dependence obtained in the Arrhenius plots, activation energy was calculated using the Vogel-Tammann-Fulcher (VTF) equation.²³⁻

²⁵ This equation is commonly applied to describe the temperature dependence of

conductivity in highly concentrated electrolyte solutions, as follows:

$$\sigma = AT^{1/2}\exp[-B/(T-T_0)] \quad (2)$$

where A and B are constants, and T_0 is ideal glass transition temperature in free-volume theory. Mizuhata et al. provided a detailed description of the method for calculating the parameters in the VTF equation.^{26,27} The VTF parameters were determined with a nonlinear Gauss-Newton inverse matrix optimizing method.²⁷ The calculation was carried out on $\ln \sigma$ vs. T plots with respect to the following equation, which is the logarithmic function of Eq. 3:

$$\ln \sigma(T) = A' - (\ln T)/2 - B/(T-T_0) \quad (3)$$

where $A' = \ln A$ in Eq. 2. Three partial derivative functions with respect to parameters, A' , B , and T_0 were introduced for this operation as follows

$$\frac{\partial}{\partial A'} [\ln \sigma(T)] = 1 \quad (4)$$

$$\frac{\partial}{\partial B} [\ln \sigma(T)] = -\frac{1}{T-T_0} \quad (5)$$

$$\frac{\partial}{\partial T_0} [\ln \sigma(T)] = -\frac{B}{(T-T_0)^2} \quad (6)$$

The data processing was carried out by the BASIC program, which includes the functions of Eqs. 4-6, with emulator ANEX86 in personal computer. The calculation was processed until the relative error became within $10^{-3}\%$. After these parameters were determined, ΔE_a was calculated from the differential coefficient at 30 °C in Eq. 7;

$$\frac{d(\ln \sigma)}{d(1/T)} = -\frac{\Delta E_a}{R} = -\frac{1}{2}T - B\left(\frac{T}{T-T_0}\right)^2 \quad (7)$$

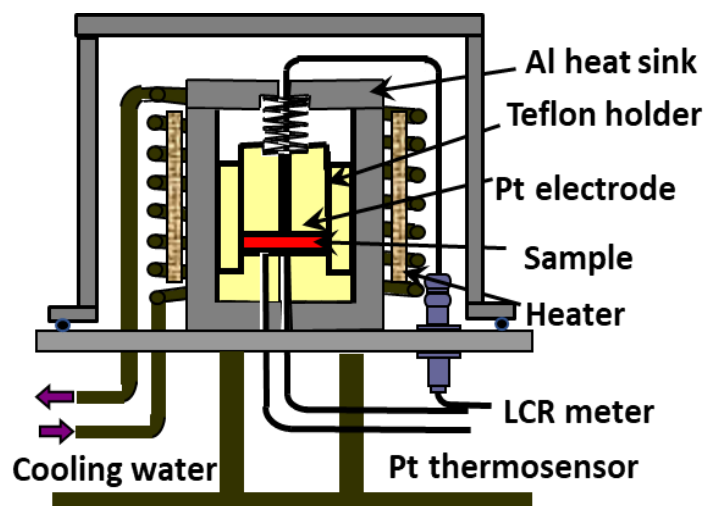


Figure 2. Schematic diagram of the cell used for testing solid-liquid coexistence samples. The cylindrical sample has a platinum electrode at both the top and bottom, maintained in full contact with the sample through springs and applied constant external force. The internal temperature of the cell is monitored in real time using a thermometer, and the temperature is controlled by a heater. Once the thermometer reading reaches the target temperature, it is maintained for 5 minutes to ensure that the sample temperature is consistent with the cell temperature.

2.5 Spectroscopy measurement

Raman spectra were recorded using a T-64000 Raman spectrometer (HORIBA, Ltd.) equipped with a Nb: YVO₄ laser and a charge-coupled device cooled using liquid nitrogen as a detector. The 532 nm line was used for excitation. The solution samples were loaded into glass tubes and spectra were recorded in the back-scattering geometry. The monochromator was calibrated using the CCl₄ peak at 459 cm⁻¹. All experiments were performed at room temperature.

To further understand the behavior of water molecules in solid-liquid coexistence systems, we employed diffuse reflectance spectroscopy to analyze the near-infrared spectra of water molecules. The near-infrared spectra of water molecules in pure solution were measured using total internal reflection. The ZnSe prism was employed at an incidence angle of 45° , with three reflections. In contrast, the near-infrared spectra of water molecules in a solid-liquid coexistence system were measured using a diffuse reflectance attachment (DR-600B) in an N_2 atmosphere. All near-infrared spectra were obtained using a JASCO FT-IR-615 spectrometer, with a resolution of 2 cm^{-1} , and averaged over 64 scans. The O–H stretching vibrations of water molecules are highly sensitive to changes in surrounding interactions, such as the formation or disruption of hydrogen bonds. Therefore, we examined the combination frequency of the OH symmetric and antisymmetric stretching vibrations of water molecules in the range of $6000\text{--}8000\text{ cm}^{-1}$.^{21,28} Using Gaussian functions and referencing the deconvolution results of pure water, we attributed the four components obtained from the deconvolution to different hydrogen bonding states of water molecules.²¹ To enhance the signal-to-noise (S/N) ratio, the Savitzky-Golay smoothing method was applied to the near-infrared spectra of all water samples.

The spin-spin relaxation time T_2 of ^1H NMR in both pure solution and solid-liquid coexistence samples was measured using Acorn Area (Xigo Nanotools). The magnetic

field strength was set to 0.3 T, with a measurement frequency of 13 MHz, a time of integrations of 4 times, and the measurement temperature was maintained at 30 °C. All samples were measured 10 times, and the average of these 10 results was taken. Due to instrument precision, the volume fraction of the liquid phase in the tested samples ranged from 40 vol% to 100 vol%.

3. Result and discussion

3.1 The conductivity of Lithium electrolyte solutions in solid-liquid coexistence systems.

Figures 3 display the Nyquist plots of the electrochemical impedance for 1 mol kg⁻¹ and 20.5 mol kg⁻¹ LiTfSA electrolyte at 30 °C. All samples exhibit a semicircular feature at high frequencies and a linear portion at low frequencies in their Nyquist plots. Additionally, as the liquid phase volume fraction decreases, the diameter of the semicircular part increases. In the case of 20 vol% liquid content, TiO₂ powder/ 20.5 mol kg⁻¹ LiTfSA aqueous electrolyte system showing a resistance of ca. $8 \times 10^5 \Omega$, normal polarization in the low frequency range is unlikely to occur, and there is little im

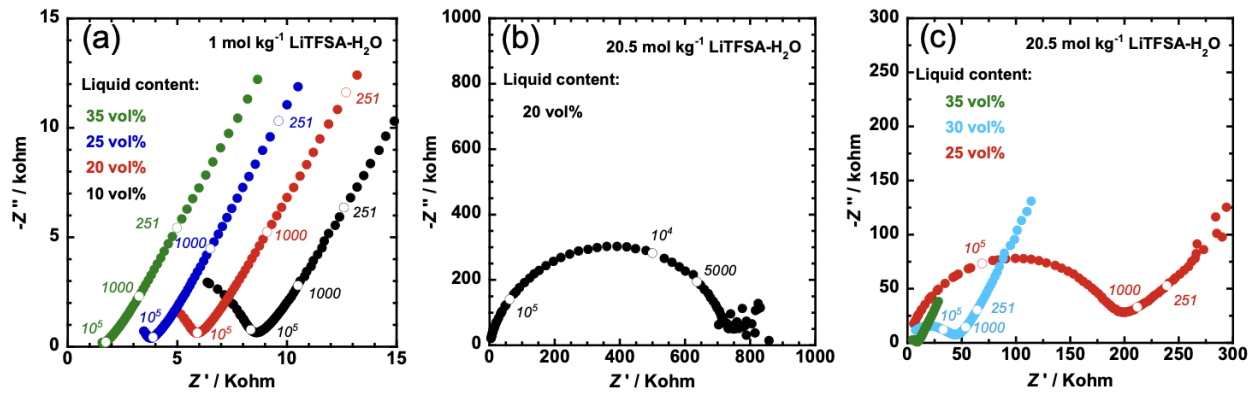


Figure 3. Nyquist plot obtained by impedance measurement of (a) TiO₂ powder / 1 mol kg⁻¹ LiTFSA-H₂O electrolyte; (b) TiO₂ powder/ 20.5 mol kg⁻¹ LiTFSA aqueous electrolyte coexisting system at the liquid phase volume fraction of 20 vol%; (c) TiO₂ powder/ 20.5 mol kg⁻¹ LiTFSA aqueous electrolyte coexisting system at liquid phase volume fractions greater than 20 vol%. The italicized numbers in the three figures indicate the measurement frequencies for AC impedance.

impedance indicative of solution diffusion, as shown in Fig. 3b. All Nyquist plots at high frequency range are considered as the resistance of the electrical conductivity of the solid-liquid coexistence system caused by ionic conduction of the aqueous liquid phase. In TiO₂ powder/ 20 vol% 20.5 mol kg⁻¹ LiTFSA aqueous electrolyte system, the excessively high resistance value leads to an inability to accurately detect results as the low frequency approaches the DC region. The electrical conductivity in each solid-liquid coexistence system is calculated using the following formula:

$$\sigma = L / RS \quad (8)$$

where L represents the thickness of the sample, R is the resistance of the sample obtained through Nyquist analysis, and S is the cross-sectional area of the sample. The

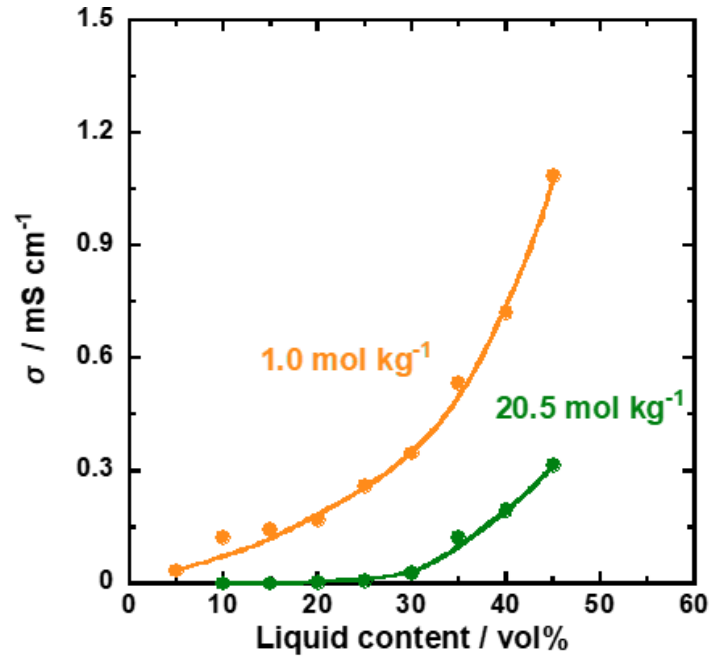


Figure 4. The variation of the electrical conductivity with the liquid content of the TiO₂ powder/ LiTFSA aqueous electrolyte coexistence system. The concentration notations in the figure are for LiTFSA electrolyte solution.

results of the conductivity of the solid-liquid coexistence systems as a function of the liquid phase volume fraction are shown in Fig. 4. For both LiTFSA aqueous electrolyte solutions of the concentrations of 1 mol kg⁻¹ and the 20.5 mol kg⁻¹, the electrical conductivities increase with the liquid content exponentially, so to assess the effect of TiO₂ on the conductivity of the 20.5 mol kg⁻¹ LiTFSA electrolyte, we introduced Archie's empirical formula.²⁹ Archie's empirical formula is widely recognized in geology and is typically used to evaluate the relationship between the porosity of rocks and the conductivity of the interstitial water, as shown in Eq. 9:

$$\sigma/\sigma_{\text{liq.}} = a\phi_l^m \quad (9)$$

that is:

$$\log (\sigma / \sigma_{\text{liq.}}) = m \log \varphi_l + \log a \quad (10)$$

where σ is the measured conductivity of the solution in the solid-liquid coexistence system, $\sigma_{\text{liq.}}$ is the conductivity of the bulk solution, a is a constant, φ_l is the volume fraction of the liquid phase in the solid-liquid coexistence system, and m , known as the cementation index, is typically considered to be a constant related to the intrinsic properties of the solid phase. However, due to the limitations of Archie's equation, it is typically used to discuss aqueous solutions with concentrations similar to that of seawater. In these solutions, the electrolyte concentration is low, and the interactions between ions, as well as between ions and solids, are relatively weak, resulting in minimal influence from the solid phase. In this regard, Deki et al. found that the cementation index, m , indicates the interactions between the solid and liquid phases, as well as by changes in the structure of the liquid phase solution, when studying the conductivity of solid-liquid coexistence systems with varying concentrations, temperatures, and ionic species.³⁰ Figure 5a illustrates the effect of changes in the volume fraction of the liquid phase on the conductivity of 1 mol kg⁻¹ and 20.5 mol kg⁻¹ LiTfSA aqueous electrolyte coexisting with TiO₂, corresponding to the relationship described in Eq. 10. For ease of comparison, Fig. 5b shows the influence of the TiO₂ solid phase on the conductivity of 1 mol kg⁻¹ LiCl and 20.5 mol kg⁻¹ LiCl aqueous solti-

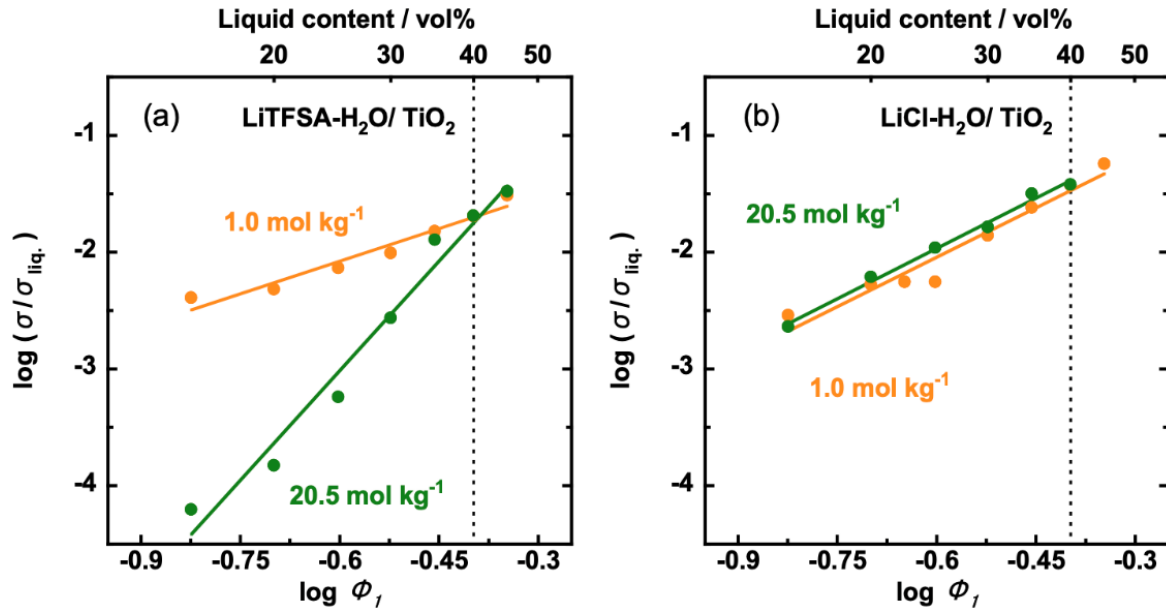


Figure 5. Archie's plots for the system of (a) TiO_2 powder/ LiTFSA aqueous electrolyte solution coexistence system and (b) TiO_2 powder/ LiCl aqueous electrolyte solution coexistence system. The concentration notations in the figure are each electrolyte solution.

ons. Values of a and m in Archie's equation for the TiO_2 powder/ Li^+ electrolyte systems are shown in Table 4. The conductivity for the 20.5 mol kg^{-1} LiTFSA solution are shown to decrease by a factor of about 1/1000 as the liquid phase volume fraction decreases from 45 vol% to 15 vol%, which indicates a significant decrease compared to results for other systems.³⁰ This indicates that the influence of TiO_2 on the 20.5 mol kg^{-1} LiTFSA aqueous electrolyte is much greater than that on other aqueous solutions of the same concentration, such as LiCl solutions.

On the other hand, the activation energy of ion mobility in the solution, ΔE_a , typically reflects the energy barrier for ion transport. Therefore, to obtain the activation energy

Table 2. Values of a and m in Archie's equation, $\sigma/\sigma_{\text{liq.}} = a\phi_l^m$, for TiO₂ powder/ Li electrolyte solution coexisting systems.

Electrolyte	a	m
1.0 mol kg ⁻¹ LiTfSA	0.11	1.86
20.5 mol kg ⁻¹ LiTfSA	5.54	6.26
1.0 mol kg ⁻¹ LiCl	0.45	2.83
20.5 mol kg ⁻¹ LiCl	0.57	2.88

of ion mobility in the solid-liquid coexistence system, the conductivity of the samples was measured at different temperatures, as shown in Fig. 6. Since the relationship between conductivity and temperature for all samples exhibited nonlinearity, the relationship between the conductivity and temperature of all samples was fitted using the VTF equation given in Eq. 2 and 7, with the results shown in Fig. 7. Whereas the value of activation energy is ca.24 kJ mol⁻¹ in 20.5 mol kg⁻¹ LiTfSA aqueous solution, it can be observed that the activation energy for the conductivity at the liquid phase of 45 vol% in the 20.5 mol kg⁻¹ LiTfSA aqueous electrolyte is ca. 35 kJ mol⁻¹ and higher than that in the 1 mol kg⁻¹ solution (ca.28 kJ mol⁻¹). These differences are observed across all liquid phase volume fractions. Furthermore, when the liquid phase volume

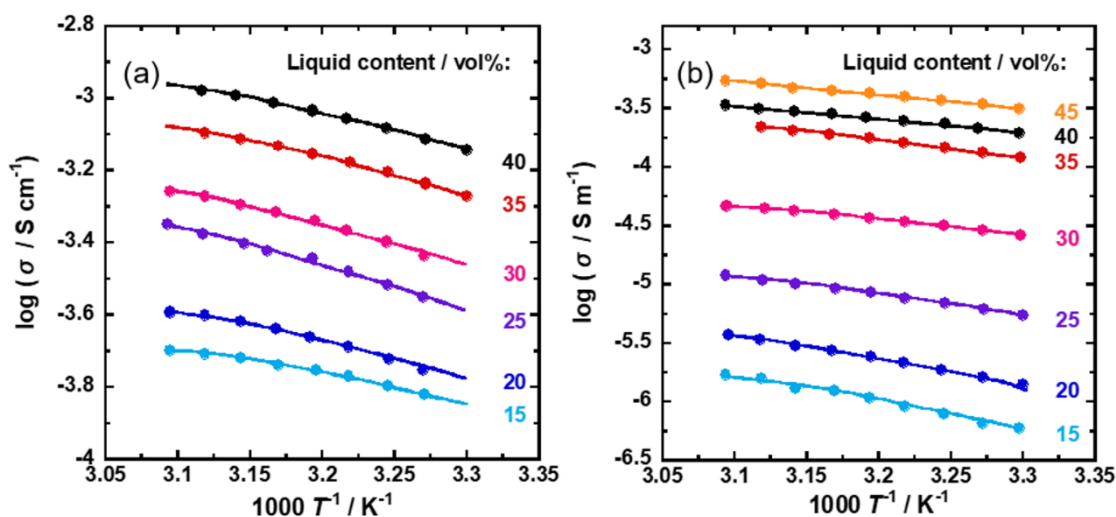


Figure 6. Temperature dependence of the electrical conductivity of TiO₂ powder/ LiTFSA aqueous electrolyte coexistence system. Concentration of LiTFSA: (a) 1 mol kg⁻¹ and (b) 20.5 mol kg⁻¹ at various liquid contents.

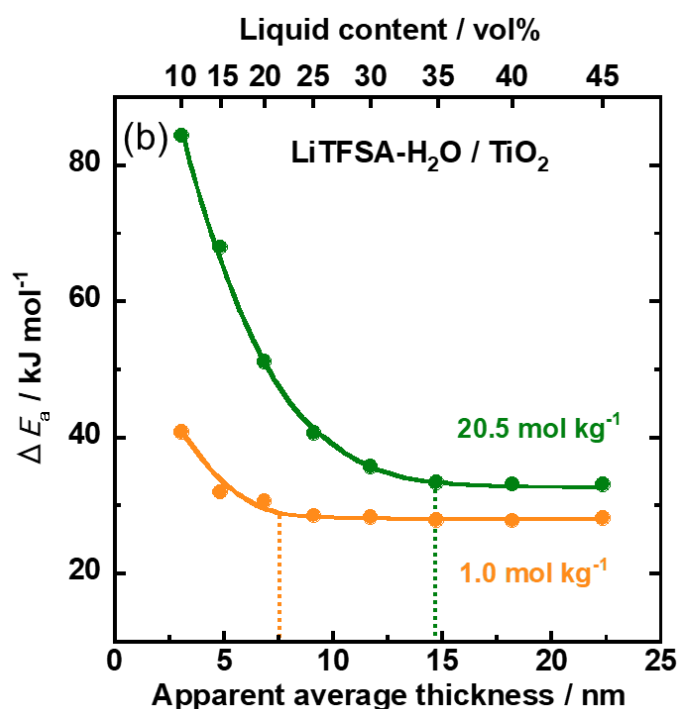


Figure 7. Variations of the activation energy of the electrical conductivity with the apparent average thickness of the liquid phase for the system of TiO₂ powder/ LiTFSA aqueous electrolyte coexistence system.

fraction is below 35 vol%, i.e., the apparent average thickness of the liquid phase of ca. 15 nm, the ΔE_a value increases rapidly, which corresponds well with the anomalous decrease in the conductivity for the system using 20.5 mol kg⁻¹ LiTFSA. To discuss the influence of the solid phase on the solution, we considered an ideal model in which all TiO₂ particles can be approximated as uniformly sized spheres. Under the assumption of homogeneous mixing of the solid and liquid phases, the thickness of the liquid phase distributed on each particle's surface remains consistent, referred to as the apparent average thickness. The detailed model and calculation formulas are provided in the supporting information, as shown in Fig. 8. Figure 7 illustrates the variation of activation energy at different apparent average thicknesses calculated based on the mix-

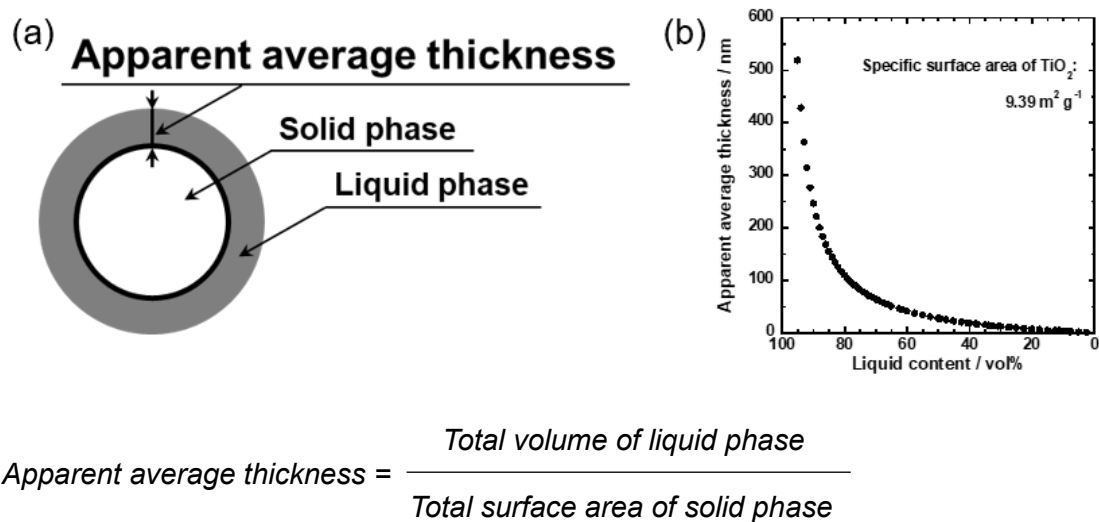


Figure. 8 (a) Schematic drawing of the solid-liquid coexistence system; (b) Relationship between average thickness of liquid phase and volume fraction of liquid.

-ing ratio of the liquid and solid phases, as well as the specific surface area of the solid phase. Compared to the 1 mol kg⁻¹ LiTFSA solution, which shows a significant increase in activation energy at an apparent average thickness of ca. 7.5 nm, 20.5 mol kg⁻¹ LiTFSA aqueous electrolyte begins to exhibit a significant influence from the solid phase at a liquid thickness of ca. 15 nm. This observation contrasts with the trend noted by Mizuhata in CaCl₂ aqueous solutions.²⁶ Considering the structural changes reported at the electrode interface¹⁶ and the mica surface²⁰ in 21 mol kg⁻¹ LiTFSA aqueous electrolyte, we further propose that the anomalous decrease in the conductivity of the 20.5 mol kg⁻¹ LiTFSA aqueous electrolyte is closely related to its interaction with the TiO₂ solid phase, which leads to significant alterations in the solution structure at the solid phase interface compared to the bulk solution. This change disrupts the original ionic transport mechanism in the bulk 20.5 mol kg⁻¹ LiTFSA electrolyte,^{7-9,31-34} making ion transport significantly more difficult.

3.2 The behavior of TFSA⁻ in solid-liquid coexistence systems

To further understand the effect of TiO₂ on the solution structure of 20.5 mol kg⁻¹ LiTFSA aqueous solution, we analyzed the molecular vibrations of water molecules and TFSA⁻ under the influence of the TiO₂ solid phase within the solid-liquid coexisting

system. Fig. 9 presents the Raman spectral peak changes of the S-N-S bending vibration, δ_{SNS} , of TFSA⁻ at different concentrations and liquid phase volume fractions.^{35,36} According to Suo et al., the S-N-S vibration near 749 cm⁻¹ in 20.5 mol kg⁻¹ LiTFSA aqueous electrolyte is highly sensitive to the anion environment and is thought to be related to the formation of a permeable TFSA⁻ anionic network⁶. As shown in Figure 6a, with increasing bulk LiTFSA concentration, the peak wavenumber of the bending vibration shifts from 746 cm⁻¹ at 1 mol kg⁻¹ to 749 cm⁻¹ at 20.5 mol kg⁻¹. The deconvolution of the S-N-S bending Raman peak into two Gaussian components is shown in Fig. 9b. We assign the component at 750 cm⁻¹ to TFSA⁻ in ion pairs, including CIP and AGG, and the component at 746 cm⁻¹ to free TFSA⁻, the deconvoluted spectra are shown in Fig. 10. The results indicate that no significant Li⁺-TFSA⁻ interaction is observed in LiTFSA solutions below 5 mol kg⁻¹. At concentrations above 5 mol kg⁻¹, TFSA⁻ begins to participate in Li⁺ solvation, forming CIP or AGG, with increasing ion-ion interactions at higher concentrations. This observation aligns well with the findings of Borodin et al.⁷

When the liquid phase volume fraction in the solid-liquid coexisting system is reduced to 10 vol%, as shown in Fig. 9c and 9d, the peak wavenumber of the S-N-S bending vibration shifts from 749.3 cm⁻¹ to 746.7 cm⁻¹. The deconvolution results reveal

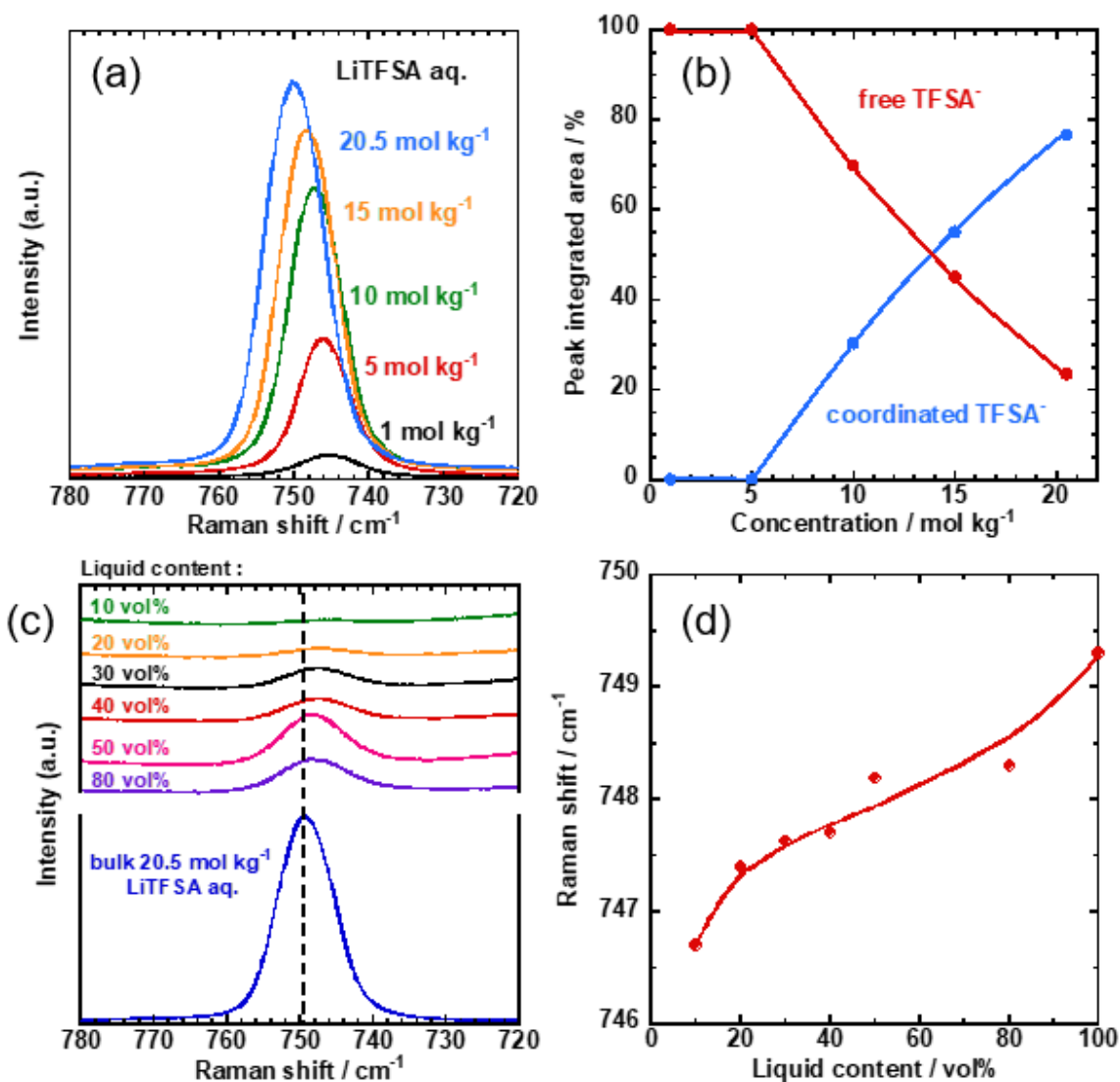


Figure 9. Raman spectrum of the S-N-S bending vibration in TFSA⁻. (a) Raman spectral changes in the S-N-S bending vibration of TFSA⁻ in LiTFSA aqueous electrolyte solutions at different concentrations. The deconvoluted spectra are shown in Fig. S4. (b) The deconvolution ratios in Raman spectra (a) using Gaussian functions. The deconvolution was performed with two Gaussian components: the high-frequency component is assigned to TFSA⁻ involved in the Li⁺ solvation shell (blue), and the low-frequency component is assigned to free TFSA⁻ not interacting with Li⁺ (red). (c) Raman spectra of the S-N-S bending vibration of TFSA⁻ in the TiO₂/ 20.5 mol kg⁻¹ LiTFSA aqueous electrolyte solution coexistence system at different liquid phase volume fractions. (d) The change in the wavenumber of the maximum Raman signal of the S-N-S bending vibration measured in (c) as a function of the liquid phase volume fraction

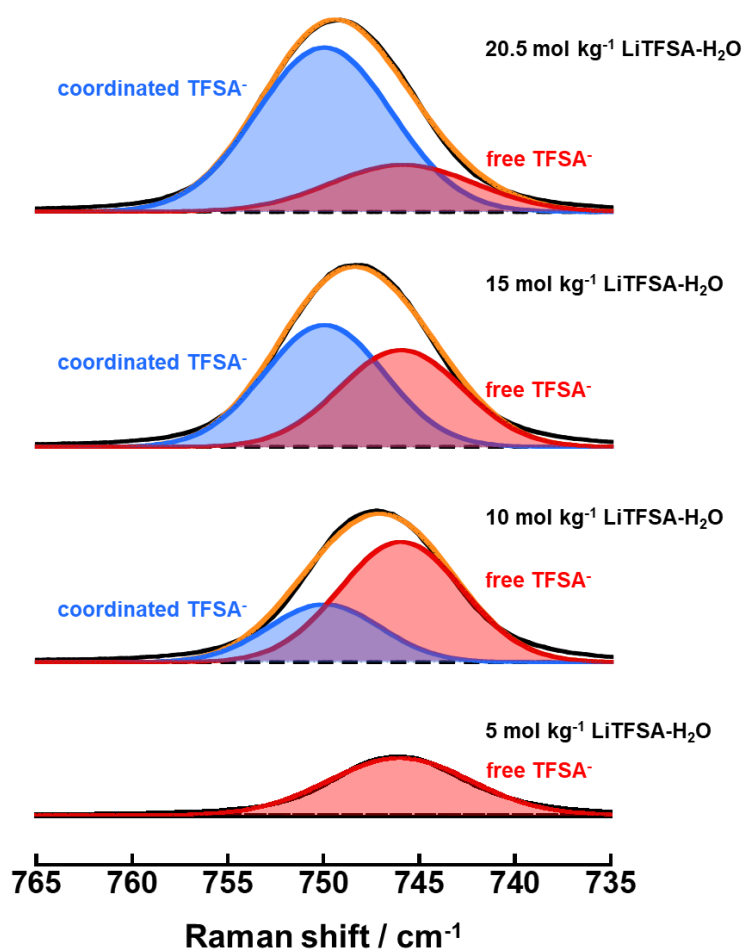


Figure 10. Deconvoluted bands of the Raman spectra of the S-N-S bending mode in TFSA⁻ anion in different concentrations of LiTFSA aqueous solutions. The red band represents free TFSA⁻ without interaction of Li⁺, and the blue band represents TFSA⁻ interacted with Li⁺ ion.

that as the liquid phase volume fraction decreases, interaction between TFSA⁻ and Li⁺ is weakened, resulting in an increase in free TFSA⁻, as illustrated in Fig. 11. Results of changes in conductivity and activation energies with the amount of HTFSA added to LiTFSA aqueous electrolyte solution of 1 mol kg⁻¹ and 20.5 mol kg⁻¹ at a liquid phase volume fraction of 30 vol% as shown in Fig.12. The horizontal axis indicates the loga-

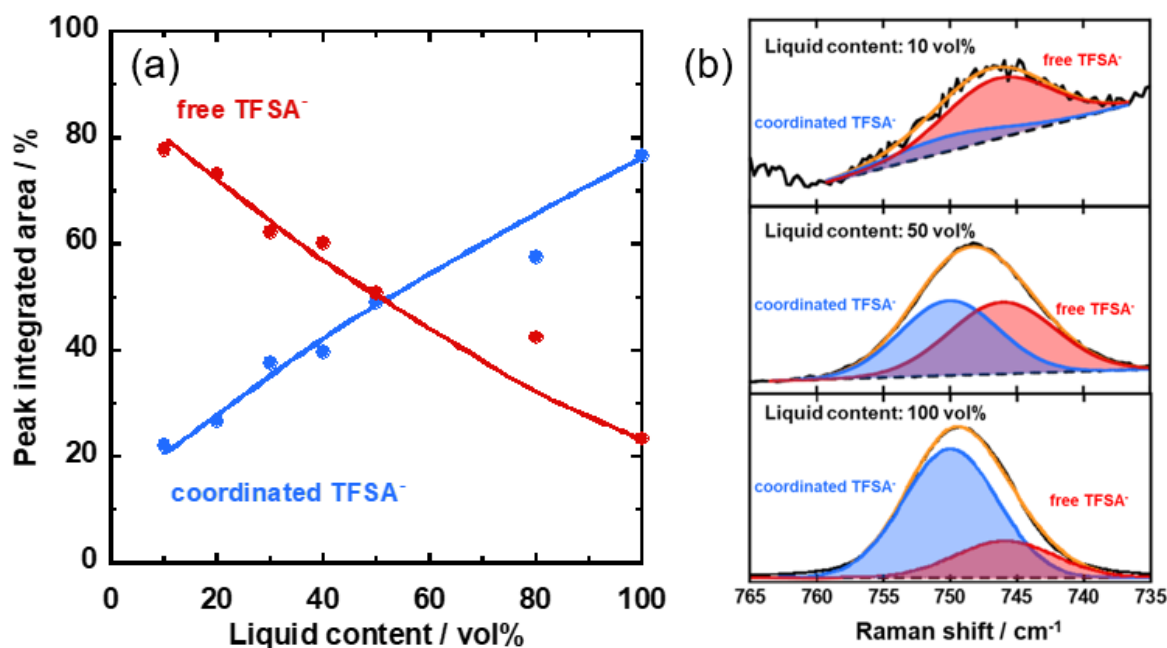


Figure 11. The deconvolution results of the Raman spectra of the S-N-S bending vibration of TFSA⁻ at different liquid contents in Fig. 6c.

-rhythmic opposite of the HTFSA added to the bulk solution. Results for conductivity and activation energies without HTFSA addition are shown at “ ∞ ” on the right side of the graph. The electrical conductivity and the apparent activation energy calculated from the temperature dependence of the electrical conductivity of TiO₂ powder / LiTFSA solution systems with a liquid phase volume fraction of 30 vol% are shown as a function of HTFSA addition. In the system without HTFSA, the pH of the 1.0 mol kg⁻¹ and 20.5 mol kg⁻¹ solutions had pH values of 6.3 and 2.4, respectively, indicating that H⁺ is released from water molecules between TFSA⁻ ions and the pH decreases with increasing LiTFSA concentration, as indicated by Han et al.³⁷ The fact that the pzc of TiO₂ in commonly used Li salts, e.g. LiCl and LiClO₄, shows a pzc of ca. 6,³⁸ suggests

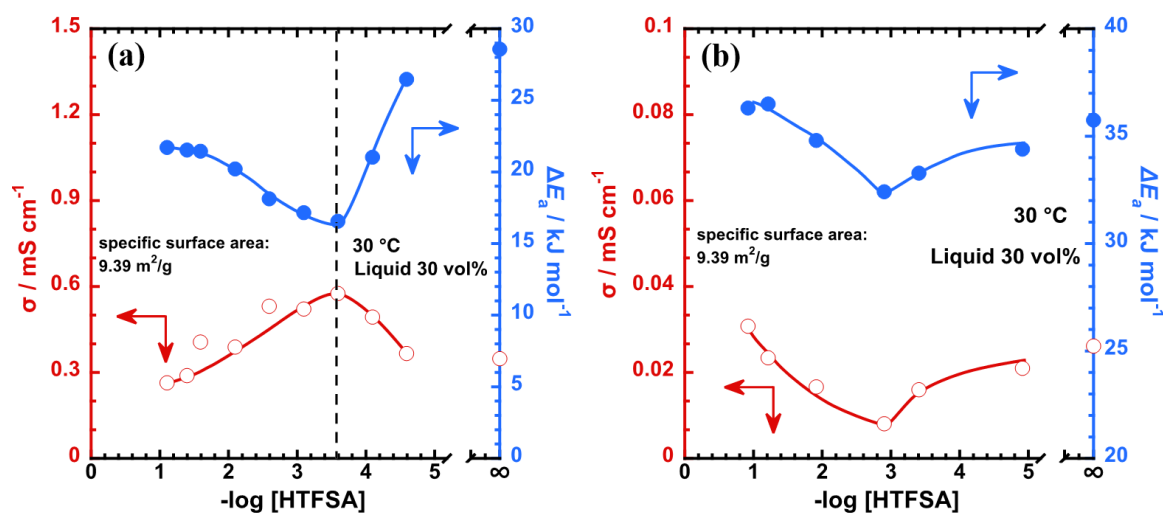


Figure 12. Results of changes in conductivity (red) and activation energies (blue) with the amount of HTFSA added to LiTFSA aqueous electrolyte at a liquid phase volume fraction of 30 vol%. (a) 1 mol kg^{-1} , (b) 20.5 mol kg^{-1} . The solid-liquid coexistence samples with a liquid phase volume fraction of 30 vol% were prepared by adjusting the pH of the solution with the addition of HTFSA to the aqueous electrolyte of LiTFSA and mixing the pH-adjusted aqueous solution with TiO_2 powder. The horizontal axis indicates the logarithmic opposite of the HTFSA added to the bulk solution. Results for conductivity and activation energies without HTFSA addition are shown at “ ∞ ” on the right side of the graph. The pH of the aqueous electrolytes of LiTFSA for bulk 1 mol kg^{-1} and 20.5 mol kg^{-1} without pH adjustment were 6.3 and 2.4, respectively, and the pzc of TiO_2 was ca. 6.

that the surface charge becomes negative (in the base side) at low concentrations and positive (in an acid side) at high concentrations with increasing concentration in LiTFSA solutions. In this case, the specifically adsorbed ions are H^+ or OH^- in aqueous systems, whereas Li^+ and TFSA^- are not specifically adsorbed ions and the effect of electrostatic interactions with the surface charge must be considered. As shown in Fig. 12(a), when small amount of HTFSA ($\log [\text{HTFSA}] = -3.6$, i.e., $2.5 \times 10^{-4} \text{ mol L}^{-1}$) is added in a 1.0 mol kg^{-1} LiTFSA solution, the surface charge is neutralized, which mean

the surface charge of LiTFSA is mostly neutral. On the other hand, as shown in Fig. 12(b), when HTFSA is added to a solution of 20.5 mol kg^{-1} , the surface charge becomes even more positive when HTFSA is added, the electrical conductivity falls. If the decrease in electrical conductivity is due to viscous effects, then the activation energy should increase in this case, but in fact the activation energy decreases. This suggests that the TFSA^- is adsorbed on the solid phase, and that the activation energy is further lowered because the Li^+ ions with low activation energy are the major conducting species.

From these results, the influence of the solid phase on the addition of TiO_2 at each concentration can be considered as follows: in a solution system of 1.0 mol kg^{-1} with a solution pH close to pzc, the activation energy hardly increases even with a high content of solid phase until the average thickness decreases to about 7 nm, as shown in Fig. 7, and the solid phase is considered to be very insensitive to the effect of the solid phase. However, in the 20.5 mol kg^{-1} solution system, the addition of the solid phase causes the activation energy to increase from about 15 nm, Deki et al. found that the increase in activation energy due to electrostatic interactions depends on the thickness of the electric double layer, so that at higher concentrations the activation energy increases at a greater distance from the solid. They stated that the activation energy rises from a closer distance.²⁶ In contrast, the results of Fig. 5 suggest that the decrease in the solid-

phase dependence of the electrical conductivity is caused by a significant decrease in the pH of the high-concentration solution, which increases the surface charge of the solid phase and makes it easier for TFSA⁻ ions to adsorb onto the solid phase.

3.3 The behavior of H₂O in solid-liquid coexistence systems

The NIR spectra for TiO₂ powder/ 20.5 mol kg⁻¹ LiTFSA aqueous solution coexisting systems are shown in shown in Fig. 13a, each component is assigned as follows;

I_0 : free water molecules with no hydrogen bond

I_1 : water molecules with one hydrogen bond

I_2 : water molecules with two or three hydrogen bond

I_3 : water molecules with four hydrogen bonds

We further categorize the four types of water molecules into two major classes: I_0 and I_1 are considered as water molecules interacting with ions, while I_2 and I_3 are those are not influenced by ion interactions. The results of the peak intensity ratios as a function of liquid phase volume fraction are shown in Fig. 12b. It can be observed that the addition of solids increases the number of hydrogen-bonded water molecules on the low-frequency side, while the number of water molecules with fewer hydrogen bonds decreases.

It is generally known that the electric double layer at the oxide/ aqueous solution interface and the surface potential based on it depend on the pH value due to the potential-determining ions, i. e., H^+ and OH^- .^{39,40} However, the contribution of dissolved ions cannot be ignored for the surface potential in highly concentrated aqueous solutions. For example, studies have shown that TFSA⁻ ions exhibit physisorption due to electrostatic interactions with solid surfaces. Additionally, a series of investigations on the structure of a 21 mol kg⁻¹ LiTFSA aqueous electrolyte at the interface have reported that, under positive potentials, water molecules are excluded from the layer closest to the electrode surface.^{16-18,36} The decrease in ion-ion interactions near the solid surface obtained from the Raman scattering results described in Section 3.2 is a result that supports the promotion of phase separation between the domains of TFSA⁻ ions forming the hydrophobic phase and the hydrophilic phase formed by Li⁺ hydration structure. In this situation, the Li⁺ ions originally interacting with TFSA⁻ would migrate to the hydrophilic phase, forming a more concentrated domain of hydrated Li⁺ ions. However, in stoichiometric condition of $[H_2O]/[Li^+] = ca.2.7$ in 20.5 mol kg⁻¹ LiTFSA aqueous solution, the water molecules are under the influence of multiple Li⁺ ions. In Fig. 11, it is suggested that the interaction between anions and cations is weakened as they coexist with the solid phase, while Fig. 13 shows that a hydrogen bonding network is partially formed. If coexistence with the solid phase

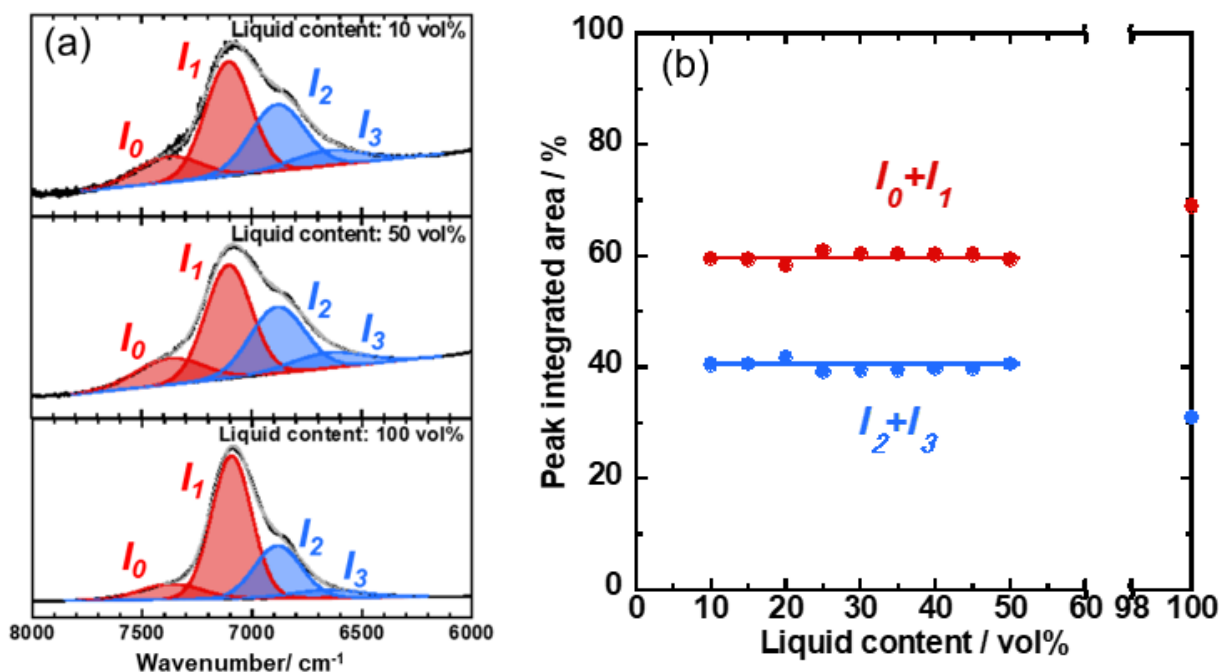


Figure 13. Near-infrared spectrum of water molecules in the TiO_2 powder/ LiTFSa aqueous electrolyte solid-liquid coexistence system, featuring the absorption peak associated with the combination frequency of the symmetric stretching and antisymmetric stretching vibrations of OH groups. (a) After deconvoluting the near-infrared absorption peak of OH, four Gaussian components were obtained, attributed to: the component I_0 on the high wavenumber side represents free water molecules with no hydrogen bonding, I_1 represents water molecules with one hydrogen bond, I_2 corresponds to water molecules with two or three hydrogen bonds, and I_3 denotes water molecules with four hydrogen bonds. (b) Dependence of the relative peak area of water molecules with fewer hydrogen bonds ($I_0 + I_1$, in red) and water molecules with more hydrogen bonds ($I_2 + I_3$, in blue) on liquid phase volume fraction.

leads to adsorption of water molecules to the solid phase or to the development of a hydration structure, the values of $I_2 + I_3$ should decrease and the space where water can assemble, which does not contribute to solid phase adsorption or orientation to ions, should be taken into account.

The results of electrical conductivity suggest that TFSa⁻ ions are in a state where

they can easily assemble near the solid phase. It follows that Li^+ ions excluded from the TFSA⁻ domain can only be incompletely hydrated, and water molecules gather to form hydrogen bonding networks in the repulsive field among Li^+ ions, resulting in an increase in I_2+I_3 already when the liquid phase volume fraction is reduced to 50%.

In bulk 21 mol kg⁻¹ LiTFSA aqueous electrolyte, the presence of nanoscale water channels results in a conductivity of nearly 10 mS cm⁻¹ even at high concentrations and viscosities.⁹ Consequently, the behavior of water molecules in the solid-liquid coexistence system plays a decisive role in ionic transport. Studies utilizing proton nuclear magnetic resonance (¹H NMR) to detect the spin-spin relaxation time (T_2) of water molecules in the aqueous solution have been widely reported.⁴¹ Since the spin-spin relaxation process of hydrogen nuclei is a dipolar relaxation process, T_2 of the hydrogen nuclei is highly sensitive to changes in the dipole interactions surrounding the water molecules.⁴² Therefore, we aim to clarify the behavioral changes of water molecules by measuring T_2 in the solid-liquid coexistence system. Due to the different interactions between various electrolytes and water molecules, the T_2 relaxation times of hydrogen in these bulk aqueous solutions vary. Therefore, to discuss the effect of TiO₂ solids on the T_2 relaxation times of H₂O in each solution more intuitively, all T_2 times measured at various liquid volume fractions were normalized using the values result of each bulk solution as a reference. The unnormalized T_2 results for all conditions

are provided on Fig. 14.

Due to the typical strong hydrophilicity of TiO_2 , water molecules readily interact with TiO_2 , leading to their ordering structure at the surface and the formation of hydrogen bonds, which restricts the thermal motion of the water molecules. Consequently, as the volume fraction of TiO_2 increases, a significant decrease in the T_2 relaxation time of water molecules in all solutions can be observed, as shown in Fig. 14a and 14b. This indicates that the mobility of water molecules in the electrolyte is reduced due to confinement by the solid phase. Fig. 15a compares the relative changes in T_2 relaxation times of 20.5 mol kg^{-1} $\text{LiCl-H}_2\text{O}$ and 20.5 mol kg^{-1} LiTFSA aqueous electrolyte, highlighting their liquid volume fraction dependency. Notably, although LiCl and LiTFSA have the same number of ions per water molecule, the relative T_2 relaxation times of water molecules in the 20.5 mol kg^{-1} LiTFSA aqueous electrolyte vary with volume fraction more similarly to pure water than those in LiCl . By examining the changes in the relative T_2 relaxation times of H nuclei in LiCl solutions of different concentrations, we conclude that increasing concentration leads to more water molecules participating in interactions with cations or anions. This electrostatic interaction is evidently stronger than that between water molecules and TiO_2 , resulting in a limited interaction with TiO_2 . Consequently, water molecules in highly concentrated solutions are less influenced by the solid phase, yielding a more gradual

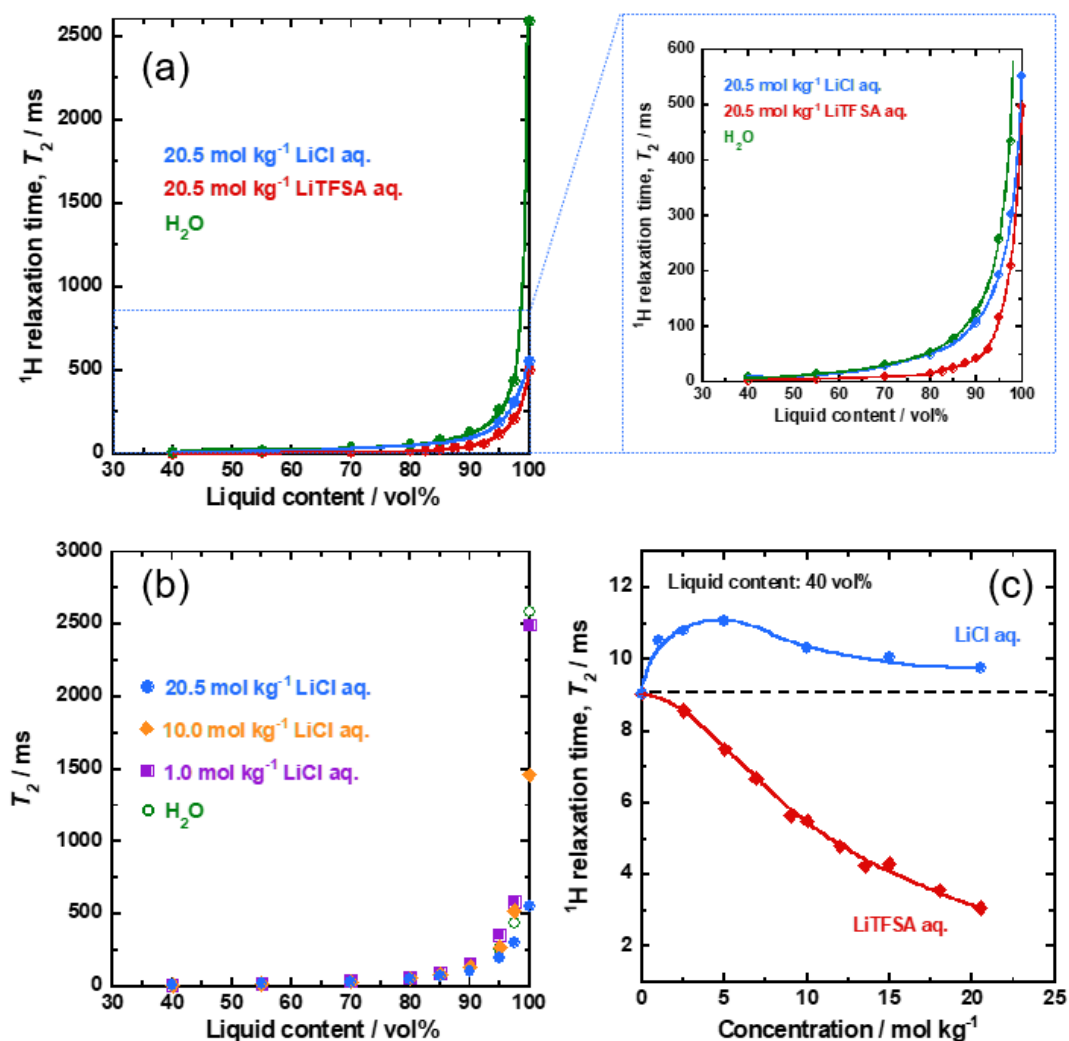


Figure 14. T_2 relaxation times of hydrogen nuclei in water molecules within the $\text{TiO}_2/\text{LiCl-H}_2\text{O}$ and $\text{LiTFSA-H}_2\text{O}$ solid-liquid coexistence systems. (a) The relationship between the T_2 relaxation time of hydrogen nuclei in water molecules and liquid phase volume fraction in the 20.5 mol kg⁻¹ $\text{LiCl-H}_2\text{O}$ (blue), 20.5 mol kg⁻¹ $\text{LiTFSA-H}_2\text{O}$ (red), and pure water (green) / TiO_2 coexistence systems. (b) Variation of T_2 relaxation time of hydrogen nuclei in different concentrations of $\text{TiO}_2/\text{LiCl-H}_2\text{O}$ solid-liquid coexistence systems with liquid phase volume fraction. (c) The T_2 relaxation times of water molecules (H) in 20.5 mol kg⁻¹ $\text{LiCl-H}_2\text{O}$ (blue) and 20.5 mol kg⁻¹ $\text{LiTFSA-H}_2\text{O}$ (red) as a function of electrolyte concentration at a liquid phase volume fraction of 40 vol%.

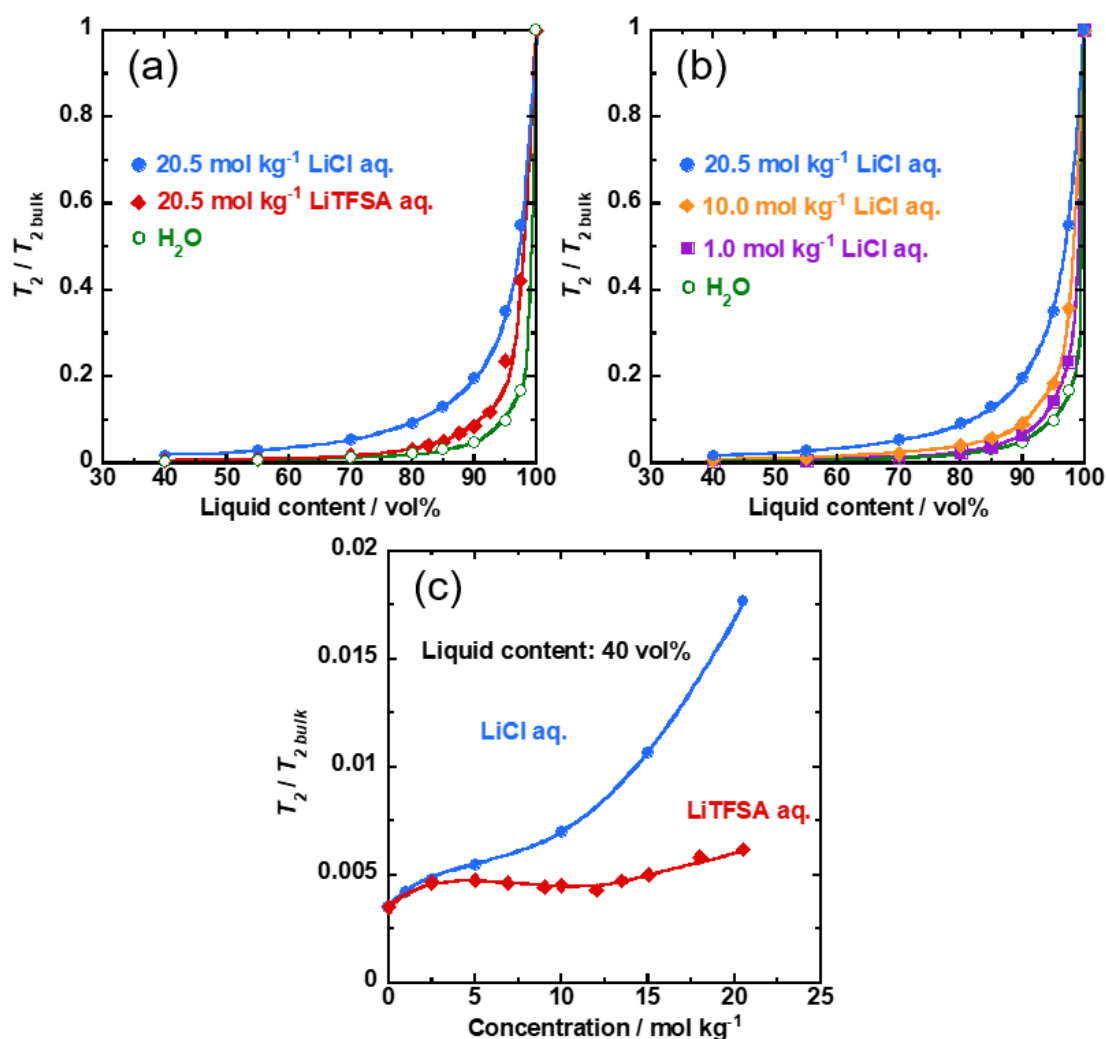


Figure 15. Variation of the T_2 relaxation time of hydrogen nuclei in water molecules within the solid-liquid coexistence system. To compare the results of different electrolytes, the T_2 relaxation times for all liquid phase volume fractions were normalized using the respective bulk solution T_2 relaxation times as a reference, expressed as $T_2 / T_{2, \text{bulk}}$. (a) T_2 relaxation time dependence on liquid phase volume fraction for pure water (green), 20.5 mol kg⁻¹ LiTfSA aqueous electrolyte (red), and 20.5 mol kg⁻¹ LiCl aqueous solution (blue) in conjunction with TiO₂ powder. (b) Dependence of the T_2 relaxation time of hydrogen nuclei in water molecules on liquid phase volume fraction in TiO₂/ LiCl aqueous solution coexistence systems with different concentration. (c) Dependence of the T_2 relaxation time of hydrogen nuclei in water molecules on concentration for LiCl aqueous solution (blue) and LiTfSA aqueous electrolyte (red) at a liquid phase volume fraction of 40 vol %.

change in T_2 relaxation times compared to dilute solutions, as shown in Fig. 15b. In the 21 mol kg⁻¹ bulk LiTFSA aqueous electrolyte, the water molecules in the hydrophilic regions are less influenced by contact ion pairs and exhibit weaker interactions with TFSA⁻ and Li⁺ concentration being significantly lower than the apparent concentration of the solution. Therefore, we believe that the addition of TiO₂ causes water molecules in the hydrophilic regions to aggregate on the TiO₂ surface, resulting in relative T_2 relaxation time changes that resemble those of water molecules in dilute solutions.

Additionally, at a liquid phase volume fraction of 40 vol %, we investigated the effect of solution concentration on the T_2 relaxation times of water molecules. As mentioned earlier, increasing the solution concentration reduces the impact of the solid on the water molecules, causing $T_2 / T_{2, \text{bulk}}$ to approach 1, as illustrated for LiCl (blue) in Fig. 15c. However, as the concentration increases, a decrease in $T_2 / T_{2, \text{bulk}}$ is observed in LiTFSA aqueous electrolyte. At low concentrations, the ionic interactions are weak, so the LiTFSA solution does not exhibit significant differences compared to LiCl. Han et al. indicated that phase separation in concentrated LiTFSA aqueous solution over ca. 5 mol kg⁻¹, ionic aggregates form leading to hydrophilic(water) and hydrophobic(ionic) domains.³⁷ Consequently, more water molecules are excluded from the hydrophobic regions, making them more susceptible to the influence of TiO₂, resulting in a slight decrease in T_2 . As the concentration continues to increase, the expanding interface

between the hydrophilic and hydrophobic regions raises the proportion of interfacial water, thereby inhibiting the interaction between water molecules and TiO_2 . However, overall, the inhibitory effect of Li^+ and TFSA^- on the interaction between water molecules and TiO_2 is still significantly less than that of LiCl .

4. Conclusions

To discuss the influence from solid phase on ionic conduction in highly concentrated aqueous solutions, we measured the electrical conductivity and its activation energy of solid-liquid coexistence systems consisting of 20.5 mol kg^{-1} LiTFSA aqueous electrolyte and TiO_2 powder and correlated them with various spectroscopic results indicating interactions between dissolved species.

The electrical conductivity of the 20.5 mol kg^{-1} LiTFSA aqueous electrolyte increased exponentially with an increase of the volume fraction of the liquid phase up to ca. 40 vol %, and the activation energy of electrical conductivity increased with a decrease of the liquid phase below 35 vol %.

S-N-S bending mode in TFSA^- anions at ca. 750 cm^{-1} in Raman spectra shifts toward to lower wave number, which indicates weakened ion-ion interactions with TFSA^- and Li^+ due to the coexistence of a solid phase. In the near-infrared spectra ($\nu_1 + \nu_3$) of water

molecules in the 6500-7500 cm^{-1} region, which indicate the hydrogen-bonding network state, the intensity at lower wavenumbers, indicating the formation of hydrogen-bonding network structure among water molecules, increases with the coexistence of the solid phase. These results suggest that the ion-water interaction is weakened, and Li^+ ions are released from the hydrophobic TFSA^- anions and concentrated in the hydrophilic region. As a result, water molecules form hydrogen bonds with each other in the repulsive field of high concentration of Li^+ ion, and the near-infrared band at lower wavenumber side is considered to increase. As for the spin-spin relaxation in ^1H -NMR measurement in the electrolyte coexisting with the solid phase, the relaxation time (T_2) is significantly reduced due to the reduced mobility of water molecules, which is more pronounced in the order of $\text{H}_2\text{O} > \text{LiTFSA} > \text{LiCl}$. This may be due to the hydration structure of LiCl which weakens the solid effect relatively, while LiTFSA , due to the high hydrophobicity of TFSA^- , has a less pronounced effect on water molecule dynamics, leading to a more pronounced effect from the solid phase. These results indicate that in the $\text{TiO}_2/20.5 \text{ mol kg}^{-1} \text{ LiTFSA}$ solid-liquid coexistence system with a liquid phase volume fraction below 40 vol%, the presence of TiO_2 disrupts the nanoscale water channel structure in the water-enriched regions of the bulk solution, resulting in an unusual decrease in electrical conductivity. The strong influence of the solid phase on the electrical conduction of the highly concentrated LiTFSA electrolyte

was found to be significant only in the region below 50 vol% in the liquid content, while in the region above 50 vol%, there were no differences due to electrolyte concentration and ion species, indicating the influence of the solid phase on electrical conduction.

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Summary

In this study, the authors conducted a quantitative evaluation of the effects of ions on water molecules in electrolyte solutions using near-infrared (NIR) spectroscopy. Furthermore, NIR spectroscopy was successfully employed to detect trace amounts of water molecules in high-concentration electrolyte solutions within solid-liquid coexistence systems involving metal oxides. The study provides a detailed investigation of how solid phases disrupt ion-water interactions in highly concentrated solutions.

In Chapter 1, we measured the detection rate of solvent molecules in a solid-liquid coexistence system formed by mixing pure water, propylene carbonate (PC), and the highly volatile organic solvent dimethyl ether with silica in the gas phase using near-infrared spectroscopy. By comparing the detected solvent proportions with their actual proportions in the mixed system, we verified the excellent quantitative detection capability of NIR spectroscopy. However, application of the method to aqueous solutions containing different electrolytes revealed that the concentrations of water molecules detected in all solutions were consistently lower than the values calculated from the density and concentration data. Furthermore, the difference between the detected and calculated concentrations clearly depended on the type and concentration of ions present. Detailed analysis of lithium-based solutions containing different anions

showed that the number of undetected water molecules in each solution was in the order $\text{TFSA}^- < \text{ClO}_4^- < \text{Cl}^- < \text{NO}_3^- < \text{SO}_4^{2-}$. This order agrees well with the known order of ion-water interaction strengths. Therefore, we suggest that strong ion-water interactions affect the generation of OH stretching vibrational combinatorial tones, leading to a decrease in the intensity of the NIR spectrum.

The study in Chapter 2 focuses on the effect of competitive ionic interactions on the water molecules in the mixed molten salt hydrate system, especially the $\text{CaCl}_2\text{-ZnCl}_2$ mixture $(\text{Ca}_{1-x}\text{Zn}_x)\text{Cl}_2 \cdot 6\text{H}_2\text{O}$. The water molecules in the mixture were detected by using NIR spectroscopy in the same way as in Chapter 1. The results showed that the detected water concentration gradually approached the theoretical value when $x < 0.5$, while the detected concentration started to decrease when $x > 0.5$. The results showed that the water molecules in the mixture were detected by NIR spectroscopy. Raman spectra of $[\text{ZnCl}_4]^{2-}$ and $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ species showed that Zn^{2+} preferentially interacted with Cl^- to form $[\text{ZnCl}_4]^{2-}$ complexes when $x < 0.5$. This disrupts the $\text{Ca}^{2+}\text{-Cl}^-$ contact ion pair (CIP), allowing more water molecules to hydrate with Ca^{2+} . Spectroscopically, this manifests itself as weakening or breaking hydrogen bonds in the water molecules. In addition, the involvement of Cl^- in the formation of the complex reduces its interaction with the water molecules, leading to an increase in the detected water concentration. At $x > 0.5$, water molecules begin to incorporate into the $[\text{ZnCl}_4]^{2-}$ complex. The strong

Zn-O interaction weakens the OH bonds and the H^+ generated by hydrolysis again forms hydrogen bonds with the water molecules, leading to a significant increase in the low-frequency intensity in the NIR spectrum. However, since the weakening of the OH bond by the strong Zn-O interaction is similar to the interaction between anions and OH groups, the detection of water decreases further. This finding confirms the hypothesis presented in Chapter 1 about the reason for the decrease in the detection rate of water molecules.

In the first section of Chapter 3, the authors investigated the effects of TiO_2 solid phases on ion-water interactions in highly concentrated LiTFSa aqueous solutions with heterogeneous nanoscale structures, analyzing these effects through conductivity changes. When increasing the TiO_2 content in the solid-liquid coexisting system, it was found that the conductivity of the 20.5 mol kg^{-1} LiTFSa aqueous solution decreased significantly more than in diluted solutions or LiCl aqueous systems. This indicates that the nanoscopic heterogeneity of the LiTFSa solution is strongly influenced by the TiO_2 solid phase. Raman spectroscopy of TFSa⁻ showed that the presence of TiO_2 promoted the dissociation of Li^+ -TFSa⁻ ion pairs. Near-infrared (NIR) spectroscopy revealed that the addition of the solid phase led to strengthened hydrogen bonding among water molecules. Moreover, the proton spin-spin relaxation time T_2 results demonstrated that water molecules in the 20.5 mol kg^{-1} LiTFSa solution were significantly affected by

the TiO₂ solid phase compared to those in a LiCl aqueous solution of the same concentration. These findings suggest that the influence of TiO₂ on water molecules disrupts the nanoscale heterogeneous structure, which is the primary reason for the substantial reduction in conductivity observed in the 20.5 mol kg⁻¹ LiTfSA system.

In the second section, the authors further explored the effect of TiO₂ surface charge on conductivity. In dilute solutions, modifying the solution pH to alter the surface charge of TiO₂ revealed a clear pH dependence for both the system's conductivity and the activation energy of ion transport. However, in highly concentrated LiTfSA aqueous solutions, the strong ion-ion interactions led to a markedly different relationship between conductivity and H⁺ concentration compared to that observed in dilute aqueous solutions.

Based on the above chapters, the authors demonstrate that interactions between ions and water molecules reduce the absorption coefficient of water molecules compared to bulk water. Consequently, the reduction in water molecule detection values relative to theoretical values, as measured by near-infrared spectroscopy, can be used to quantitatively evaluate the strength of ion-water interactions in solutions. Furthermore, the study reveals that the relaxation time of water molecules in highly concentrated solutions is significantly shorter than that of bulk water, indicating reduced mobility of water molecules influenced by ions. In solid-liquid coexistence systems, the solid phase

also restricts water molecule mobility; however, this effect diminishes as ion-water interactions become stronger. The authors conclude that these findings provide a novel perspective and methodology for understanding ion-water interactions in aqueous solutions. Additionally, they highlight the potential of these insights to contribute to the development of next-generation aqueous electrolytes for advanced batteries.

Publication list

Anion Species Dependence of Non-detected Water Molecules along the Hofmeister Series in Various Lithium Salts in Near-infrared and Nuclear Magnetic Resonance Spectroscopy

Jingchao Xu, Youngchol Koh, Shinya Takayose, Hideshi Maki, and Minoru Mizuhata

Electrochemistry, in submitted

Quantitative Study on the Behavior of Water in CaCl₂-ZnCl₂ Binary Hydrate melt

Jingchao Xu, Haruto Matsunami, Hiro Minamimoto, Hideshi Maki,

and Minoru Mizuhata

(in preparation)

Effect of Coexisting TiO₂ Powder on Ionic Conduction of Highly Concentrated LiTFSA Aqueous Electrolyte (20.5 mol kg⁻¹)

Jingchao Xu, Hideshi Maki, Hiro Minamimoto, and Minoru Mizuhata

Electrochemistry, in press

<https://doi.org/10.5796/electrochemistry.24-00115>

Related publication

Single-Nanometer-Sized Boron and Phosphorus Co-Doped Silicon Nanoparticles for Negative Electrode of Lithium-Ion Batteries

Hiroki Yoshikawa, Taiki Ueshima, Hiroshi Sugimoto, Jingchao Xu, Minoru Mizuhata,
and Minoru Fujii

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Presentation list

- [1] Quantitative evaluation of solvent molecules in a heterogeneous coexistence system using near-infrared spectroscopy**

J. Xu, Y. Suzuki, H. Maki, and M. Mizuhata

The 3rd Workshop of Electrochemical Society of Kansai in 2021, online, December 2021

- [2] Validation of a quantitative analysis for intramolecular vibrations of electrolytes in the heterophase systems by the near-infrared (NIR) spectroscopy**

J. Xu, H. Maki, and M. Mizuhata

The 102nd Chemical Society of Japan Annual Meeting in 2022, online, March 2022

- [3] Effect of anions on absorption intensity of aqueous lithium solutions by near-infrared spectroscopy**

J. Xu, S. Takayose, H. Maki, and M. Mizuhata

The 93rd Materials Tailoring Committee, Karuizawa, August 2022

- [4] Influence of anions on absorption intensity of aqueous electrolyte solutions by near-infrared spectroscopy**

J. Xu, H. Maki, and M. Mizuhata

The 2022 Electrochemical Society of Japan Fall Meeting, Yokohama, September 2022

- [5] Effect of ions on absorption intensity of aqueous solutions by near-infrared spectroscopy**

J. Xu, H. Maki, and M. Mizuhata

The 3rd Workshop of Electrochemical Society of Kansai in 2022, online, December 2022

[6] Ion transport at Water-in-salt/ solid interface: Surface Charge Dependency

J. Xu, H. Minamimoto, H. Maki, and M. Mizuhata

The 64th Battery Symposium in Japan, Osaka, November 2023

[7] Ion transport at Water-in-salt/ solid interface

J. Xu, H. Minamimoto, H. Maki, and M. Mizuhata

The 3rd Workshop of Electrochemical Society of Kansai in 2023, Kobe, December 2023

[8] Quantitative study on the behavior of water in $\text{CaCl}_2\text{-ZnCl}_2$ binary hydrate melt

J. Xu, H. Matsunami, H. Minamimoto, H. Maki, and M. Mizuhata

The 92nd Electrochemical Society of Japan Annual Meeting, Tokyo, March 2025

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