



Properties and Interfacial Behavior of Condensed Liquid System Based on Hydrate Melt and Ionic Liquid

Kunikata, Nobuaki

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博士論文

**Properties and Interfacial Behavior of
Condensed Liquid System
Based on Hydrate Melt and Ionic Liquid**

凝集系水和物溶融体およびイオン液体に関する
物性と界面挙動

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神戸大学大学院工学研究科

國方 伸亮

(Nobuaki KUNIKATA)

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General introduction

The physico-chemical properties of condensed electrolyte liquid system are relatively uncharted territory compared with dilute solution where approximations such as the Debye-Hückel theory appropriate. Highly concentrated electrolyte solution, especially hydrate melt and molten salt, are condensed systems of ionic interaction, and have attracted much attentions because their properties would be sufficiently distinct from dilute system.¹⁻⁷ Many authors have studied them vigorously from the viewpoint of thermal storage, promising applications such as solvents for cellulose, feed phase for the solvent extraction of rare-earth ions, and electrolytes in next-generation rechargeable batteries have been also reported in recent years.⁸⁻²²

In addition, it is well known that the restricted layer of the liquid phase exists near the solid surfaces in solid/liquid coexisting system.²³ The liquid layer is remarkably influenced by the solid phase, and show different properties compared with that of bulk liquid. The liquid properties in solid/liquid interfaces are very important because liquid materials are generally utilized in the contact system with solid phase. For example, electrochemical devices like lithium-ion batteries contain large amount of active materials and concentrated electrolyte solution in limited volume to obtain high power density. In such solid/liquid coexisting system, concentrated electrolyte solution was impregnated into small void spaces and confined by the solid surfaces, where solid phase affects the liquid properties. Electrochemical reaction occurs within such solid/liquid interfaces. Consequently, liquid phase confined by a lot of solid surface can be considered as condensed dispersion system. Mizuhata et al. has been studied the interfacial liquid layer using various liquid materials and solid materials from the

perspective that the influence of the solid phase to the vicinal liquid layer in solid/liquid coexisting system is conceptually similar to the ion-solvent interaction in the concentrated solution.²⁴⁻²⁶ They pointed out that the thicknesses of the layers are in the order of tens nm, which are not the same as interfacial restructuring water confirmed by X-ray technique or electrical double layer.^{27, 28}

In the previous studies of our group, particles with a diameter of micrometer size were used as solid phase, and we defined the “apparent average thickness” which varies with the surface area of solid phase and liquid content as follows,

$$[\text{apparent average thickness}] = \frac{[\text{total volume of liquid phase}]}{[\text{total surface area of solid phase}]}$$

Above equation shows that the apparent average thickness has a length dimension and means a distance from the surface of solid phase as shown in Fig.1-1. This simple model described the relationships between solid/liquid volume fraction and properties such as activation energy of the electrical conductivities, phase transition temperature, depolarization ratio of depolarized Raman spectroscopy, and so on. Here in this study, we used the fumed metal oxide nanoparticles as solid phase to get much thinner apparent average thickness because they have a large specific surface area. The fumed metal oxides are prepared by flame synthesis, and many researchers have studied solid-liquid composite materials composed of fumed oxides such as “soggy sand” electrolytes, gel electrolytes which suppressed dendrite formation on metal anode, gelled fuels, the crosslinked hybrid electrolyte material, and so on.²⁹⁻³⁵ The dispersion of fumed oxides in water showed high stability even at 95 vol% of liquid content, therefore the spatial model shown as Fig. 1-1 is not valid. Considering that only one solid sphere of radius a exists on the diagonal line of a cube with one side length $2A$ including the liquid sphere of radius A , $2\sqrt{3} - 2A < 2a$. Consequently, this model is applicable when

the liquid volume fraction is 60 vol% or less.

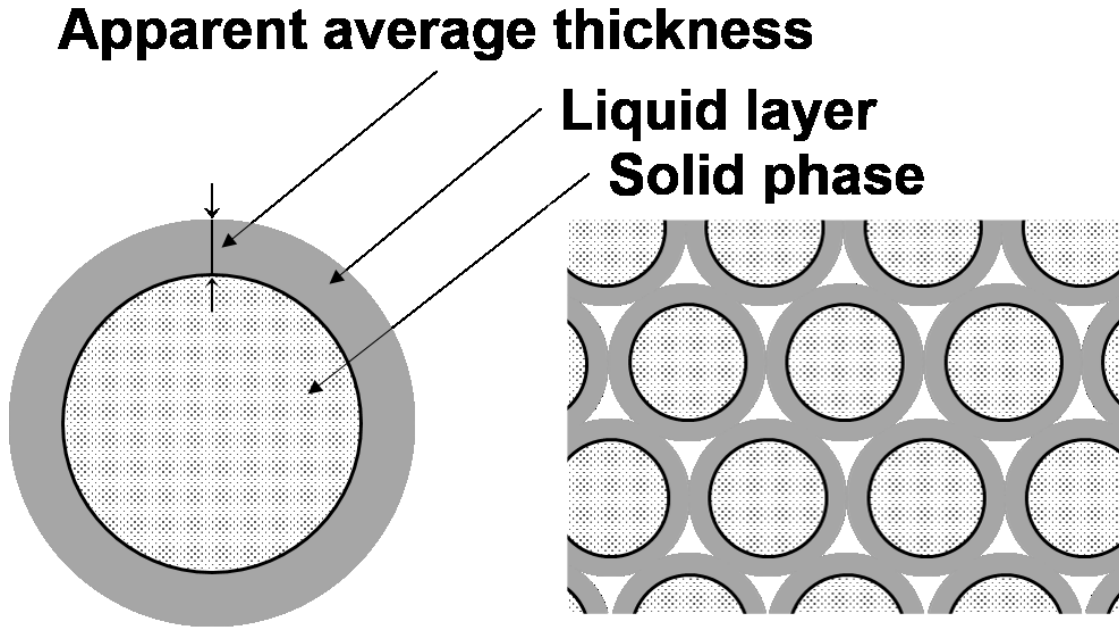


Fig. 1-1. Schematic model of the apparent average thickness of the liquid layer and the model of solid/liquid coexisting dispersion system.

Thus we proposed the new spatial model for nanoparticle dispersion system that liquid particles are monodispersed as hexagonal close-packed as described in Fig. 1-2. Consequently, we re-defined the parameter called “apparent average thickness” by the following equations. This parameter replaces volume fraction with the overall liquid layer distance, which has a dimension of length. Here, due to the condition $d/r > 0$, V_L must be greater than 26 vol%.

$$V = 16\sqrt{2}(r + d)^3$$

$$d = r \left[\left(\frac{\pi}{3\sqrt{2}} \cdot \frac{1}{1 - V_L} \right)^{\frac{1}{3}} - 1 \right]$$

d : Apparent average thickness

r : solid radius

V : unit cell volume

V_L : liquid phase volume

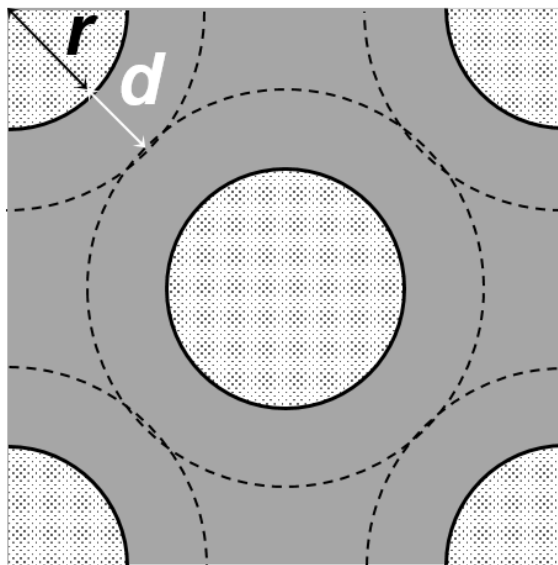


Fig. 1-2. Schematic model of solid/liquid coexisting system; d and r means the “apparent average thickness” based on hexagonal close-packed model and solid particle radius, respectively.

The purpose of the present study is to investigate the physico-chemical properties of two condensed systems, “condensed electrolyte liquid system” and “condensed dispersion system”, focusing on their similarity. Both of them are mixed systems which are composed of a main component and subcomponents. These are characterized by having nano-heterogeneity in their structure, such as micro-phase separation and disproportion of charge density, and it would dominate the properties of the whole system.^{29, 36-40}

In Chapter 1, the isomerization behavior of anionic binary ionic liquid was discussed in terms of ideal glass transition temperature T_0 derived from VTF equation. Ionic liquids are condensed electrolyte liquid system because they have no solvent molecules. They are known to show micro-phase separation and crystal polymorphism.

We used TPAFSA looking forward to relatively high conductivity, and we added TFSA⁻ for the purpose of lowering the phase transition point. We obtained the phase diagram of the binary ionic liquid employing thermal analyses and compared with composition dependences of T_0 , similar to the report by Angell et al.⁴¹ Phase transition behavior was investigated using X-ray diffraction patterns with temperature controlling unit and discussed comparing with other anion. In addition, the quaternary ionic liquid system was also studied.

As Chapter 2, we focused on ZnSO₄ aqueous electrolyte system coexisting with metal oxide nanoparticles: condensed dispersion system. ZnSO₄ is one of the most frequently used zinc compound for a variety of applications and plays a significant role in biochemistry, fertilization for plants as inorganic nutrition, hydrometallurgical production of zinc.⁴²⁻⁴⁸ Moreover, ZnSO₄ aqueous solution is of interest because there is significant ion pairing, thus many researchers have studied academically.⁴⁹⁻⁵³ In addition, 2:2 electrolyte solution has not been investigated in our solid/liquid coexisting experimental system. In Section 1 of Chapter 2, we employed Raman spectroscopy to investigate the ion pair forming tendencies caused by adding SiO₂ nanoparticles. Salt concentration dependences of ¹H NMR relaxation time was observed to confirm the effects from solid phase. In Section 2 of Chapter 2, we dealt with ZnSO₄ aqueous solution as ZnSO₄ based hydrate melt and observed the spectroscopic properties of metal oxide nanoparticles/ZnSO₄·15.7H₂O coexisting system to discuss the competitive effect on water molecules from ionic species and metal oxide solid surfaces.

In Chapter 3, we focused on LiClO₄ based non-aqueous binary solvent electrolytes nanoconfined by SiO₂ solid surfaces. In the previous chapter, we confirmed that ionic species and metal oxide solid surfaces interact competitively with neutral solvent

molecules in the interfacial liquid layer and such liquid layer region is several tens nm. Moreover, the binary solvent system consisted of high permittivity PC and low viscosity DME, it is used as electrolyte solution of Li-ion batteries, might show quite different behavior compared to a single solvent system in condensed dispersion system. We tried to elucidate the heterogeneity of each solvent molecules in solid/liquid interfaces by analyzing the ^1H NMR spectra quantitatively. In addition, we carried out the resonance shear measurement using a home-built apparatus owned by Kurihara lab. in Tohoku Univ. This apparatus can measure the length of the interfacial liquid structure with high accuracy by observing the shear stress at resonance frequencies.⁵⁴⁻⁵⁶ Through the above discussion on the physical properties of various condensed systems composed of ions, solvent molecules and solid phases, we report the heterogeneous phases on the nanometer scale which appears by adding the second component to the basic component.

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CHAPTER 1

Thermophysical Properties of Binary Amide Anion-Based Ionic Liquids; TPAFSA_xTFSA_{1-x}

1. Introduction

Ionic liquids are expected as next-generation liquid material for various kinds of utilization and have become an expanding topic of chemical research because of their attractive and unique properties; a negligible vapor pressure, nonflammability, electrical conductivity, good solubility, and so on.¹⁻⁹ Ionic liquids are generally recognized as salts which have melting point below 100°C, and their physical properties depend on the choice of ionic species. Aliphatic quaternary ammonium is known as one of the cationic species and their good electrochemical stability was reported.¹⁰⁻¹²

In the past decade, ionic liquids including bis(fluorosulfonyl)amide ion (FSA⁻) have attracted much attention due to its higher fluidity and conductivity compared with bis(trifluoromethanesulfonyl)amide ion (TFSA⁻) which is famous as a constituent of hydrophobic, low viscosity, and low melting temperature ionic liquids.^{13, 14} The flexibilities by internal rotations with respect to the C–S–N–S dihedral angle are key factor for lowering melting temperature or viscosity as well as delocalization of charge. However, with *N,N,N*-trimethyl-*N*-propylammonium ion (TPMA⁺), there is an obstacle for operation in room temperature because the melting point of *N,N,N*-trimethyl-*N*-propylammonium bis(trifluorosulfonyl)amide (TMPAFSA) is 43.2 °C. In the past, authors found that mixture of TMPAFSA and *N,N,N*-trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)amide (TMPATFSA) showed phase transition at lower temperature than each pure substance, and reported the phase diagram.¹⁵ From the viewpoint of practical applications, mixing several materials is beneficial to design desired performances.^{16, 17} Although many studies have been investigated focusing on binary or ternary ionic liquid systems these are mainly limited in transport properties, and there are few studies about basic

properties overlooking the whole composition.¹⁸⁻²⁶ Because both FSA⁻ and TFSA⁻ possess isomerization by intramolecular rotation, it is important to understand that how anionic composition affect the properties.^{27, 28} Hence, in chapter 1, we investigated anionic binary ionic liquid; TPAFSA_xTFSA_{1-x} (x means mole fraction of FSA⁻) focusing on the relationship between anionic composition and phase transition behavior. For reference purposes, other ionic liquids which have different shape of anion were also studied.

In addition, binary amide anion-based ionic liquid system containing lithium ion was investigated. The lithium secondary batteries have to be treated carefully for temperature management to ensure the credibility and safety because the conventional electrolytes contain organic solvents prone to decompose. Therefore, a possible alternative for high temperature operation might be ionic liquid based electrolytes.²⁹ We discussed how the coexistence of two different anions affect phase transition temperature and coordination around lithium ion.

2. Experimental

2.1 Materials

TMPAFSA and TMPATFSA were synthesized by an anion-exchange method.³⁰ LiFSA and LiTFSA were purchased from Kishida Chemical Co., Ltd. and Morita Chemical Industries Co., Ltd., respectively. The recovered organic phase was dried under vacuum for 12 h at 95 °C and then TMPAFSA and TMPATFSA were gained. They were stored in an argon filled glove box. Appropriate amounts of the ionic liquids were mixed and stirred for 3 h at 50 °C in the glove box to prepare the anionic binary ionic liquid; TMPAFSA_xTFSA_{1-x}. Ionic liquid system containing lithium ion; Li_yTMPA_{1-y}TFSA and Li_yTMPA_{1-y}FSA_{0.33}TFSA_{0.67} (here, *y* means mole fraction of Li⁺ against cation composition) were also prepared in a similar way keeping the anion ratio constant. *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium tetrafluoroborate (DEMEBF₄) was purchased from Kanto Kagaku Co., LTD, and *N,N,N*-trimethyl-*N*-propylammonium (fluorosulfonyl) (trifluoromethylsulfonyl)amide (TMPAFTA) was provided as product. All chemical structures are shown in Fig. 2-1.

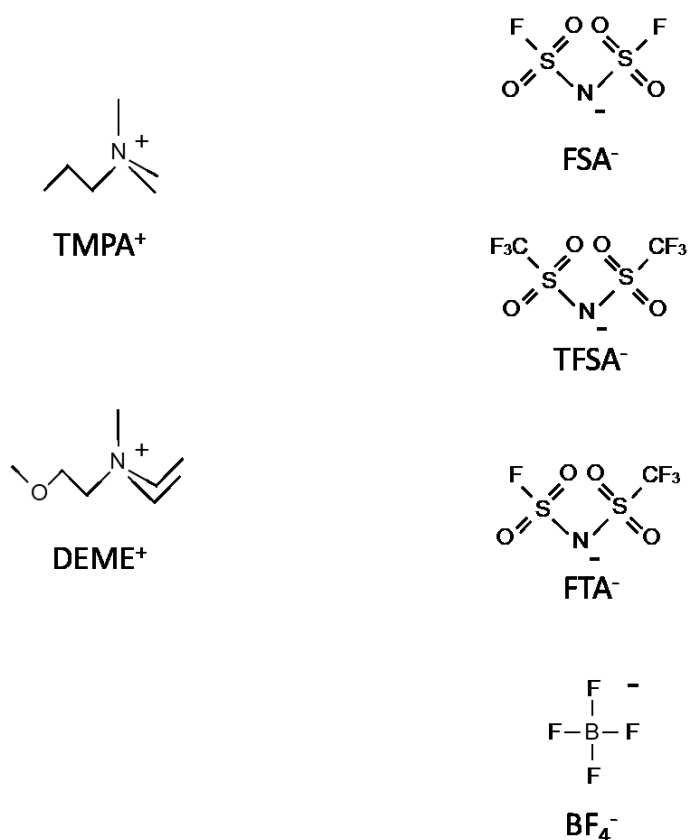


Fig. 2-1. Chemical structures of the cations (TPMPA⁺ and DEME⁺) and anions (FSA⁻, TFSA⁻, FTA⁻ and BF₄⁻).

2.2 Thermal characterization

Phase transition of ionic liquids were investigated by differential scanning calorimetry (DSC) measurements with a Thermo Plus DSC 8230L (Rigaku Denki Co., Japan) with liquid nitrogen cooling. Sealed aluminum pans were prepared in the glove box. The employed scanning temperature range was between -50 and 50 °C and the scan rate was 5 °C min⁻¹. Cooling and heating processes were repeated more than three times in dry nitrogen atmosphere.

2.3 X-ray diffraction analysis

XRD patterns were measured using X-ray generator RINT-TTR (Rigaku Co., Ltd., Japan) equipped with semiconductor detector and low temperature control unit (PTC30). The sample was investigated by focusing method (CuK α , 50 kV, and 300 mA) with a Ni filter. A scanning speed of 20° min⁻¹ was used within the range of 10° < 2 θ < 60°. We measured XRD patterns at every 20 °C as stepwise procedure between -100 °C and 50 °C and heating and cooling rates were 1 °C min⁻¹. All measurements were carried out under vacuum condition to avoid dew condensation. At each measurement temperature, the sample was retained for 10 min before measurement. The stepwise procedure was repeated to confirm the effect of the heating and cooling cycles. We analyzed the degree of variation using a simple statistical method to estimate the reproducibility in the obtained XRD patterns. We calculated the sample standard deviations for the root mean square of the d -value (D_k) derived from diffraction angles of each repeated XRD measurements for each ionic liquid as shown below:

$$D_k = [\text{root mean square of } d - \text{value in } k\text{th cycle}] = \sqrt{\frac{\sum_{i=1}^n d_i^2}{n}}$$

$$[\text{sample standard deviation}] = \sqrt{\frac{\sum_{k=1}^N (D_k - \overline{D})^2}{N - 1}}$$

where n and N are the number of diffraction peaks in each cycle and the number of measurement repetitions, respectively. Repeated XRD measurements with higher reproducibility in diffraction angles tend to result in relatively lower sample standard deviation value. When no diffraction peaks appeared due to the glassy state, we applied zero value instead of the root mean square to calculate the sample standard deviation.

This represents there was big difference between crystal and glassy state. The calculation was carried out within the range of $10^\circ < 2\theta < 40^\circ$.

2.4 Raman Spectroscopy

Raman vibrational spectra were recorded by a T-64000 Raman spectrometer (Horiba Ltd., Japan) with a charge coupled device detector cooled using liquid N₂. The neodymium-doped yttrium aluminium garnet (i.e., Nd:YVO₄) laser with a wavelength of 532 nm was used for excitation. Samples were loaded into 5 mm diameter glass tubes and set into the Raman cell (#2000-A of AABSPEC) in the 180° scattering geometry. The laser power and integration time were 20 mW and 10 sec., respectively. The wavenumber of monochromator was calibrated by F2g mode of Si at 520 cm⁻¹ using silicon powder.

2.5 Ionic conductivity and viscosity measurements

The ionic conductivities were measured by AC impedance measurement using a precision LCR meter (4284A and 4285A of Agilent Technology, USA) with a 16452A test fixture. The electrode area was 38 mm and the distance was 0.5mm. The cell was calibrated by using a 0.01 mol L⁻¹ KCl aqueous solution at 25°C. The viscosities were measured by a cone-plate digital viscometer (TVE-22L of Toki Sangyo Co., Ltd., Japan). A cone rotor 1°34' × R24 was used and the rotating speed was 5 rpm. The fluidities were gained as the reciprocal of viscosities. The nonlinear temperature dependences of the electrical conductivities and fluidities showed were analyzed using Vogel-Tamman-Fulcher (VTF) equation given as following:

$$W = A\sqrt{T} \exp[-B/(T - T_0)]$$

where W is conductivity or fluidity and A , B and T_0 are constants. The VTF parameters were determined with a nonlinear Gauss-Newton inverse matrix optimizing method similarly to our previous study.³¹

3. Results and discussion

3.1 Thermal analyses

Excepting the single or eutectic salts, two endothermic peaks were observed in the heating process of $\text{TMPAFSA}_x\text{TFSA}_{1-x}$ from the DSC measurement. Peaks appeared at lower temperature were assigned to the liquidus line on the phase diagram, and higher ones were linked with the solidus line. From the all results of DSC spectra, the phase diagram of $\text{TMPAFSA}_x\text{TFSA}_{1-x}$ was obtained as Fig. 2-2. The binary anion system showed the binary phase diagram composed of two kinds of immiscible crystals and completely miscible melt. The eutectic point of $x = 0.33$ was confirmed at $5.5\text{ }^\circ\text{C}$ and it was lower than that of TMPAFSA and TMPATFSA ; $43.2\text{ }^\circ\text{C}$ and $19.8\text{ }^\circ\text{C}$, respectively. Bayley et al. reported that the binary anion system based on *N*-methyl-*N*-propylpyrrolidinium ion showed the phase diagram and the eutectic composition around an anion ratio of 2:1 (FSA^- : TFSA^-).¹⁸ The eutectic composition of $\text{TMPAFSA}_x\text{TFSA}_{1-x}$ had much TFSA^- content compared with their report. Slight difference in cation structure; two methyl groups or pyrrolidine, made a difference for interaction among the constituent ions. It could be due to the difference of randomness between TMPA^+ and *N*-methyl-*N*-propylpyrrolidinium ion because TMPA^+ based system showed higher phase transition points, and TMPA^+ might need much TFSA^- which exhibits more randomness than FSA^- to get the eutectic mixture. Fig. 2-3 represents two endothermic curves of same composition with and without the small peak which appeared below the temperature corresponding to the solidus line. The peak suggested that there is minor phase transition below the phase transition temperature, and more

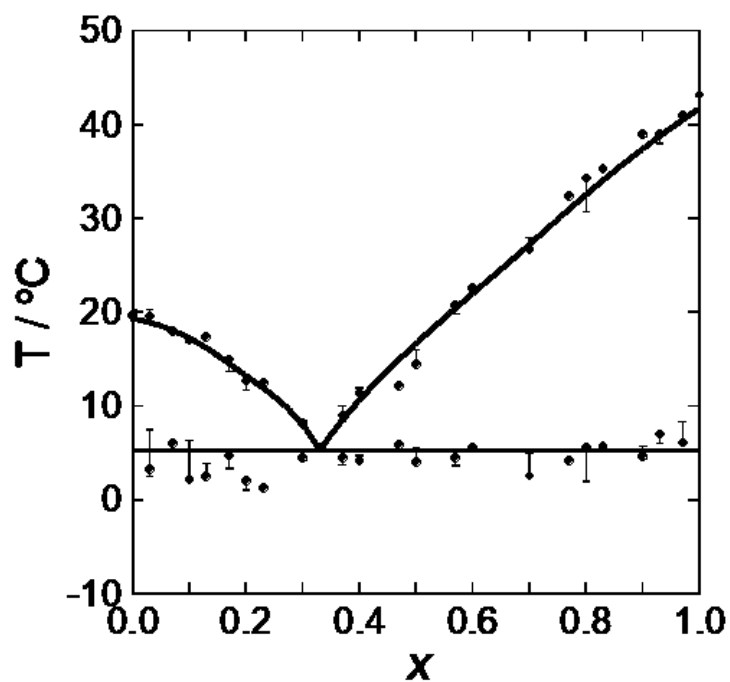


Fig. 2-2. Phase diagram of TPAFSA_xTFSA_{1-x}.

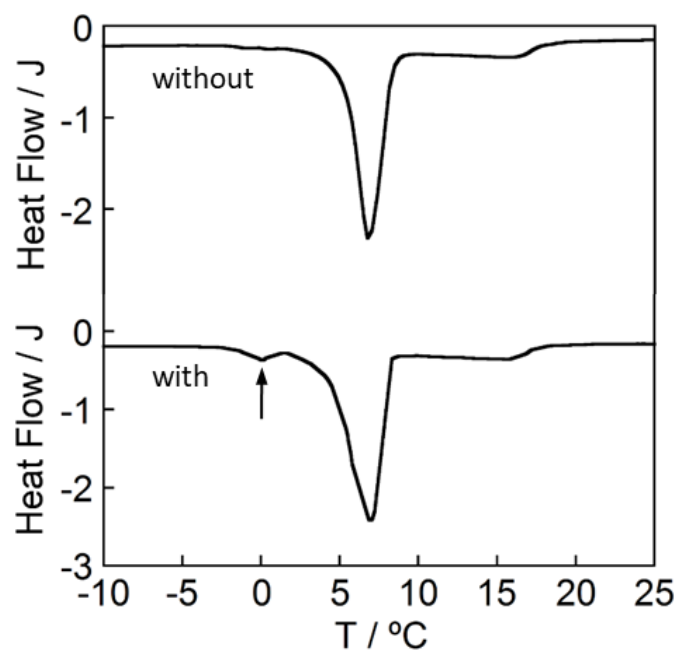


Fig. 2-3. Calorimetric curves of TPAFSA_{0.50}TFSA_{0.50} without and with small endothermic peak both in a heating process at 5°C min^{-1} . The black arrow represents the existence of a small peak.

than one metastable crystal structure in solid state. Such melting behavior is particularly common in materials which exhibit polymorphism. Recently, it is well reported that ionic liquid exhibits polymorphic behavior.³²⁻³⁹ Also in this work, there are several solid phases which have different segmental motion due to polymorphism, such solid phase exhibited melting behavior below the temperature corresponding to the solidus line. Additionally, we got composition dependence of heat of fusion as Fig. 2-4 from integration of endothermic peaks. The eutectic composition showed the lowest value as shown in the figure. It suggests that eutectic composition can solidify more easily than other composition. The small peak was hardly found near the eutectic composition. It seems that the magnitude of polymorphism is related to the composition. The polymorphism of TPAFSA_xTFSA_{1-x} is discussed in a later section with XRD patterns.

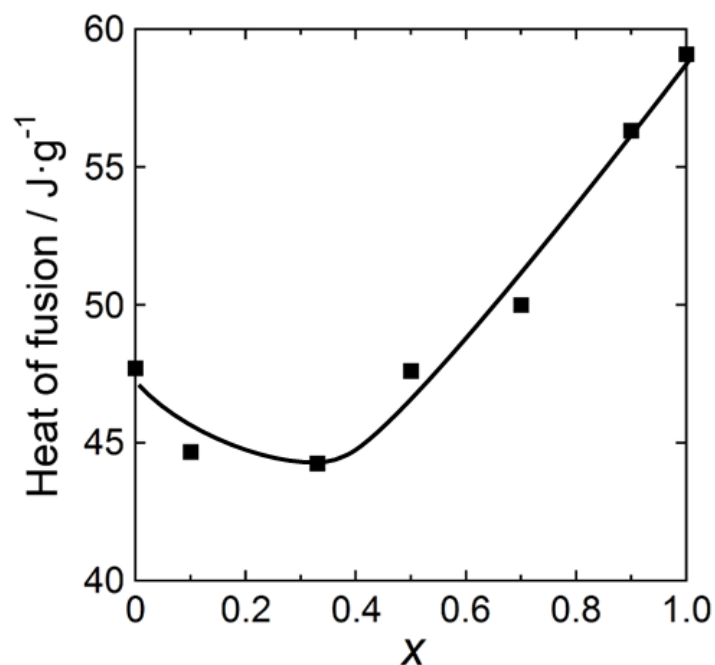


Fig. 2-4. Composition dependence of heat of fusion of TPAFSA_xTFSA_{1-x}.

3.2 Phase transition behavior of $\text{TMPAFSA}_x\text{TFSA}_{1-x}$

We observed the XRD patterns on cooling process shown in Fig. 2-5. TMPATFSA got glassy state until $-100\text{ }^\circ\text{C}$ despite its melting point at $19.8\text{ }^\circ\text{C}$. On the other hand, TMPAFSA which has a melting point at $43.2\text{ }^\circ\text{C}$ also got glassy state but to a lesser extent. Although phase behavior of ionic liquids is affected by pressure, the difference between TFSA^- and FSA^- is due to the intramolecular rotation of each anion.⁴⁰ Each retention times before XRD measurement was seemed to be sufficient because the time scale of crystallization for the domains of ionic liquid was reported to be about 100 second.⁴¹ Effect by intramolecular rotation of TFSA^- is supposed to be more drastic than FSA^- because of its intrinsic bulkiness, therefore it makes the solidification of TMPATFSA unsettled. Interestingly, the eutectic composition hardly got glassy state. This composition seems to be relatively stable for crystallization, and that corresponded with the composition dependence of heat of fusion.

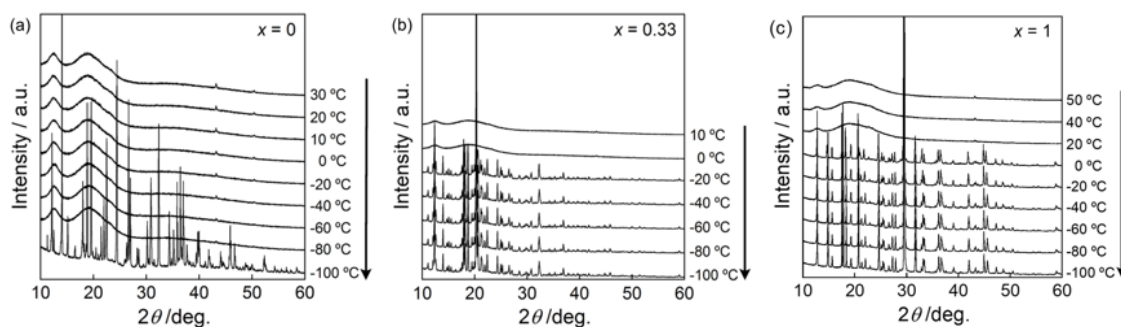


Fig. 2-5. XRD patterns of $\text{TMPAFSA}_x\text{TFSA}_{1-x}$ at (a) $x = 0.00$; (b) $x = 0.33$; (c) $x = 1.00$ under 6th cooling process. Diffraction patterns are vertically displaced for clarity. Peaks from copper substrate was also detected at around $2\theta = 43^\circ$ and 50° .

The separated solid phases of TMPATFSA and TMPAFSA should melt above the solidus temperature because the system showed binary phase diagram as Fig. 2-2. Consequently, we carried out XRD observation in heating processes. Some diffraction peaks of mixed composition disappeared along with the temperature increase, while TMPAFSA did not show such behavior until 40 °C. This suggested that different solid phases exist in mixed composition.

Fig. 2-6 represents cycle-dependent XRD patterns observed at -100 °C in each cycle. It is obvious that TMPATFSA showed different XRD patterns depending on cycles, while TMPAFSA showed XRD patterns at relatively same angles shown as Fig. 2-6(c). We confirmed that there is an influence from sample orientation for X-ray. However, the cycle dependences of the XRD patterns are unexplained by just the sample

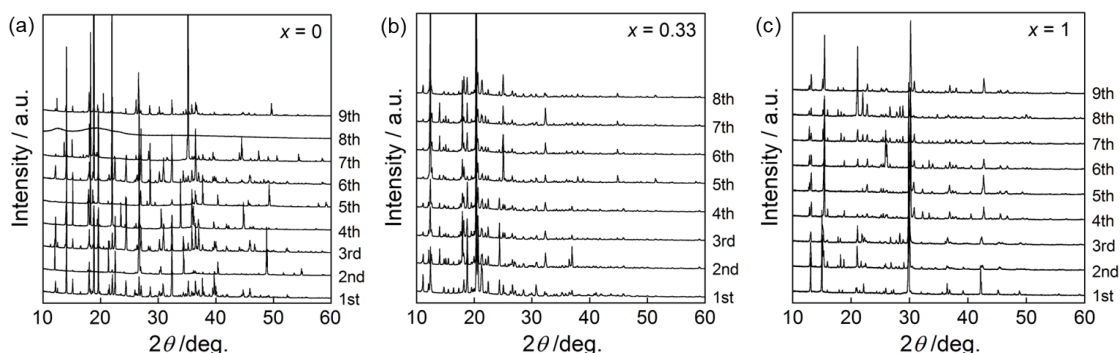


Fig. 2-6. XRD patterns of TMPAFSA_xTFSA_{1-x} at (a) $x = 0.00$; (b) $x = 0.33$; (c) $x = 1.00$ at -100°C in each measurement cycle. Diffraction patterns are vertically displaced for clarity.

orientation. It suggested that various solid phases existed and the phase transition was not fixed clearly by the varieties of the molecular conformation. Nishikawa et al. reported unique thermal phenomena of 1-isopropyl-3-methylimidazolium bromide using

a laboratory-made DSC with nanowatt stability and sensitivity.^{41, 42} They pointed out that domains of different conformers existed and could be closely related with phase transition behavior. Their indication would be more remarkable in $\text{TMPAFSA}_x\text{TFSA}_{1-x}$ than 1-isopropyl-3-methylimidazolium bromide because amide anions have more complicated structure. It was reported that TMPAFSA and TMPATFSA exhibit isomerization equilibria displacement depending on temperature, and alter its liquid structure depending on the isomerization equilibria displacement.¹⁵ It was supposed that isomerization equilibria occurred during cooling processes until just before solidification and resulted in polymorphic behavior. We found difficulty to determine the crystal structure due to the polymorphism. On the other hand, XRD patterns of eutectic mixture represented in Fig. 2-6(b) showed relatively good reproducibility for each cycle. Hence, the polymorphic tendency of FSA^- and TFSA^- might be suppressed. Cycle-dependent XRD patterns of TMPAFTA , which has asymmetric anion structure and melting point at $-27.3\text{ }^\circ\text{C}$, were shown as Fig. 2-7(a). Solidification did not occur even in heating process from $-100\text{ }^\circ\text{C}$ except for first two cycles and kept glassy state until end of measurement. Matsumoto et al. pointed out that introducing asymmetry into an amide anion is one of effective strategies to reduce the melting point of ionic liquid.⁴³ The solidification difficulty of TMPAFTA was due to the asymmetric molecular structure of FTA^- . On the other hand, ionic liquid based BF_4^- , which has simple and symmetric structure, exhibited with high reproducibility in XRD patterns as displayed in Fig. 2-7(b). BF_4^- seems to get the most stable structure easily. We estimated the reproducibility of the obtained XRD patterns for each ionic liquid shown in Figs. 2-6 and 2-7 with the simple statistical method. If material exhibits polymorphic behavior, it would show XRD patterns in different angles randomly for each measurement cycle,

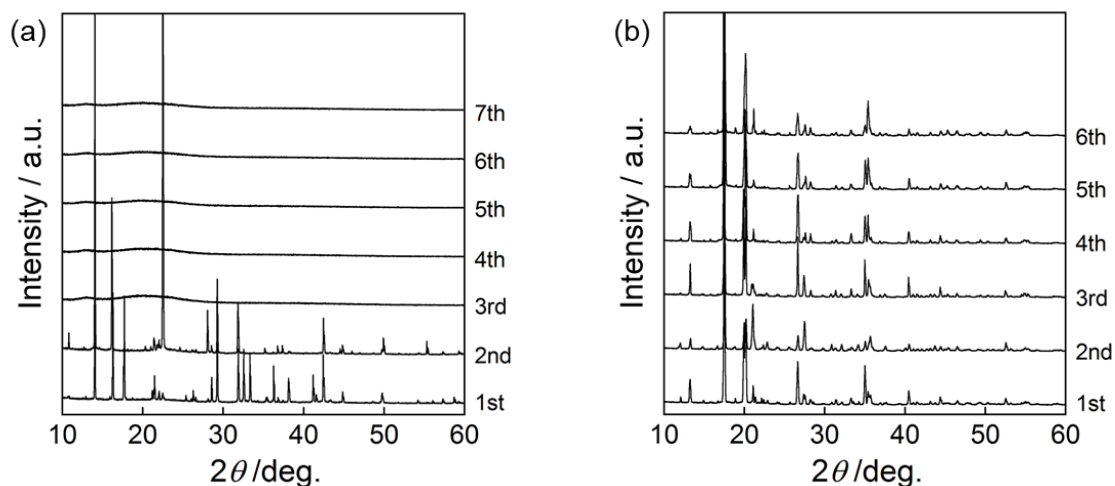


Fig. 2-7. XRD patterns of (a)TPAFTA and (b)DEMEBF₄ at -100°C in each measurement cycle. Diffraction patterns are vertically displaced for clarity.

and the sample standard deviation tend to be large value. Thus, we can qualitatively compare the tendency to show polymorphism for each ionic liquid. The results are shown in Table 2-1. We confirmed the variations of diffraction angles were less in order of TPAFSA_{0.33}TFSA_{0.67}, DEMEBF₄, TPAFSA, TMPATFSA and TPAFTA. From the above estimation, conformational change by intramolecular rotation plays a critical role on crystalline structure of ionic liquid, and mixing different anions had a more significant influence.

Table 2-1. Values of the sample standard deviations for ionic liquids. Zero value were applied instead of root mean square for no diffraction patterns due to the glassy state.

Ionic liquids	Root mean square of the d -value for each measurement cycle									Sample standard deviation
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	
TMPATFSA	1.92	1.46	1.84	1.65	1.42	1.73	1.71	1.73	0	0.58
TMPAFSA _{0.33} TFSA _{0.67}	2.17	2.33	2.30	2.37	2.34	2.34	2.34	2.26	-	0.06
TMPAFSA	1.49	1.47	1.58	1.52	1.63	1.81	1.73	1.72	1.61	0.12
TMPAFTA	1.69	1.57	0	0	0	0	0	0	-	0.75
DEMEBF ₄	1.59	1.48	1.43	1.32	1.31	1.35	-	-	-	0.11

3.3 Electrical conductivities and fluidities

Fig. 2-8 represents composition dependences of conductivities and fluidities for TMPAFSA _{x} TFSA_{1- x} at 60 °C. The conductivities and fluidities increased with FSA⁻ mole fraction. It was due to the better mobility of the FSA⁻. The inflection points were found near $x = 0.3$, and this suggests that there are two regions depending on anion composition; FSA⁻ is dominant in one region and TFSA⁻ is so in the another region. At each composition, temperature dependences of conductivity and fluidity showed obvious curvatures that follow VTF behavior as shown in Figs. 2-9(a) and 2-9(b), respectively. Fig. 2-10 exhibits the composition dependences of $T_{0,\sigma}$ and $T_{0,\phi}$ determined by conductivity and fluidity, respectively. Here, T_0 is known as an ideal glass transition temperature at which the fluidity would fall to zero.^{31,44,45} Cohen et al. proposed from a series of their investigations that free volume means requirement for molecular movements, and it depends on the difference between T_0 and measuring temperature under constant pressure.⁴⁶⁻⁴⁹ Although $T_{0,\sigma}$ in low FSA⁻ mole fraction and $T_{0,\phi}$ were

almost constant, $T_{0,\sigma}$ above the composition of $x = 0.33$ showed dependence with FSA⁻ content as shown in Fig. 2-10. The eutectic composition seemed to exhibit the lowest hindrance for ionic transport. The composition dependences of $T_{0,\sigma}$ and $T_{0,\phi}$ corresponded with the results of XRD of Fig. 2-6. TMPATFSA, which kept glassy state and then crystallized at a temperature lower than $T_{0,\sigma}$ and $T_{0,\phi}$, seems to exhibit phase transition under highly restricted condition.

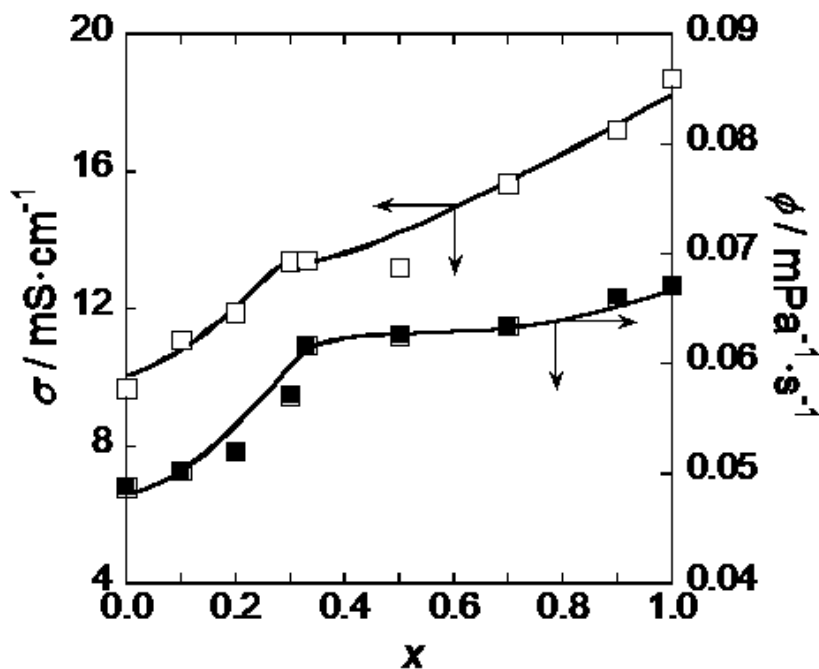


Fig. 2-8. Composition dependences of conductivity(□) and fluidity(■) of TMPAFSA_xTFSA_{1-x} at 60°C.

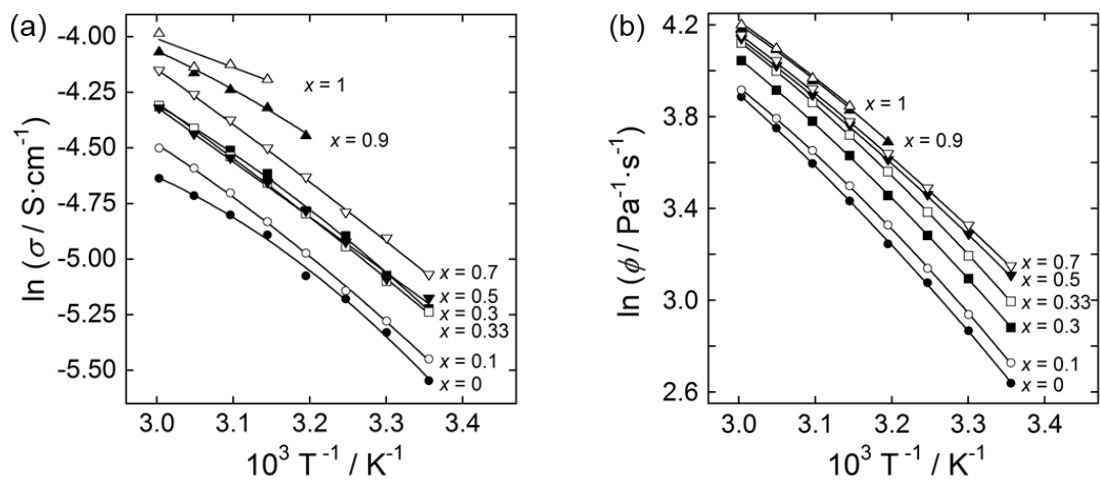


Fig. 2-9. Temperature dependences of (a)conductivity and (b)fluidity for TPAFSA_xTFSA_{1-x}.

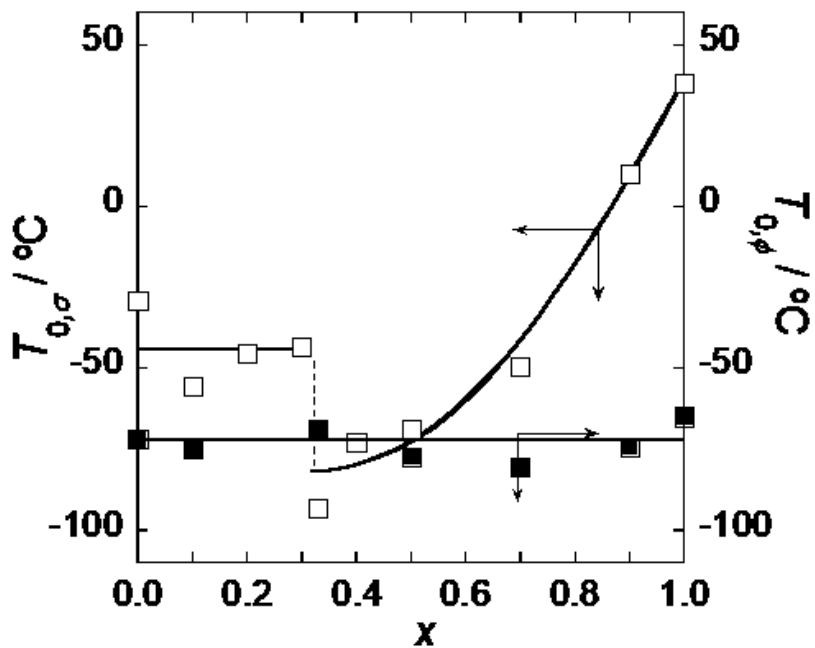


Fig. 2-10. Composition dependence of $T_{0,\sigma}(\square)$ and $T_{0,\phi}(\blacksquare)$.

3.4 Phase transition of binary anion system containing lithium cation

For application of ionic liquids as lithium ion battery electrolytes, lithium salt is usually mixed with ionic liquids. However, the increase of salt concentration generally induces unfavorable changes such as increase of viscosity, decrease of ionic conductivity, and rise of melting point. Mixing ionic liquids can lower the phase transition temperature especially at the eutectic composition as above mentioned, therefore we compare the phase transition of the system with single anion and binary anion. As binary anion system composed of FSA^- and TFSA^- , FSA^- mole fraction of $x = 0.33$ was employed because this anion ratio, which was found as the eutectic composition in Fig. 2-2, seemed to be stable in TMPA^+ based system. Fig. 2-11 represents two phase diagrams; $\text{Li}_y\text{TMPA}_{1-y}\text{TFSA}$ and $\text{Li}_y\text{TMPA}_{1-y}\text{FSA}_{0.33}\text{TFSA}_{0.67}$. The liquidus and solidus lines of the binary anion system were lower than that of the single anion system. This means binary anion could keep liquid state in wider temperature range. It is one good example of practical application for binary anion. In the binary anion system, $y = 0.5$ did not show definite phase transition and showed liquidity at room temperature, while the single anion system solidified completely.

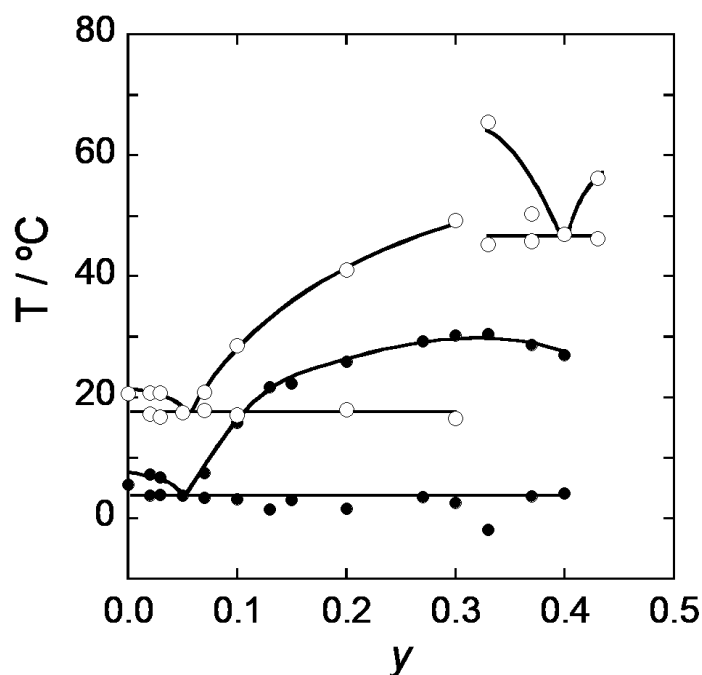


Fig. 2-11. Phase diagrams of $\text{Li}_y\text{TMPA}_{1-y}\text{FSA}_{0.33}\text{TFSA}_{0.67}$ (●) and $\text{Li}_y\text{TMPA}_{1-y}\text{TFSA}$ (○).

3.5 Interaction between lithium cation and binary anion

In FSA^- and TFSA^- coexisting system, it is important to know which anion interacts with Li^+ preferably. From the results of Raman spectroscopy shown as Fig. 2-12, the band assigned to the CF_3 bending vibration of TFSA^- was observed at 742 cm^{-1} , while the new band in the higher frequency side appeared depending on mole fraction of Li^+ . The new band around 750 cm^{-1} is ascribed to the TFSA^- bound to the Li^+ .⁵⁰ This behavior was same whether FSA^- coexists or not. On the other hand, the Raman band of 1217 cm^{-1} assigned to the SO_2 symmetric in-phase stretches of the bulk (*free*) FSA^- did not show any changes between lithium mole fraction of $y = 0.1$ and $y = 0.0$, although the band ascribed to the FSA^- solvated to the Li^+ appeared around 1242 cm^{-1} and

overlapped with the decreasing band of *free* FSA⁻ above $y = 0.3$.⁵¹ Previous reports say that the lithium ion may be coordinated through two TFSA⁻ and that of FSA⁻ is three in corresponding ionic liquids.^{52, 53} As Li⁺ mole fraction of $y = 0.1$ in the binary anion system, there is enough TFSA⁻ to coordinate with Li⁺. However, Li⁺ and TFSA⁻ lose numerical balance above $y = 0.3$ and consequently form a pair with FSA⁻. Therefore, Li⁺ seems to interact with TFSA⁻ preferably in binary amide anion-based ionic liquid. This consideration is appropriate to the findings proposed by Tsuzuki et al. that the interaction between FSA⁻ and Li⁺ is weaker than between TFSA⁻ and Li⁺.⁵⁴ Thus, in Li_yTMPA_{1-y}FSA_{0.33}TFSA_{0.67}, Li⁺ solvated cluster composed of TFSA⁻ seemed to exist in somewhat FSA⁻-rich binary ionic liquid.

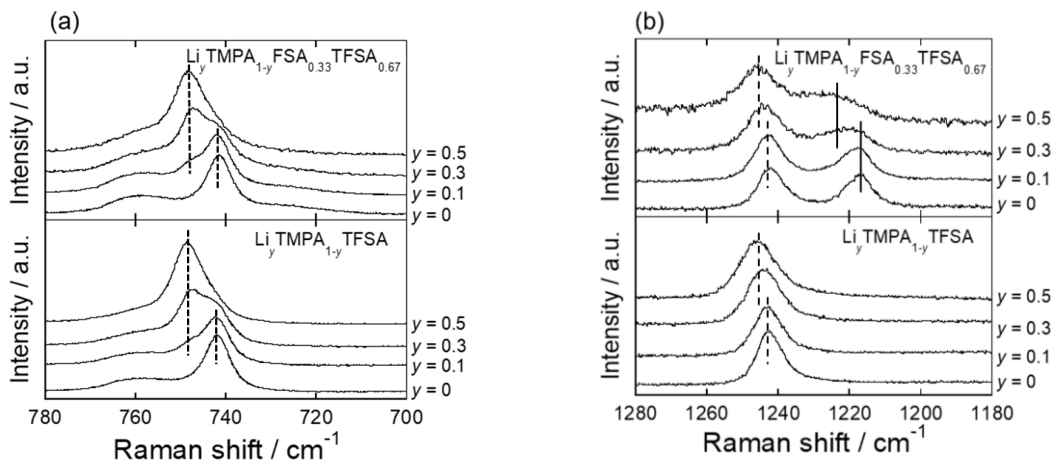


Fig. 2-12. Raman spectra of Li_yTMPA_{1-y}TFSA_{0.33}TFSA_{0.67} and Li_yTMPA_{1-y}TFSA in the frequency ranges (a) 700–780 and (b) 1180–1280 cm⁻¹ at 25°C. Characteristic bands of free TFSA⁻ (742 cm⁻¹), bound TFSA⁻ (750 cm⁻¹), free FSA⁻ (1217 cm⁻¹), bound FSA⁻ (1242 cm⁻¹), and TMPA⁺ (759 cm⁻¹) are shown. Vertical dashed line and vertical straight line in the figure represents contribution from TFSA⁻ and FSA⁻, respectively.

Conclusion

Thermophysical properties of binary amide anion-based ionic liquid; TMPAFSA_xTFSA_{1-x} were investigated in whole composition. From DSC measurements, TMPAFSA_xTFSA_{1-x} showed the binary phase diagram which had the eutectic point at the mole fraction of $x = 0.33$. In order to investigate the polymorphism which was suggested by thermal analyses, we carried out XRD measurements again and again with repeated heating and cooling using temperature controlling unit. Comparing each XRD pattern with the simple statistical method, polymorphic behaviors due to the intramolecular rotation of amide anion were confirmed. A relatively good reproducibility in XRD patterns of the eutectic composition seemed to be consistent with the composition dependence of heat of fusion and of ideal glass transition temperature determined from VTF equation. Motivated by desire for a lithium secondary battery electrolyte for high temperature operation, we studied the binary amide anion system containing lithium ion. The phase transition temperature of the binary anion system was lower than TFSA⁻ system. In addition, Raman spectroscopy suggested that lithium ion interacts more preferentially with TFSA⁻ than with FSA⁻.

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CHAPTER 2

Section 1

Properties of Concentrated Aqueous Electrolyte Solution in a Vicinal Region of Coexisting Solid Surface

1. Introduction

Numerous electrochemical devices are expected to operate in higher output using large amount of active materials and concentrated electrolyte solution in limited volume. Large solid/liquid interfacial area between solid phase and liquid phase exist in these systems, and it is well-known that the solid surface affects the properties of water nearby the solid/liquid interface¹. Therefore, solution chemistry not only in bulk solution but also in vicinal area of solid surface is important. In spite of a lot of researchers have been investigating for electrolyte solution, the properties of electrolyte solution\coexisting with solid materials are not studied very well. We have been studying the coexisting systems consisting of aqueous electrolyte solution and inorganic powder, and confirmed that various kinds of solutions change their properties depending on a distance from solid surface.²⁻⁴

Recently, highly concentrated aqueous solution have attracted attention as stable aqueous electrolyte for aqueous lithium secondary batteries.⁵⁻⁷ Such electrolyte solutions are regarded as hydrate melts defined by Braunstein which behaves like molten salt in some respects.⁸ Ionic interaction of ionic species is dominant in liquid properties of such concentrated solutions. In section1 of chapter 2, we investigated zinc aqueous solution. We assumed that interaction from solid surface might be much observable because strong ionic interaction of Zn^{2+} makes large hydration sphere. In order to discuss the interaction in the vicinity of solid phase, we measured the liquid properties of ZnSO_4 aq. coexisting with metal oxide nanoparticles focusing on the numerical ratio of water molecules to one salt and interfacial liquid molecular layer thickness.

2. Experimental

2.1 Materials

ZnSO₄ aqueous solution was prepared by dissolving zinc sulfonate heptahydrate in deionized distilled water. Concentration of aqueous solutions were determined using inductively coupled plasma atomic emission spectroscopy (HORIBA). The concentration dependence of pH for ZnSO₄ aqueous solution was displayed as Fig. 3-1.

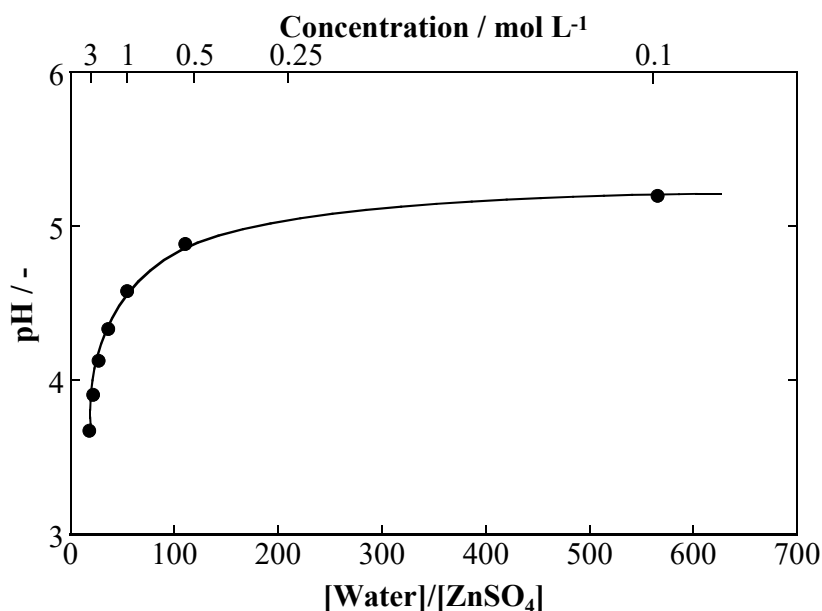


Fig. 3-1. Concentration dependences of pH for ZnSO₄ aq. at 25 °C.

Fumed metal oxides supplied from Nippon Aerosil were used as solid phase, and solid/liquid coexisting samples were obtained mixing the fumed oxides with ZnSO₄ aq. thoroughly using an agate mortar. Volume fractions of the liquid phase ranged from 85.0 to 100 vol%. The physical aspects of the oxides are shown in Table 3-1.⁹ The crystalline phases of fumed metal oxides were assigned using parallel beam X-ray

diffractometer RINT-TTR (Rigaku), following the references as shown in the Table. The relative weight fraction of rutile was 7.7 wt% as Moiseev et al. reported by Rietveld refinement.

Table 3-1. Properties of the fumed metal oxides.

Samples	Nature	Specific	Average	Origin
		surface area /	particle size /	
		m ² g ⁻¹	μm	
Fumed silica	SiO ₂ (Amorphous)	200±25	12	Aerosil 200
Fumed alumina	γ - Al ₂ O ₃ ¹⁰	130±15	10	Aeroxide Alu 130
Fumed titania	TiO ₂ (Rutile, Anatase) ¹¹	90±20	14	Aeroxide TiO ₂ P90

2.2 Thermal analysis

Phase transition behavior was observed by DSC with a Thermo Plus DSC 8230L (Rigaku) with liquid nitrogen cooling unit. The fumed metal oxides were thoroughly mixed with ZnSO₄ aqueous solution, then the solid/liquid coexisting samples were immediately sealed in an aluminum sample pan. The employed scanning temperature range was between -70 and 50°C and the scan rate was 5°C per minute. Cooling and heating processes were repeated more than three times in dry nitrogen atmosphere. Temperature and heat flow calibration were carried out using the melting points of 1,2-dichloroethylene (mp = -35.3°C) and In (mp = 156.6°C). The obtained DSC curves were corrected to determine the melting point and heat of fusion for the liquid phase by subtracting baseline.

2.3 Density measurement

Densities of liquid sample were measured using DMA 5000M with oscillating U-tube sensor (Anton Paar). We obtained vibrational frequencies and converted to densities.

2.4 Raman spectroscopy

Raman spectra were recorded by T-64000 Raman spectrometer equipped with a YVO₄ with a charge coupled device detector cooled using liquid nitrogen. The 532 nm line was used for excitation. The solid/liquid coexisting samples were loaded into glass tubes and set in the 180° scattering geometry. The wavenumber of monochromator was calibrated by silicon at 520 cm⁻¹. All experiments were performed at 25 °C.

2.5 ¹H Relaxation measurement

The spin-lattice relaxation time (T_1) and spin-spin relaxation time (T_2) in ¹H NMR were obtained by relaxation time measuring equipment Acorn area (XiGo Nanotools). The solid/liquid coexisting samples were put into 5 mm diameter glass NMR tube. All experiments were performed at 25 °C.

2.6 Zeta potential measurement

For studying surface potential of metal oxide nanoparticles, ELS-Z2 (Otsuka Electronics) based on laser Doppler method equipped with pH titrating system was used. 0.1 mol L⁻¹ NaCl aq. and 1 wt% of the metal oxide nanoparticles were utilized to

prepare the suspensions, which then were treated in an ultrasonic bath for 20 min. The low oxide content was used in order to avoid hydrodynamic and electrostatic interactions between particles. The pH values were adjusted by 0.1 mol L⁻¹ HCl or NaOH aqueous solutions containing 0.1 mol L⁻¹ NaCl. We confirmed surface potential of SiO₂ and γ -Al₂O₃ depending on pH as shown in Fig. 3-2.

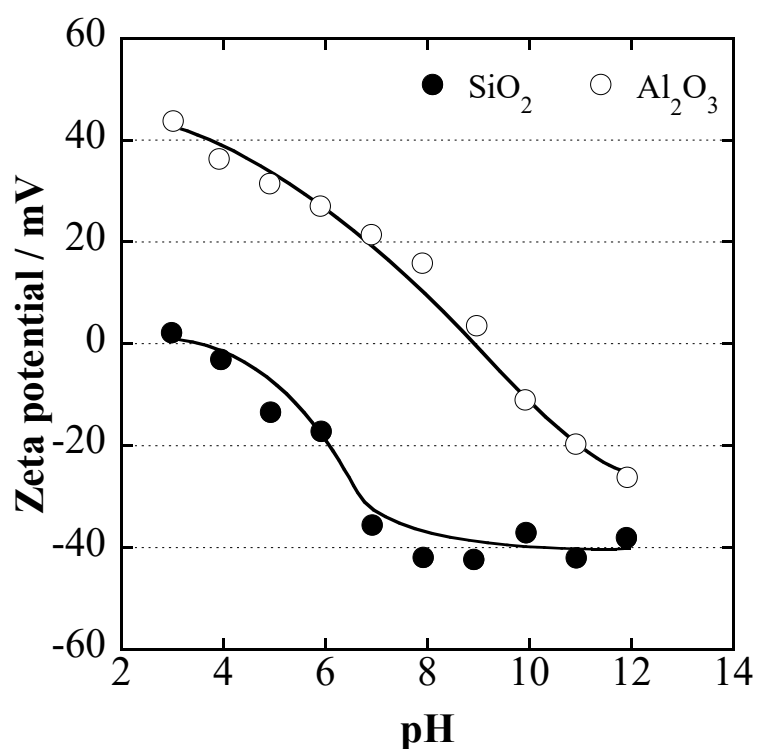


Fig. 3-2. Relationships between surface potential of 0.1 wt% of SiO₂ and γ -Al₂O₃ nanoparticles and pH of dispersion medium: 0.1 mol L⁻¹ NaCl aq.

3. Results and discussion

3.1 Phase Diagram and Electrostriction of Bulk Aqueous Solution

Water and zinc sulfate heptahydrate system showed binary phase diagram as shown in Fig. 3-3. The eutectic composition was 0.050 mole fraction of zinc sulfate. DSC measurement revealed two endothermic peaks in heating process of ZnSO_4 aq. The Peaks appeared at lower temperature were assigned to the liquidus line in the phase diagram, and the higher ones were linked with the solidus line. Kanagadurai et al. reported that crystals of heptahydrate grew by temperature lowering ZnSO_4 solution technique.¹² In addition, we didn't observe thermal transition under the solidus line temperature. The eutectic composition suggested that 19 water molecules and one salt exhibit phase transition. Rudolph et al. reported that Zn^{2+} have 6 water molecules as first hydration sphere and 12 water molecules as second hydration sphere¹³. Considering first and second hydration number, phase transition at the eutectic composition was supposed to take along almost all water molecules in liquid system. This numerical ratio of water molecules per one salt is high compared with other H_2O -salt system.¹⁴⁻¹⁸

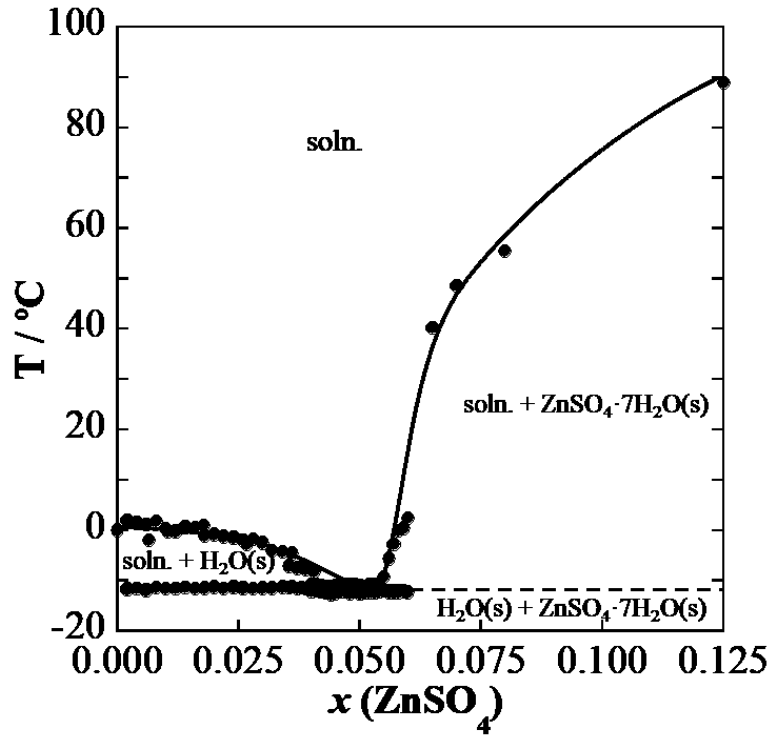


Fig. 3-3. Phase diagram of H₂O-ZnSO₄ system.

The volume subtraction was calculated by following equation using the concentration dependence of liquid density shown in Fig. 3-4, and plotted with numerical ratio of water molecules per one salt which was converted from concentration.

$$\text{Volume change by 1 mol of water} = \frac{\Delta(\text{solution volume per mol of salt})}{\Delta(\text{mol of water per mol of salt})}$$

$$= \frac{\Delta(1/\text{Concentration})}{\Delta([\text{Water}]/[\text{Salt}])} = \frac{\left| \frac{1}{\text{Concentration}} \right|_{n+1} - \left| \frac{1}{\text{Concentration}} \right|_n}{\left| \frac{[\text{Water}]}{[\text{Salt}]} \right|_{n+1} - \left| \frac{[\text{Water}]}{[\text{Salt}]} \right|_n}$$

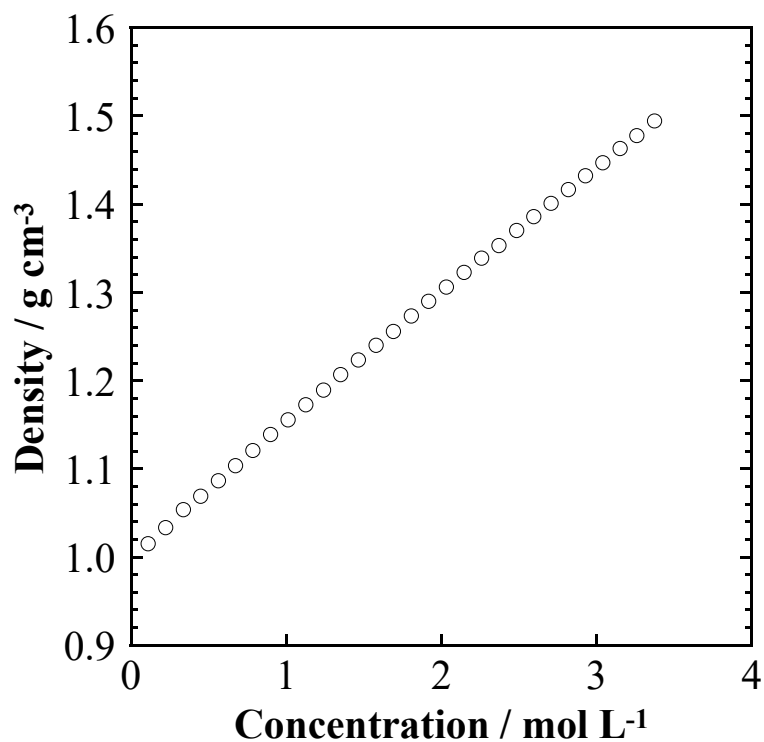


Fig. 3-4. Concentration dependence of density for ZnSO₄ aq. at 25 °C.

Fig. 3-5 represents volume increment by adding one mole of water to one mole of salt. The volume increment was 18ml mol⁻¹ in dilute solution and decreased under about 40 water molecules per one salt in Fig. 3-5(a). This decrease is known as electrostriction caused by ionic species and remarkable compared with other salt like lithium nitrate shown in Fig. 3-5(b).¹⁹ The phase diagram and the results of volume subtraction shows that zinc sulfate affects many water molecules than other salts due to its strong ionic interaction.

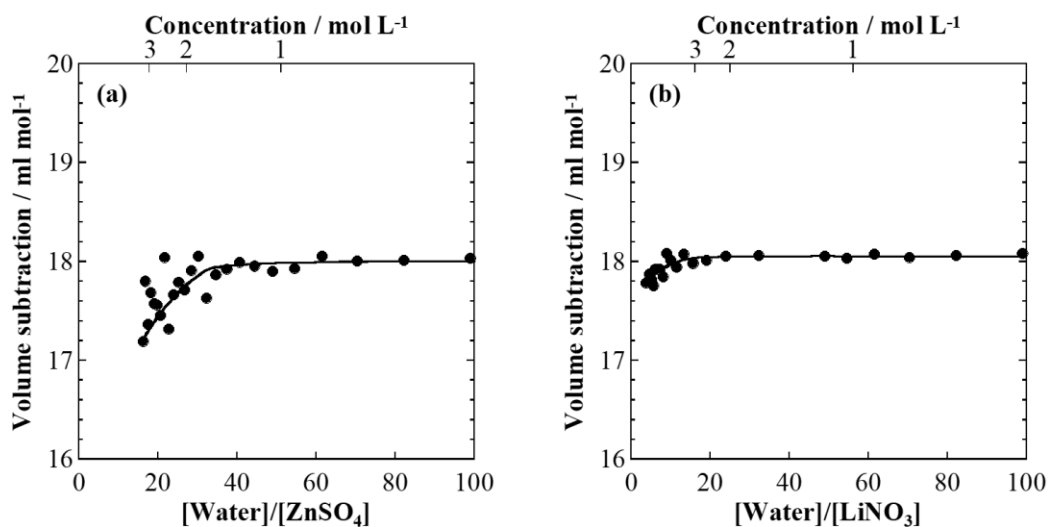


Fig. 3-5. Concentration and numerical ratio dependences of volume change for (a) $\text{H}_2\text{O}-\text{ZnSO}_4$ system and (b) $\text{H}_2\text{O}-\text{LiNO}_3$ system.

3.2 Phase Diagram and Electrostriction of Bulk Aqueous Solution

Thermal analyses were carried out for metal oxide nanoparticles/water system to investigate the influence from solid surface on water molecules. The DSC curves during heating process for various specimens are shown in Fig. 3-6. For each metal oxide sample and liquid volume fraction, the endothermic peak for fusion of ice was observed. These peaks shifted toward the lower temperature with the decrease of the liquid content. This behavior was similar to our previous studies and we reported that the thermochemical property of liquid phase depends on the hydrophilicity of the coexisting solid surface.²⁰

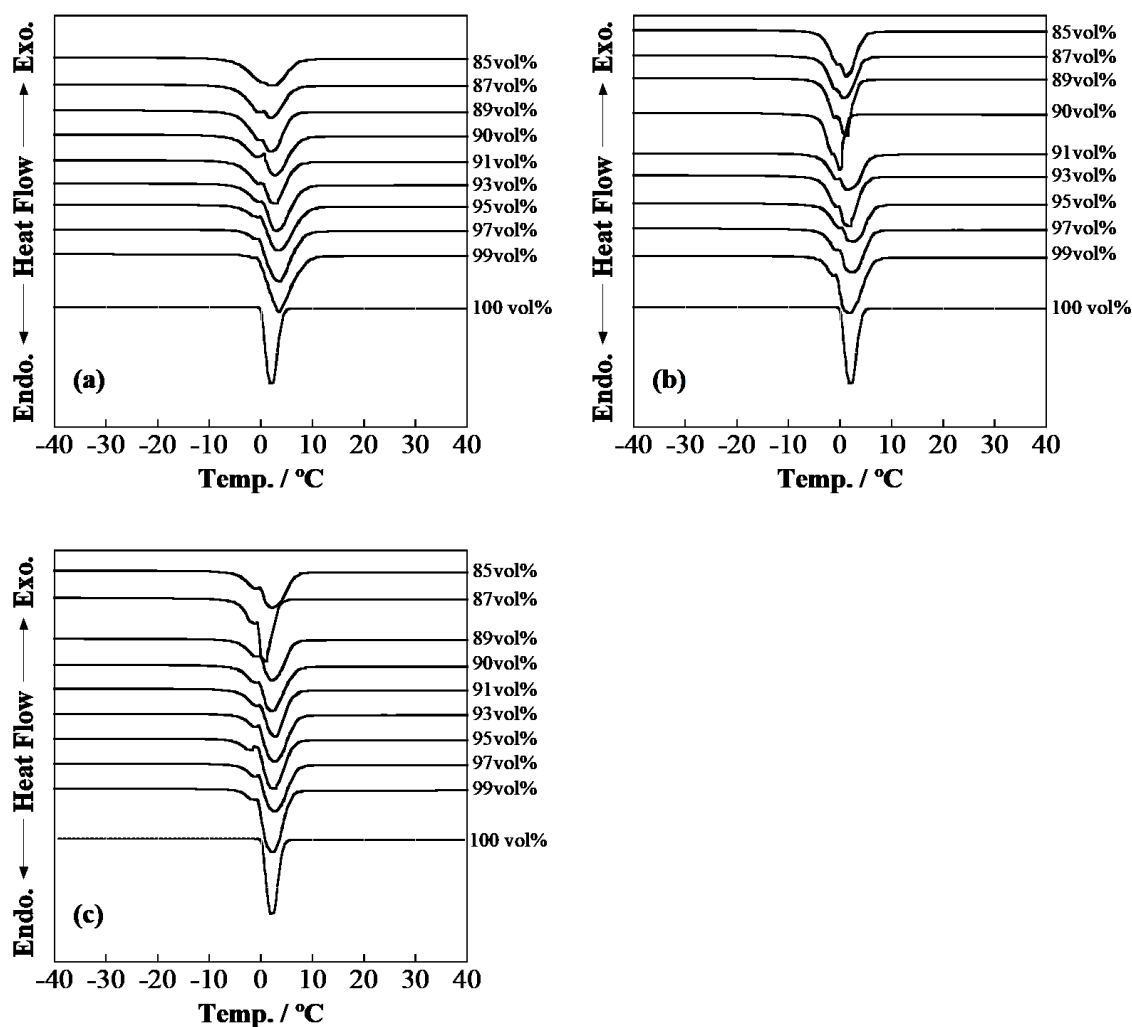


Fig. 3-6. Variations of DSC curves with liquid content for the different metal oxide nanoparticles/water system; (a) SiO₂, (b) γ -Al₂O₃, and (c) TiO₂ nanoparticles. Each curves were normalized per unit weight of liquid phase.

In order to discuss dynamics of solvent molecules in restricted area between dispersed nanoparticles, we employed the parameter “apparent average thickness” as noted in the preceding chapter. Fig. 3-7 shows relationships between the apparent average thickness and the heat of fusion of ice coexisting with metal oxide

nanoparticles; SiO_2 , Al_2O_3 , and TiO_2 . The heat of fusion showed deviation from the line of the bulk system and decreased as apparent average thickness gets smaller than about 10 or 20 nm. It suggests that the effect of coexisting solid phase reaches dozens of water molecules in the vertical direction with respect to the solid surface. Zobel reported that three to five layers of restructured water molecules exists in water–nanoparticle interfaces using spectroscopic methods like X-ray scattering.²¹ The length of liquid layer in which the effect from solid surface was observed in heat of fusion was much longer compared with the value Zobel reported. It is assumed that the effect from solid phase based on hydrogen bond networking might range over dozens of solvent molecules from solid surface, and it is hard to express only by electrical double layer or static liquid structure observed by X-ray scattering and so on.

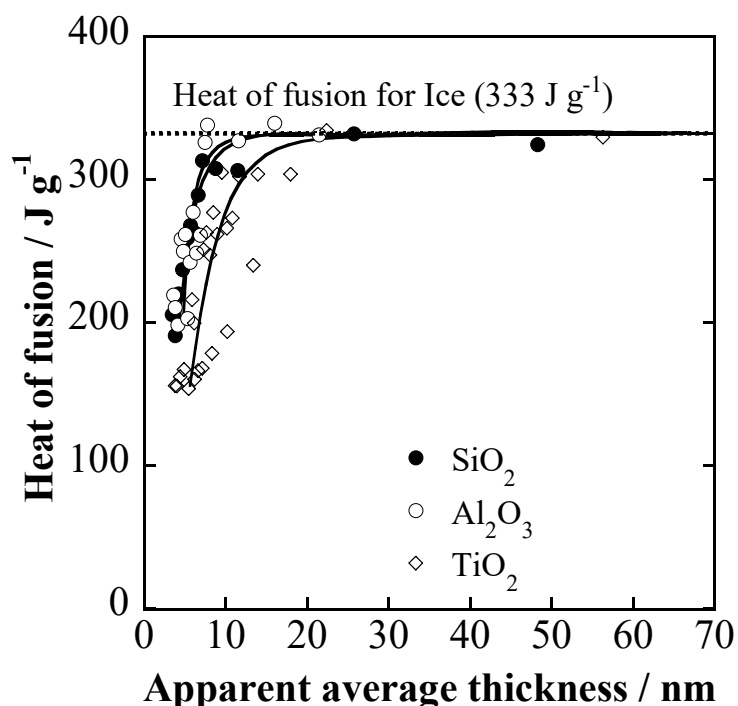


Fig. 3-7. Apparent average thickness dependences of heat of fusion of H_2O coexisting with metal oxide nanoparticles.

3.3 Raman spectra for Silica Nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ system

Fig. 3-8 shows Raman spectra for ZnSO_4 aqueous solution. Sulfate anion have four equivalent oxygen atoms and its symmetrical stretching vibration was observed around 982 cm^{-1} . As ZnSO_4 concentration increase, the peak intensity increased and wavenumber of the peaks changed to high frequency side. As Rudolph et al. reported, the symmetrical stretching vibration in ZnSO_4 aq. exhibit a small shoulder on the high

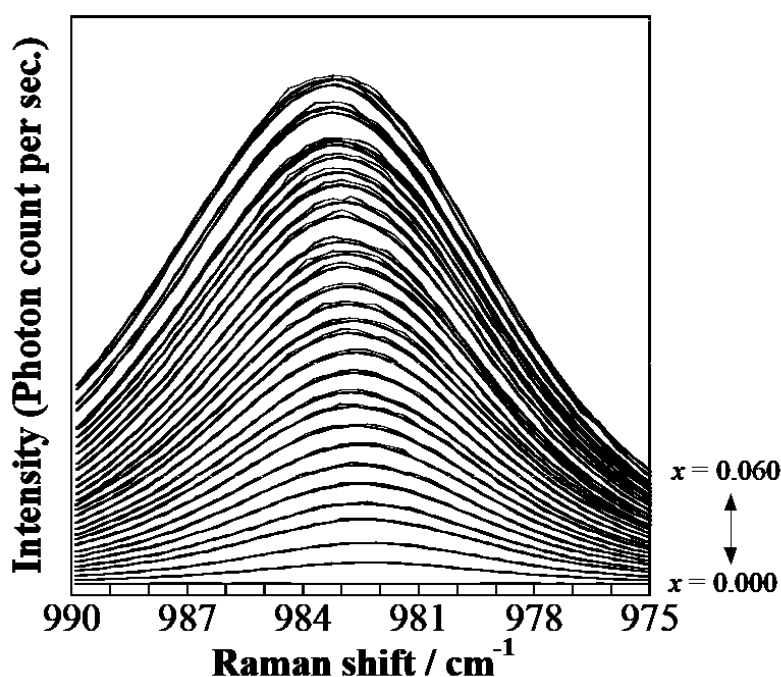


Fig. 3-8. Raman spectra of ZnSO_4 aq. at 25°C . Each curves were displaced at intervals of 0.002 mole fraction of ZnSO_4 .

frequency side with concentration increase and the high frequency shoulder is attributed to the formation of a 1:1 inner-sphere contact ion pair by Zn^{2+} and SO_4^{2-} .²²⁻²⁴ We confirmed the same behavior not only in bulk solution but also in solid/liquid coexisting system. Fig. 3-9 is concentration and numerical ratio dependences of wavenumber of peak observed for SiO_2 nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ system. The wavenumber of peak

for bulk ZnSO_4 aq. remarkably changed when number of water molecules per one salt was under ca. 40, which was similar to the results of density measurement obtained as Fig. 3-5(a). In solid/liquid coexisting system, the wavenumber of the peak changed to high frequency side in lower concentration compared with bulk ZnSO_4 aq., consequently ion pair forming tendencies seems to be enhanced. Since apparent average thickness of coexisting samples shown in Fig. 3-9 were smaller than 8 nm, these liquid phase seems to be affected by solid surface. Zn^{2+} was not supposed to make hydration sphere sufficiently due to sharing water molecules with solid surface, and ion paring tendencies seems to be enhanced in the vicinity of solid surface. This result agrees with the previous study for the $\alpha\text{-Al}_2\text{O}_3$ powder/ $\text{ZnCl}_2 \cdot n\text{H}_2\text{O}$ system, which suggested that the structural change of the ionic species affect ionic conduction behavior.²⁰

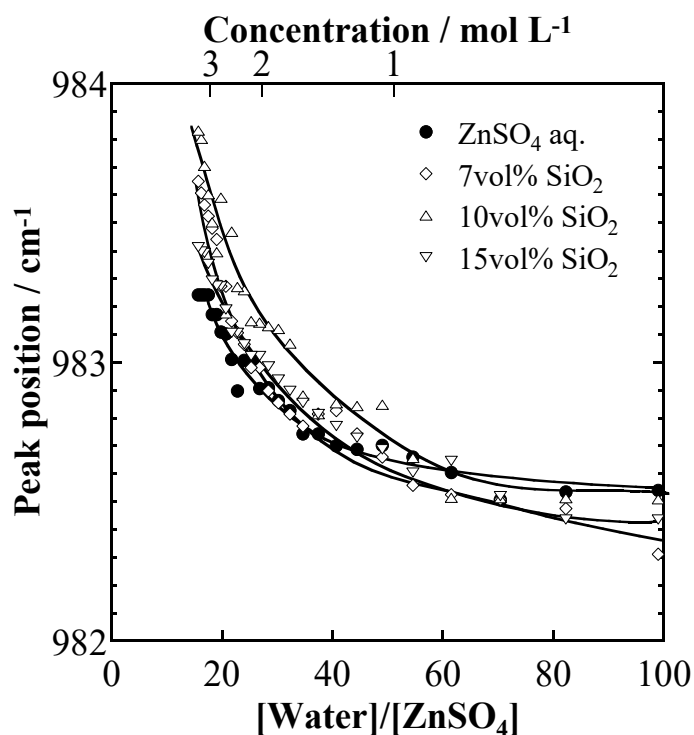


Fig. 3-9. Concentration and numerical ratio dependences of Raman band position for SiO_2 nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ system.

3.4 ^1H relaxation time for Metal Oxide Nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ system

Fig. 3-10 shows concentration and numerical ratio dependences of T_1 and T_2 for SiO_2 nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ system. T_1 and T_2 of bulk ZnSO_4 aq. decreased as the salt concentration increase. It shows mobility of water molecules in aqueous solution was suppressed by ionic interaction. T_1 of ZnSO_4 aq. coexisting with SiO_2 nanoparticles was slightly lower than the bulk value as shown in the figure, while volume fraction dependences were subtle. However, T_2 of ZnSO_4 aq. coexisting with SiO_2 nanoparticles exhibited drastic decrease depending on solid/liquid volume fraction. The water molecules in the aqueous solution reduce its mobility by not only ionic interaction but also coexisting solid surface.

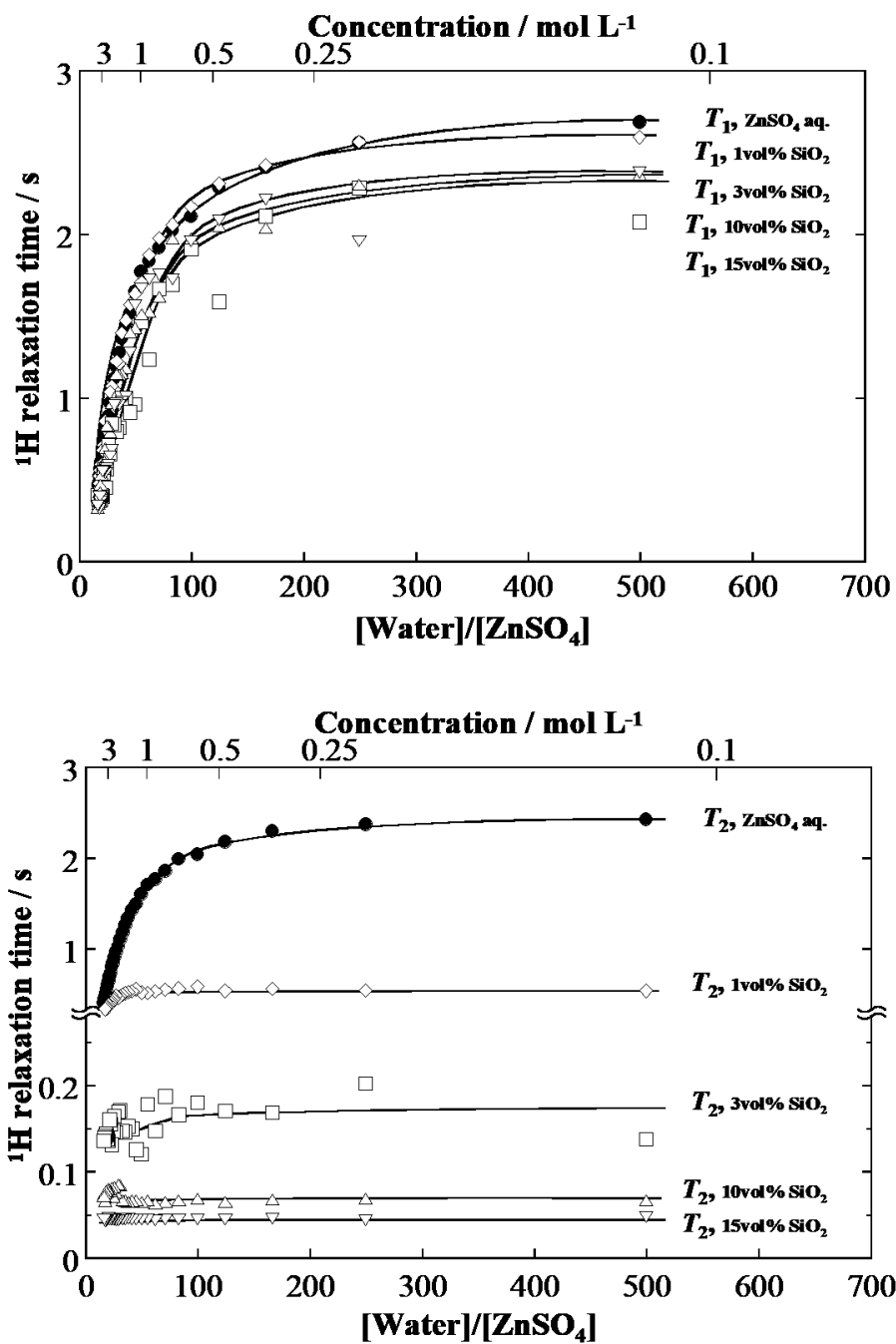


Fig. 3-10. Concentration and numerical ratio dependences of ^1H relaxation time (T_1 , T_2) for SiO_2 nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ system; (a) T_1 and (b) T_2 . The hydration number n represents the numerical ratio; $[\text{Water}]/[\text{ZnSO}_4]$ in the figure.

The concentration and numerical ratio dependences of T_1 and T_2 for the system with SiO_2 and $\gamma\text{-Al}_2\text{O}_3$ nanoparticles were obtained as shown in Fig. 3-11. Although the T_2 of ZnSO_4 coexisting with 15 vol% of SiO_2 decreased from the bulk solution, the T_1 of bulk solution and ZnSO_4 aq. coexisting with 15 vol% of SiO_2 nanoparticles approached to the same value as salt concentration increase. On the other hand, coexisting system with $\gamma\text{-Al}_2\text{O}_3$ nanoparticles showed significant decrease in both the T_1 and T_2 . $\gamma\text{-Al}_2\text{O}_3$ seems to exhibit strong effect on aqueous solution than SiO_2 and effect from solid surface is relatively large. The differences between the SiO_2 and the $\gamma\text{-Al}_2\text{O}_3$ nanoparticles might be related to surface potential of each metal oxide nanoparticles as shown in Fig. 3-2. It is well known that zinc aqueous solution indicates acidity due to the hydrolysis by Zn^{2+} . The pH in Fig. 3-1 decreased with the concentration increase. The solid surface of SiO_2 nanoparticles exhibits negative charge and approaches to zero with ZnSO_4 concentration increase, while that of the $\gamma\text{-Al}_2\text{O}_3$ nanoparticles increases a positive charge. Therefore, approaching to zero potential with salt concentration increase in SiO_2 nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ system might be related to the behavior of T_1 in Fig. 3-10; subtle volume fraction dependences and approaches to the bulk value with ZnSO_4 concentration increase. It was assumed that the effects from solid phase in solid/liquid coexisting system were affected by liquid property in itself.

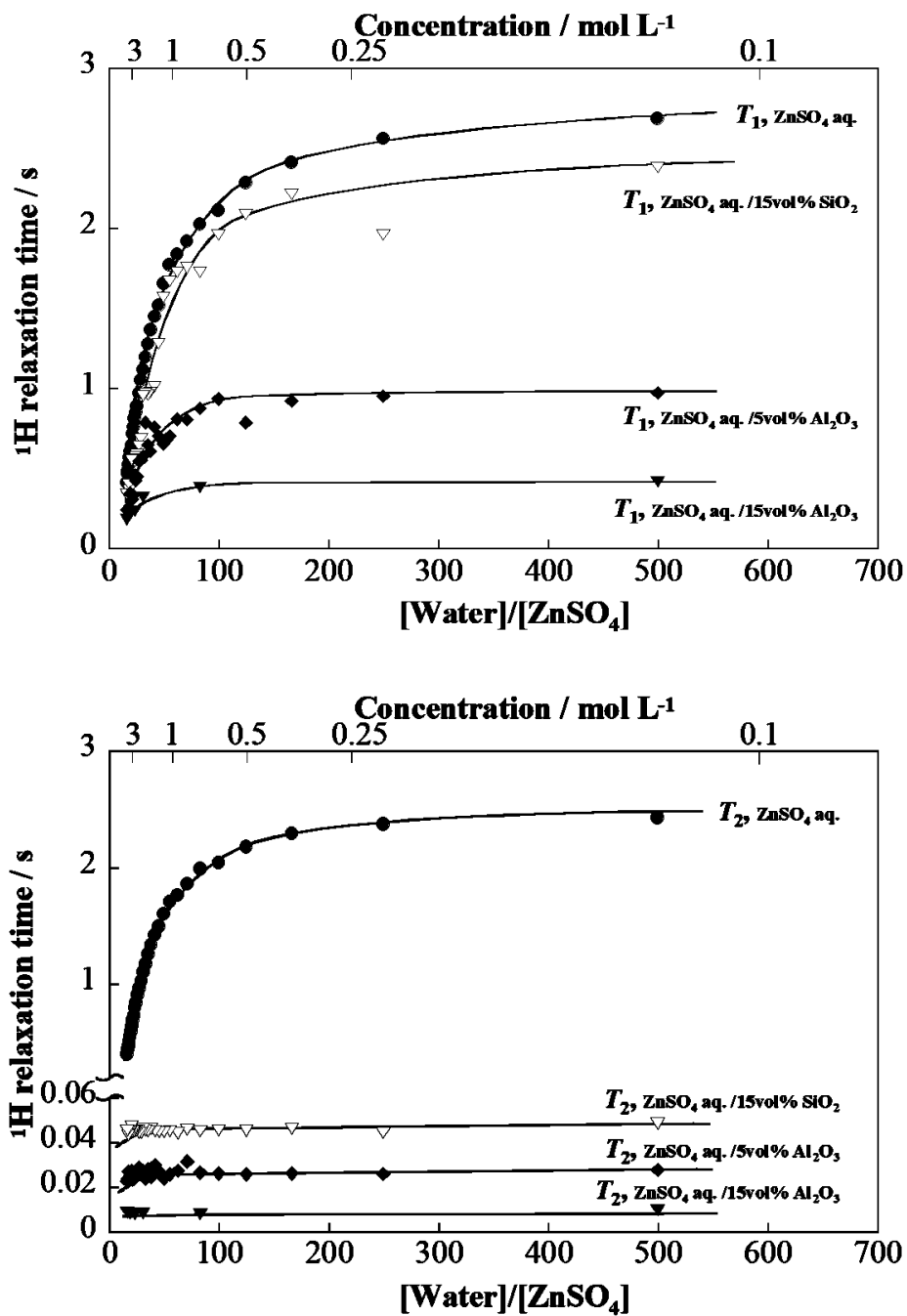


Fig. 3-11. Concentration and numerical ratio dependences of ^1H relaxation time (T_1 , T_2) for SiO_2 and $\gamma\text{-Al}_2\text{O}_3$ nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ system; (a) T_1 and (b) T_2 . The hydration number n represents the numerical ratio; $[\text{Water}]/[\text{ZnSO}_4]$ in the figure.

Conclusion

The dynamic and spectroscopic properties of metal oxide nanoparticles/ ZnSO_4 aqueous solution system were discussed within wide salt concentration range from dilute to concentrated solution. Numerical ratio of water molecules per one salt and apparent average thickness were employed to describe the liquid behavior in the vicinity of solid surface. The H_2O - ZnSO_4 system showed phase diagram which have eutectic composition at mole fraction of ZnSO_4 was 0.050 from DSC results. The volume increment by water molecules per one salt derived from density measurement represented strong interaction by electrostriction of ZnSO_4 . Raman spectroscopy in solid/liquid coexisting system suggested that ion pairing tendencies were enhanced in vicinal area of solid surface. From the relationship between ^1H relaxation in ZnSO_4 aq. and surface potential of metal oxide nanoparticles, water molecules in aqueous solution was affected by not only ionic interaction but also coexisting solid surface, and alumina exhibited strong effect than silica. Different behavior of ^1H relaxation in coexisting systems between silica and alumina might be due to the surface potential of each solid particles depending on pH of liquid phase.

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CHAPTER 2

Section2

Influence of coexisting metal oxide powder on spectroscopic properties of Zinc-based hydrate melt

1. Introduction

Many researchers have investigated the physicochemical properties of ionic species and water molecules in hydrate melts vigorously.^{1,2} Hydrate melts which are defined by Braunstein possess condensed ionic interaction and behave like molten salt in some respects.³ It is important to understand not only bulk liquid properties but also that in solid/liquid interfaces because electrolyte liquid materials are generally utilized in the system in contact with solid phase. In section 2 of chapter 2, we focused on zinc-based hydrate melt nanoconfined by metal oxide solid surfaces using fumed silica and fumed alumina. Alumina is a typical solid acid as well as silica. They have a great number of OH hydroxyl groups on their surfaces, and alumina show more complicated interaction compared with silica surfaces. ZnSO_4 is the zinc compound that is most frequently used and there are a variety of applications.⁴ Our previous report revealed from density measurement for concentrated ZnSO_4 aqueous solution that about 40 water molecules per one ZnSO_4 was influenced due to the electrostriction caused by dissolving species and it was remarkable compared with other monovalent electrolyte.⁵ Strong ionic interaction of Zn^{2+} shows pronounced hydration sphere, thus effects on dissolving species from solid surfaces might be much observable. It is interesting that how water molecules in hydrate melts which are condensed systems with ionic interaction behave in nanoconfined spaces. Here we dealt with ZnSO_4 aqueous solutions as hydrate melt analogies, and represented $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$; n means number of water molecules per one ZnSO_4 . We observed the spectroscopic properties of metal oxide nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ coexisting system within the wide range of n from dilute solution to hydrate melt to discuss the water molecular behavior in the vicinity of solid phase.

2. Experimental

2.1 Materials

$\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ was prepared by adding the deionized double distilled water to zinc sulfonate heptahydrate (Nacalai Tesque, Inc., Guaranteed Reagent) at a predetermined ratio. The solid/liquid coexisting samples were obtained in a similar way to our previous study.⁵ Fumed silica (Aerosil 200) and fumed alumina (Aeroxide Alu 130, Ni) both supplied from Nippon Aerosil were used as solid phase, and mixed with $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ using an agate mortar. The volume ratio of the liquid phase was set to 85 - 100 vol%. The crystalline phases of fumed silica and fumed alumina were assigned using parallel beam X-ray diffractometer RINT-TTR (Rigaku Co., Ltd.), as amorphous silica and $\gamma\text{-Al}_2\text{O}_3$, respectively.

2.2 ^1H NMR spectroscopy

^1H NMR spectra were obtained by a Varian INOVA 400 NMR spectrometer with 9.39 T magnet and 5mmSW probe (Varian, Inc.). To avoid mixing sample with deuterated solvent, the coaxial NMR tube (Wilmad-LabGlass CO. Inc., 516-cc-5) was used and deuterium oxide (Euriso-Top) was filled in outer tube. The ^1H NMR chemical shifts were determined with second order external standard of deionized double distilled water, as tetramethylsilane was first order standard for 0 ppm. All experiments were performed at 25 °C.

2.3 ^1H Relaxation measurement

The spin-spin relaxation time (T_2) of ^1H NMR was obtained using Acorn area

(XiGo Nanotools) with 0.3 T magnet. The solid/liquid coexisting samples were filled into 5 mm diameter glass tube and we employed the CPMG method. All experiments were performed at 25 °C.

2.4 Polarized Raman spectroscopy

Raman spectra were recorded with T-64000 Raman spectrometer using a 532 nm SHG of Nd:YVO₄ laser with a power of 20 mW as excitation source. The incident light was passed through a prism and focused onto the samples loaded into glass tube in the 180° scattering geometry. The scattered light was detected by Horiba CCD 2048 × 512–003 which has a resolution of 0.4 cm⁻¹. The wavenumber of monochromator was calibrated by *F*_{2g} mode of silicon at 520 cm⁻¹. The polarizer was rotated by exactly 90° to get the polarization geometries Y(ZZ)Y (parallel position, *I*_{//}) and Y(ZX)Y (perpendicular position, *I*_⊥), where X, Y, and Z represents the directions of polarization and propagation in accordance with Porto notation.⁶ A polarization scrambler was used between the slit and the polarizer. The Schematic was shown as Fig. 4-1 The depolarization ratio, ρ was used as an indicator of symmetry of the vibration mode and was obtained as:

$$\rho = I_{\perp} / I_{//}$$

where *I*_⊥ and *I*_{//} are the intensities of the spectra observed with the polarizer oriented parallel and perpendicular to the incident laser beam, respectively.⁷ Carbon tetrachloride (CCl₄, Nacalai Tesque, Inc., Guaranteed Reagent) was used for checking the optical system and for the comparison in polarized Raman spectroscopy measurement. All experiments were performed at 25°C. The data processing was carried out by WaveMetrics Igor Pro Ver. 3 software.

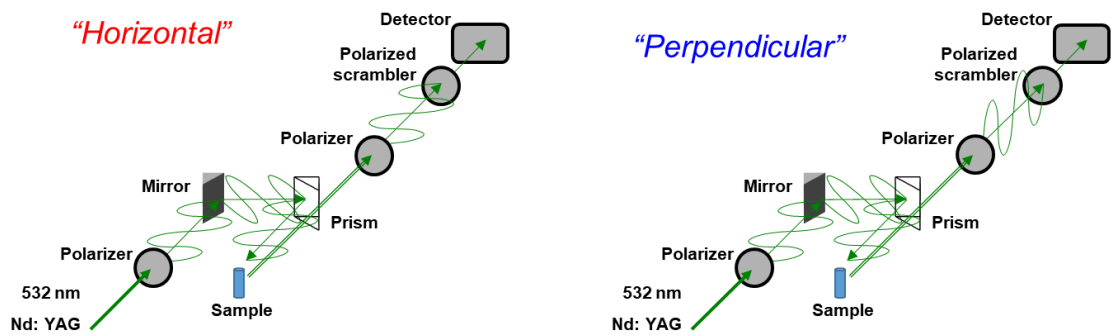


Fig. 4-1. Schematics of optical configuration as horizontal and perpendicular for polarized Raman spectroscopy to set parallel position and perpendicular position, respectively.

3. Results and discussion

3.1 pH and ^1H NMR for Metal Oxide Nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ coexisting system

The metal oxide nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ coexisting system showed gelation and showed no thixotropy, although the fumed silica is known as an excellent thixotropic agent for water. It seemed that the strong ion-solvent interaction of 2:2 electrolyte solution interrupts three dimensional network structure of fumed silica. The metal oxide nanoparticles in $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ would interact with water molecules due to their hydroxyl group.⁸ The relationship between pH and the numerical ratio, n , of bulk $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ and Metal Oxide Nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ coexisting system was show as Fig. 4-2. The pH of $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ decreased with decrease of n . It is well-known that zinc ion in aqueous system exhibits acidity due to the hydrolysis.⁹ $\text{SiO}_2/\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ coexisting system showed decrease of pH. In $\gamma\text{-Al}_2\text{O}_3$ coexisting system, lower pH was observed in dilute solution but the curve crossed the curve of bulk $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$. $\text{ZnSO}_4 \cdot 15.7\text{H}_2\text{O}$ is saturated concentration at room temperature and this composition is on the salt side rather than the eutectic composition seen in the phase diagram of section 2 of chapter 2. Fig. 4-3 showed ^1H NMR spectra for bulk $\text{ZnSO}_4 \cdot 15.7\text{H}_2\text{O}$ and Metal Oxide Nanoparticles/ $\text{ZnSO}_4 \cdot 15.7\text{H}_2\text{O}$ coexisting system. All sample showed singlet signal; $\gamma\text{-Al}_2\text{O}_3/\text{ZnSO}_4 \cdot 15.7\text{H}_2\text{O}$ shifted to the higher magnetic field compared with bulk $\text{ZnSO}_4 \cdot 15.7\text{H}_2\text{O}$ and $\text{SiO}_2/\text{ZnSO}_4 \cdot 15.7\text{H}_2\text{O}$ hardly shifted, indicating that electron density around ^1H in $\gamma\text{-Al}_2\text{O}_3$ coexisting system increased. The influences of SiO_2 and $\gamma\text{-Al}_2\text{O}_3$ on water molecules were different each other.

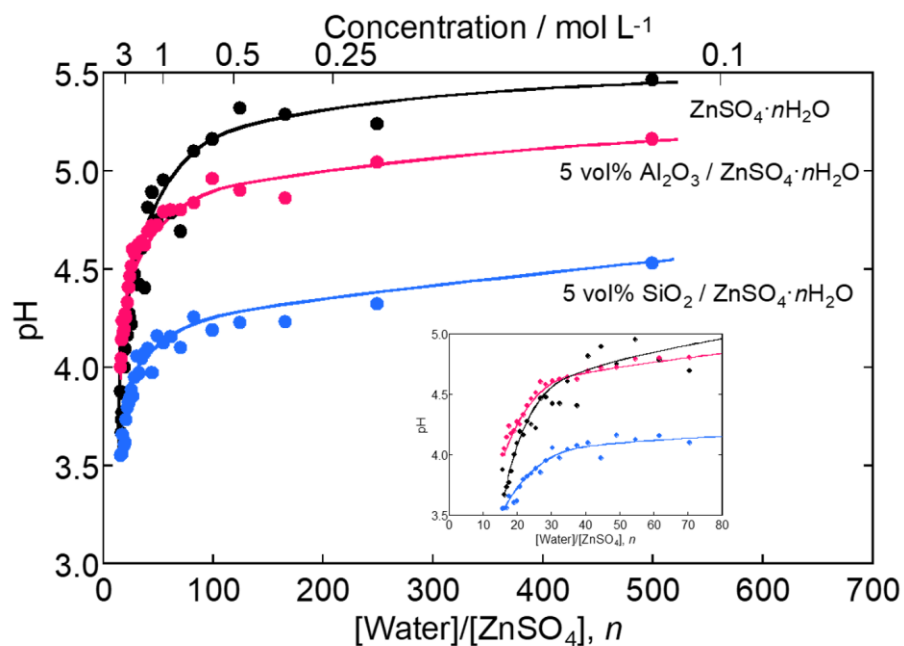


Fig. 4-2. The numerical ratio, n , dependences of pH in metal oxide nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ coexisting system. The inset shows enlarged view.

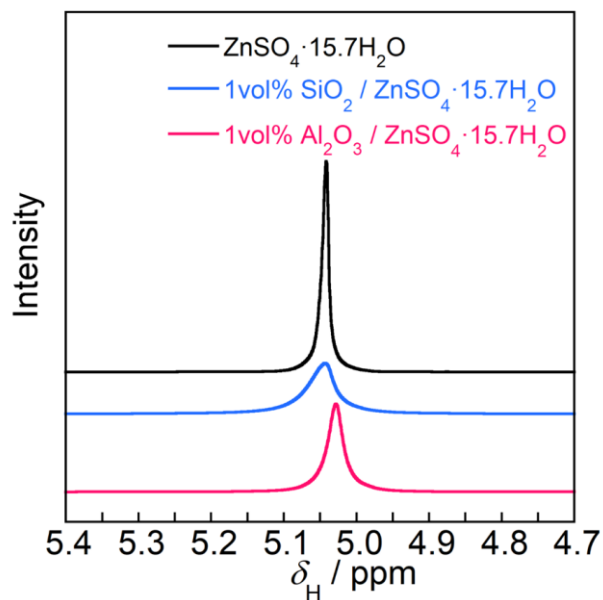


Fig. 4-3. ^1H NMR spectra of 1 vol% metal oxide nanoparticles/ $\text{ZnSO}_4 \cdot 15.7\text{H}_2\text{O}$ coexisting system and bulk $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$.

3.2 ^1H NMR relaxation for Metal Oxide Nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ coexisting system

Fig. 4-4 shows the relationship between T_2 of metal oxide nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ coexisting system and n . T_2 of bulk $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ and $\text{SiO}_2/\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ decreased depending on decrease of n and increase of solid volume fraction, indicating that the water molecules near the ions and solid surfaces reduced its mobility by not only ionic interaction but also coexisting solid surfaces as we previously mentioned.⁵ On the other hand, T_2 of $\gamma\text{-Al}_2\text{O}_3/\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ decreased with solid volume fraction and hardly depended on n . This result suggested that $\gamma\text{-Al}_2\text{O}_3$ had a so strong effect on water mobility that the influence of Zn^{2+} could not be confirmed. Using the simple spatial model that solid particles are monodispersed as hexagonal close-packed, we replaced the solid/liquid volume fraction with the liquid layer thickness, “apparent average thickness.”⁵ Fig. 4-5 represents apparent average thickness dependences of T_2 of metal oxide nanoparticles/ $\text{ZnSO}_4 \cdot 15.7\text{H}_2\text{O}$ coexisting system. In the figure, $\gamma\text{-Al}_2\text{O}_3$ exhibited more long-range interaction compared with SiO_2 , suggesting liquid layer which shows different properties from the bulk solution is on the solid surfaces and its thickness is the order of several tens nm.

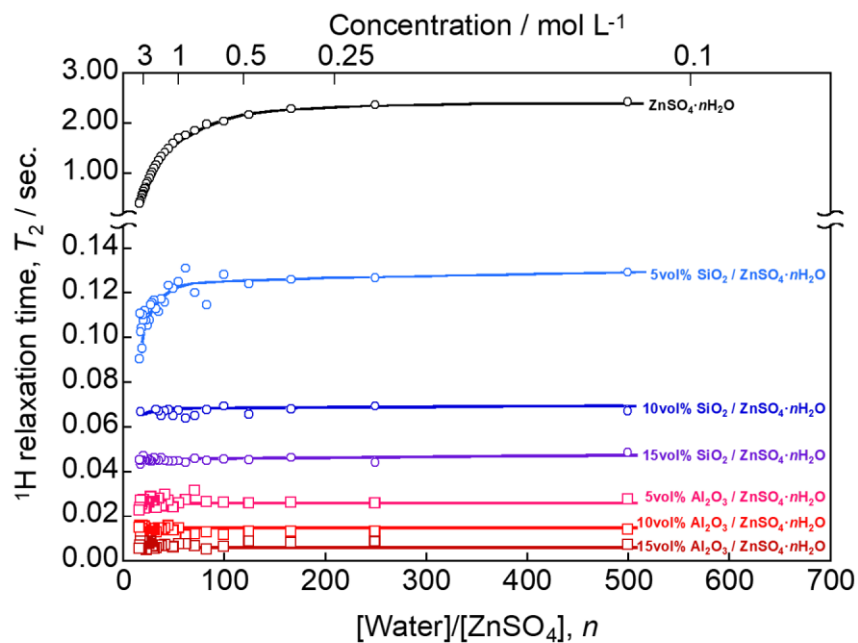


Fig. 4-4. The numerical ratio, n , dependences of ^1H relaxation time (T_2) in solid/liquid coexisting system.

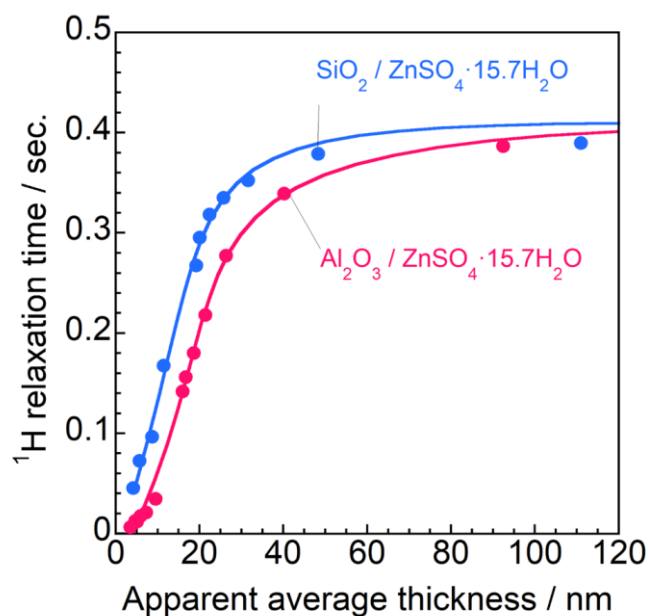


Fig. 4-5. Apparent average thickness dependences of ^1H relaxation time (T_2).

3.3 Polarized Raman spectra for Metal Oxide Nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ coexisting system

In order to investigate the effects of solid surfaces on the structure of ionic species in $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$, polarized Raman spectroscopy was carried out. The depolarization ratio obtained from polarized Raman spectra is a powerful tool to provide information on molecular symmetry in liquid states. The tetrahedral sulfate ion (SO_4^{2-}) and octahedral hydrated Zinc ion ($[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$) are known to belong to the point group T_d and O_h , respectively. Both ionic species have Raman active symmetry stretching vibrational mode, ν_1 .

Polarized Raman spectra of bulk $\text{ZnSO}_4 \cdot 15.7\text{H}_2\text{O}$ and the solid/liquid coexisting system are shown in Fig. 4-6. In Fig. 4-6(a), the peak appeared at 984 cm^{-1} , which are assigned to the symmetry stretching of SO_4^{2-} . Although the depolarization ratio calculated for bulk $\text{ZnSO}_4 \cdot 15.7\text{H}_2\text{O}$ was ca. 0.01, the coexisting systems shown as Fig. 4-6(b) and Fig. 4-6(c) showed higher depolarization ratio $\rho = 0.05$ and $\rho = 0.66$, respectively. The variation of the depolarization ratios of the $\nu_1(\text{SO}_4^{2-})$ and $\nu_1([\text{Zn}(\text{H}_2\text{O})_6]^{2+})$ as a function of the apparent average thickness were shown in Fig. 4-7. Besides the measurement of the depolarization ratios for the metal oxide nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ coexisting system, we confirmed the polarized Raman spectra for the metal oxide nanoparticles/ CCl_4 coexisting system and obtained the dependences of depolarization ratio for $\nu_1(\text{CCl}_4)$ on the apparent average thickness. The depolarization ratio in solid/liquid coexisting system is increased by diffuse reflection at the solid surfaces as we reported previously, thus such increases are not caused by the interaction with solid phase but just the optical alignment.^{10,11} Thus, the differences between CCl_4 and the samples in depolarization ratio are considered to be a significant

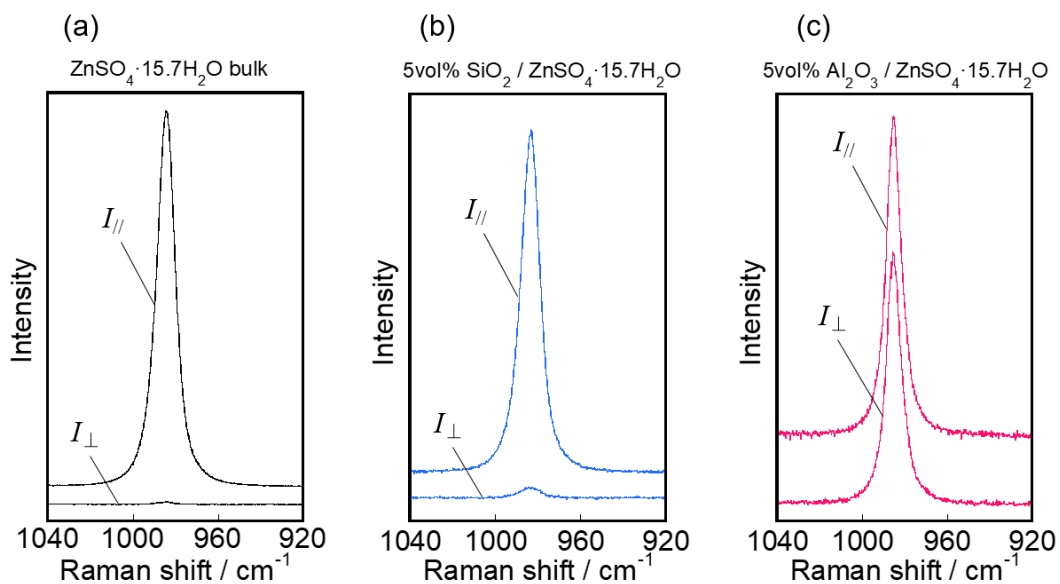


Fig. 4-6. Polarized Raman spectra of bulk $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ and solid/liquid coexisting system.

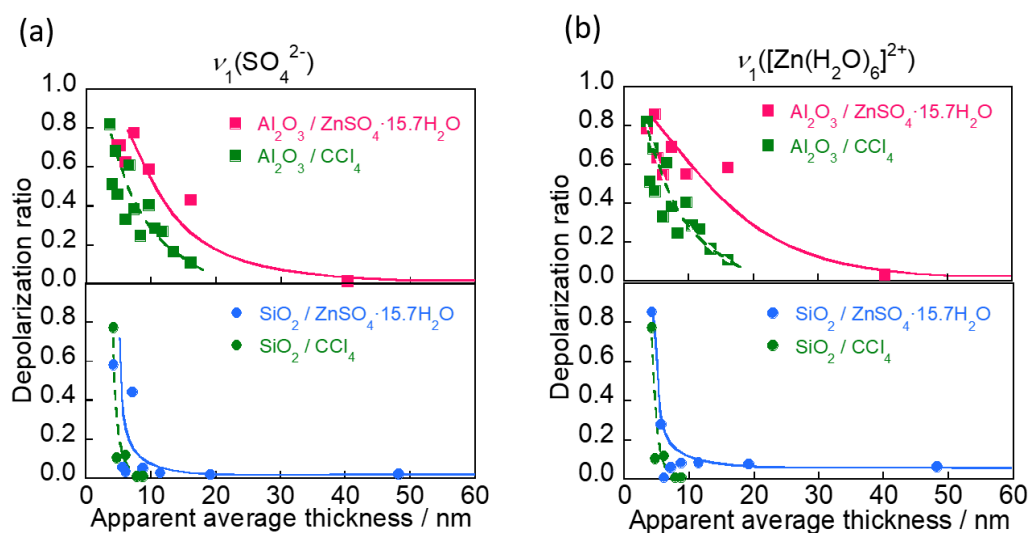


Fig. 4-7. Apparent average thickness dependences of depolarization ratio for (a) $\nu_1(\text{SO}_4^{2-})$ and (b) $\nu_1([\text{Zn}(\text{H}_2\text{O})_6]^{2+})$. The open symbols represent $\nu_1(\text{CCl}_4)$ as baseline.

difference. The depolarization ratio of $\nu_1(\text{SO}_4^{2-})$ and $\nu_1([\text{Zn}(\text{H}_2\text{O})_6]^{2+})$ in $\text{SiO}_2/\text{ZnSO}_4 \cdot 15.7\text{H}_2\text{O}$ increased compared with $\nu_1(\text{CCl}_4)$, while that of $\gamma\text{-Al}_2\text{O}_3$ coexisting system increased in longer apparent average thickness. This result indicated that the symmetry stretching of SO_4^{2-} and $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ are distorted by the presence of the metal oxides, and $\gamma\text{-Al}_2\text{O}_3$ affect more strong than SiO_2 .

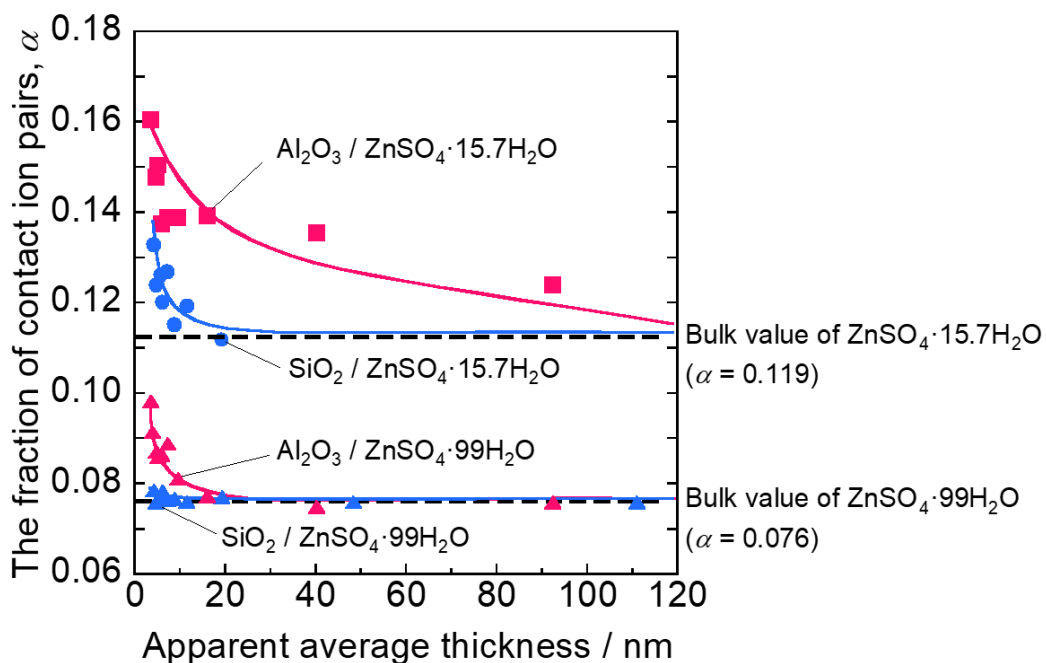


Fig. 4-8. Apparent average thickness dependences of the fraction of contact ion pairs.

It is reported that Zn^{2+} and SO_4^{2-} form a 1:1 inner-sphere contact ion pair and $\nu_1(\text{SO}_4^{2-})$ exhibit a small shoulder attributed to $[\text{Zn}(\text{H}_2\text{O})_5 \cdot \text{SO}_4]$ on the high frequency side.¹² We performed peak fitting for $\nu_1(\text{SO}_4^{2-})$ of $\text{ZnSO}_4 \cdot 15.7\text{H}_2\text{O}$ coexisting with SiO_2 and $\gamma\text{-Al}_2\text{O}_3$. Fig. 4-8 shows apparent average thickness dependences of the fraction of contact ion pairs, α , for the metal oxide nanoparticles/ $\text{ZnSO}_4 \cdot 15.7\text{H}_2\text{O}$ system. The

metal oxide nanoparticles/ $\text{ZnSO}_4 \cdot 99\text{H}_2\text{O}$ system was also plotted as a reference of concentration effect. The value of α was obtained by:

$$\alpha = (\text{concentration of } [\text{Zn}(\text{H}_2\text{O})_5 \cdot \text{SO}_4] / \text{total concentration of } \text{ZnSO}_4) \\ = I_{989} / (I_{989} + I_{981})$$

where I_{981} and I_{989} represent peak intensities of ν_1 attributed to free SO_4^{2-} and SO_4^{2-} bound to Zn^{2+} , respectively.¹² From the figure, α increased with decrease of apparent average thickness and influence of $\gamma\text{-Al}_2\text{O}_3$ are stronger than SiO_2 . Zn^{2+} in the metal oxide nanoparticles/ $\text{ZnSO}_4 \cdot 15.7\text{H}_2\text{O}$ was not supposed to make hydration sphere sufficiently due to sharing water molecules with metal oxide solid surfaces and ion paring tendencies seems to be enhanced in the vicinity of solid surfaces, suggesting that the distortion of ionic species confirmed in Fig. 4-7 resulted from ion pair formation. On the other hand, $\text{ZnSO}_4 \cdot 99\text{H}_2\text{O}$ based coexisting system, which is ca. 0.5 mol/L^{-1} aqueous solution and have a large amount of water molecules not subject to electrostriction by ZnSO_4 , showed smaller increasing ratio of contact ion pairs.

Consequently, we observed OH vibration of water molecules around 3400 cm^{-1} which significantly relates to hydrogen bonding as shown in Fig. 4-9. There has been a lot of argument due to the lack of a consensus view what these underlying absorptions represent.¹³⁻¹⁹ We carried out peak deconvolution using three-Gaussian fits based on a model reported by Walrafen et al. because OH vibration in heterogeneous solid/liquid coexisting systems might be too much complicated.²⁰⁻²² We separated peaks into 3200 cm^{-1} , 3420 cm^{-1} and 3600 cm^{-1} corresponding to hydrogen-bonded OH stretches which are in-phase between neighbor molecules, hydrogen-boded OH stretches which are not in-phase between neighbor molecules, and OH stretches of molecules whose hydrogen bonds have been broken, respectively.^{23,24} Although Raman bands at 3600 cm^{-1} in

ZnSO₄·15.7H₂O based system was little, we confirmed the band exists at 3600 cm⁻¹ by observing Raman spectra within wide concentration range as shown in Fig. 4-10. The band decreased continuously with decreasing n , i.e. ZnSO₄ concentration. Raman spectra of the metal oxide nanoparticles/ZnSO₄·99H₂O system was also observed as comparison.

Fig. 4-11 represents the relationships between the component percentages from the three-Gaussian synthesis obtained from peak deconvolution and the apparent average thickness for metal oxide nanoparticles/ZnSO₄·15.7H₂O coexisting system and metal oxide nanoparticles/ZnSO₄·99H₂O coexisting system. Comparing bulk ZnSO₄·15.7H₂O and bulk ZnSO₄·99H₂O, not in-phase hydrogen-bonded OH stretches and non-hydrogen-bonded OH stretches varied with ionic concentration, although there was no significant difference in in-phase hydrogen-bonded OH stretches. On the other hand, in-phase hydrogen-bonded OH stretches decreased with decrease of apparent average thickness, and not in-phase hydrogen-bonded OH stretches and non-hydrogen-bonded OH stretches increased in all coexisting systems. This result suggested that ionic species and metal oxide solid surfaces might have a different effect on water molecules. Additionally, γ -Al₂O₃ showed stronger interaction than SiO₂. Variations of 3600 cm⁻¹ band with apparent average thickness in ZnSO₄·15.7H₂O were small compared with ZnSO₄·99H₂O. The influence of coexisting solid surfaces on water molecules seemed to be relatively larger in the dilute solution than in the hydrate melts.

Liquid content
/ vol%

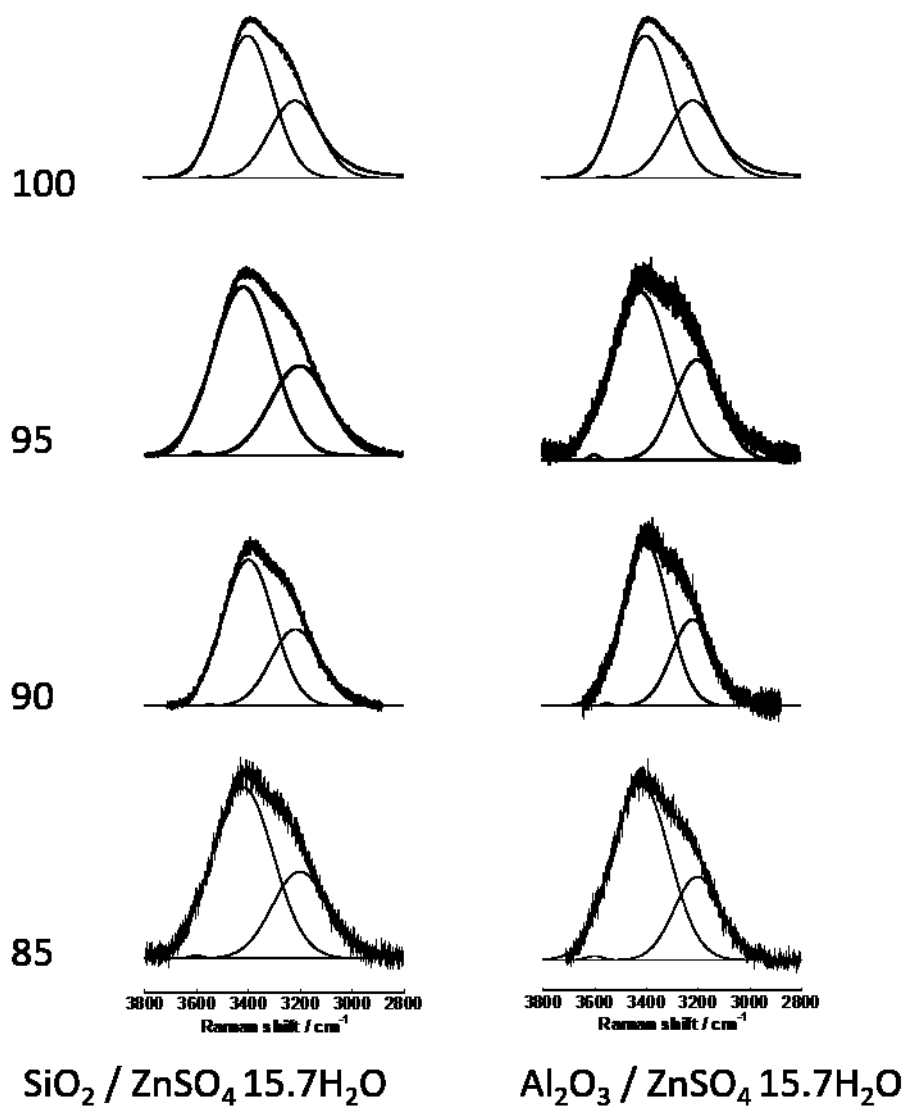


Fig. 4-9(a). The peak deconvolution of OH vibrational Raman spectra for metal oxide nanoparticles/ $\text{ZnSO}_4 \cdot 15.7\text{H}_2\text{O}$ coexisting system using three-Gaussian fits.

Liquid content
/ vol%

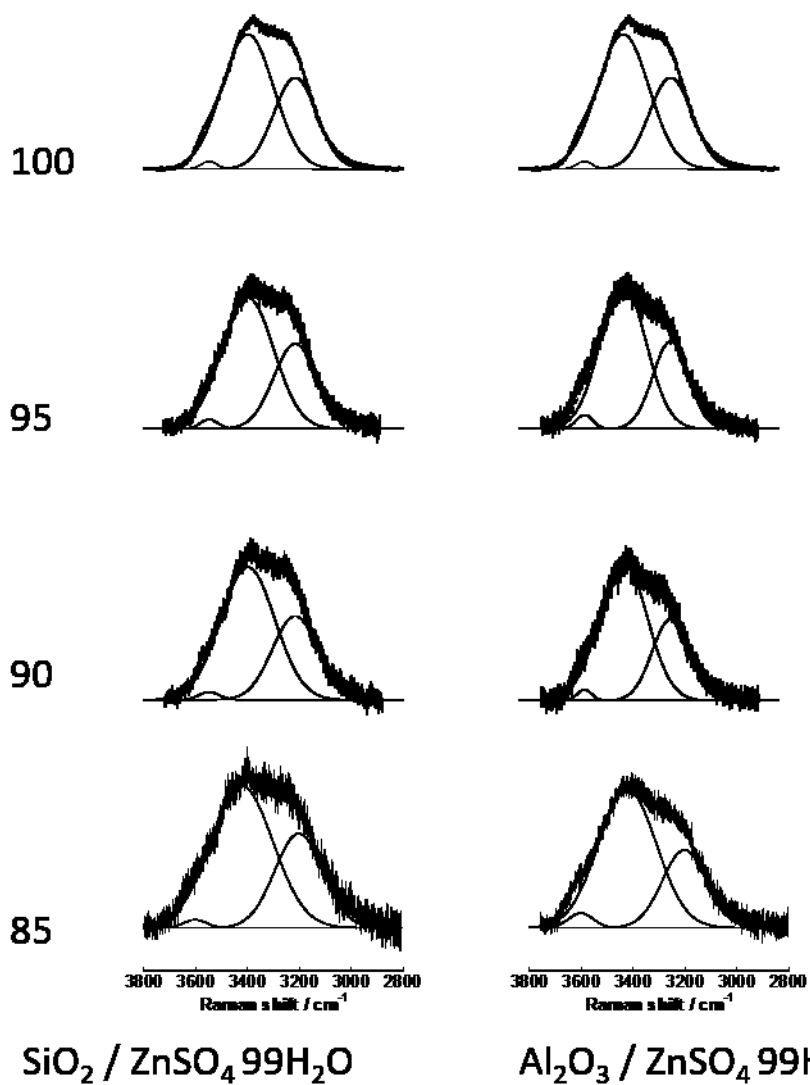


Fig. 4-9(b). The peak deconvolution of OH vibrational Raman spectra for metal oxide nanoparticles/ $\text{ZnSO}_4 \cdot 99\text{H}_2\text{O}$ coexisting system using three-Gaussian fits.

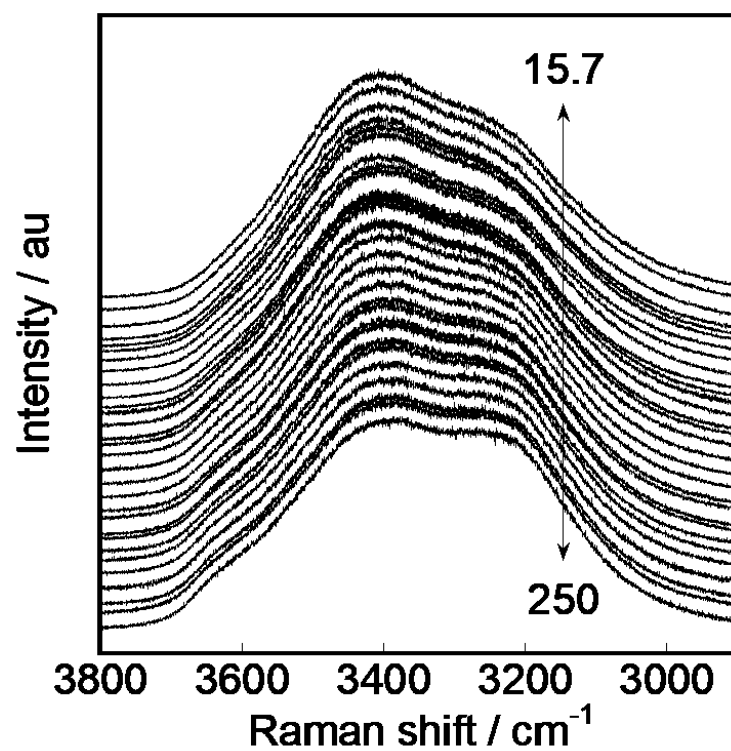


Fig. 4-10(a). Raman spectra of $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$. The numbers in the figure represents n .

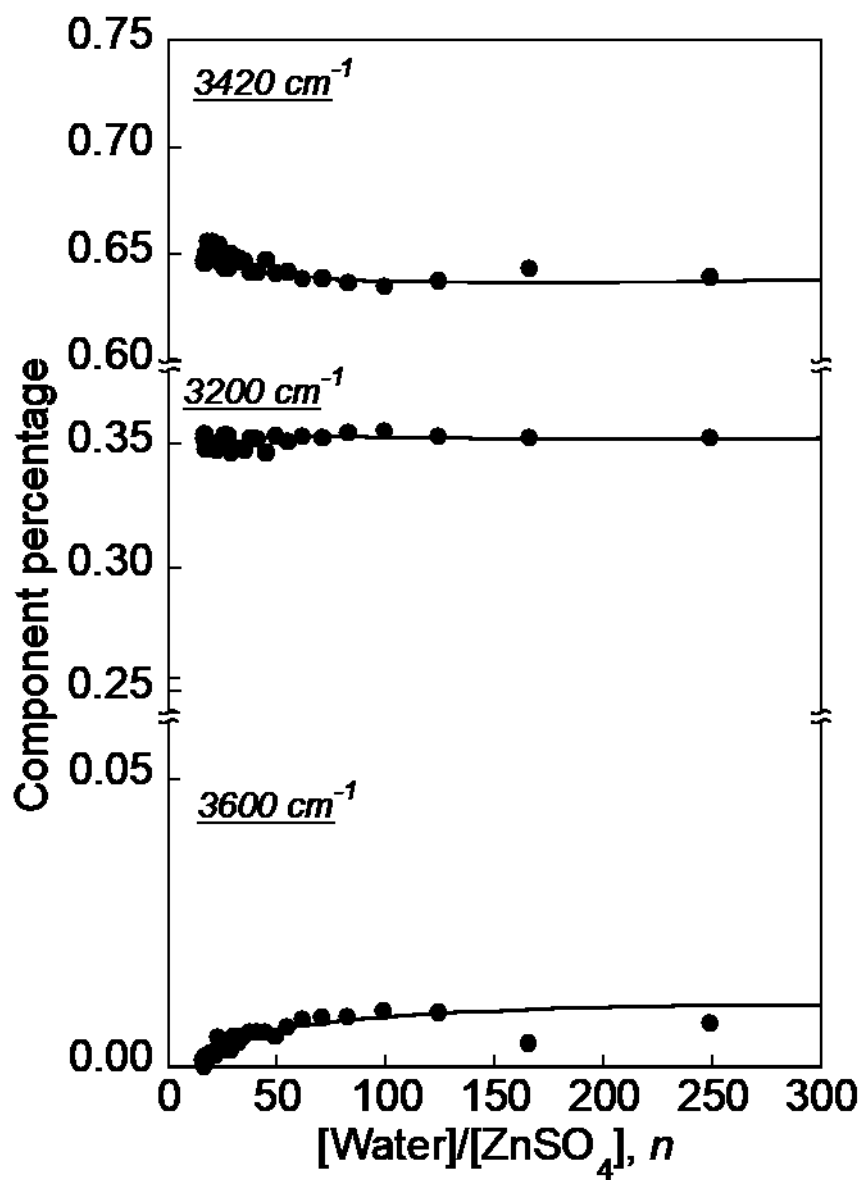


Fig. 4-10(b). The numerical ratio, n , dependences of relative intensities obtained from peak deconvolution for OH vibrational Raman spectra of $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$.

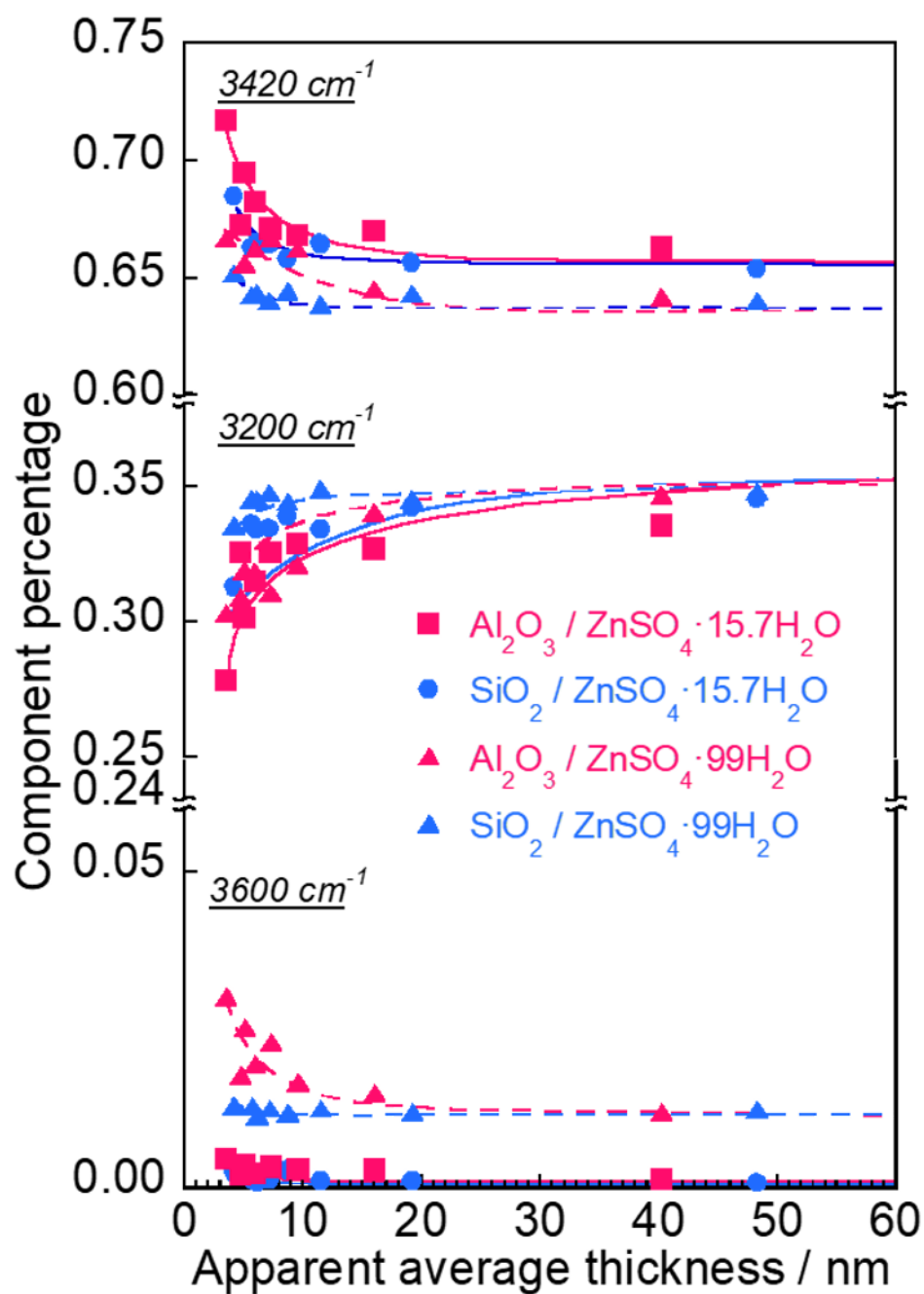


Fig. 4-11. Apparent average thickness dependences of relative intensities obtained from peak deconvolution for OH vibrational Raman spectra of metal oxide nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ coexisting system.

Conclusion

Dynamic properties and solvation structure of dissolving species in hydrate melt are influenced by coexisting solid phase. The depolarization factor suggested distortions of $\nu_1\text{-SO}_4^{2-}$ and $\nu_1\text{-[Zn(H}_2\text{O)}_6]^{2+}$ was shown in the vicinity of solid surfaces. The fraction of contact ion pairs, α increased with decrease of apparent average thickness especially in $\gamma\text{-Al}_2\text{O}_3$ coexisting system. Influence of $\gamma\text{-Al}_2\text{O}_3$ are stronger than amorphous SiO_2 . The peak deconvolution using three-Gaussian fits for OH vibration of water molecules indicated that ionic species and metal oxide solid surfaces affect OH stretching vibrational mode in different wavenumber.

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CHAPTER 3

Dynamics of Non-aqueous LiClO₄ Electrolyte Nanoconfined by Silica Surfaces

1. Introduction

Rechargeable lithium-ion batteries (LIBs) with organic electrolyte has become the widespread power sources for various electrochemical devices such as portable electronic devices, electric vehicle, stationary storage use, and so on.¹⁻³ There are various kinds of solid-liquid interfaces in LIBs. For example, electrodes were made with very high filling rate of the active material to achieve high capacity, electrolytes were impregnated into small void spaces of the solid surfaces. Liquid phase confined by a lot of solid surface can be considered as condensed dispersion system. It is well known that the restricted layer of the liquid phase exists near the solid surfaces in solid/liquid coexisting system.⁴ The liquid layer is remarkably influenced by the solid phase, and show different properties compared with that of bulk liquid. We have been studied the interfacial liquid layers using various liquid and solid materials, and confirmed that the thicknesses of the layers are in the order of tens nm, which are not the same as interfacial restructuring molecules reported by X-ray technique or electrical double layer.⁵⁻¹² In particular, the value of the activation energy for the electrical conduction of the ionic species increased nearby the hydrophilic solid surfaces.¹³ Electrochemical reaction occurs within such solid/liquid interfaces. Therefore, knowledge about dynamic properties of liquid phase in the vicinity of solid surfaces is important for improving battery performance.

In addition, mixed solvent electrolyte solutions were used for conventional LIBs for various purposes. Binary solvent systems based on ethers with low viscosity such as 1,2-dimethoxyethane (DME) and cyclic carbonates with high dielectric constant such as propylene carbonate (PC) are well known that ionic conductivity is superior to that of single solvents.¹⁴⁻¹⁷ However, liquid behavior of such binary solvent systems in the

vicinity of solid phase seems to be more complicated than single solvent system. In our previous study, the solvent composition dependence of the conductivity for binary solvent electrolyte system differed in bulk liquid state and solid/liquid coexisting system, indicating interfacial liquid layer plays a critical role on dynamic properties of the entire solution.¹⁸⁻²⁰ Our group previously reported that ethanol-cyclohexane binary liquids showed self-assembled structure of ethanol onto silica surfaces, resulting from hydrogen bonding interactions between surface silanol groups and ethanol hydroxyl groups.²¹⁻²³ Additionally, this phenomenon was applied to fabricate molecularly flat, defect-free, and thermoresponsive films.^{24,25} Similar results of self-assembled structure were obtained for other binary systems such as phenol-cyclohexane and water-cyclohexane.^{26,27} Consequently, we focused on the resonance shear measurement (RSM) based on surface forces apparatus (SFA) and observed the length of the interfacial liquid structure with high accuracy by observing the shear stress at resonance frequencies.²⁸⁻³¹ The resonance shear responses are sensitive to changes in the viscosities of confined liquids. Therefore, we can measure the thickness of the restricted layer as an increase in shear viscosity. In previous study, RSM revealed the viscosity increase of water between mica surfaces with decreasing surface separations below 1 nm.³²

In this study, we focused on dynamic properties LiClO₄ based non-aqueous binary solvent electrolytes nanoconfined by SiO₂ solid surfaces using ¹H NMR and RSM. Consequently, we elucidate the interfacial liquid structure in heterogeneous system by measuring the interfacial liquid layer thickness, and report that the binary solvent system of PC-DME showed anomalously long-range interfacial liquid layer that single solvent system of PC or DME did not have.

2. Experimental

2.1 Materials

Lithium perchlorate (LiClO_4 , Nacalai Tesque Inc.) was dried under vacuum at 130 °C for 20 h. and dissolved in propylene carbonate (PC, Nacalai Tesque Inc.) as non-aqueous solvent. 1,2-dimethoxyethane (DME, Nacalai Tesque Inc.) was used to prepare binary solvent (PC-DME), mixing PC and DME at a volume ratio of 1:1. Fumed silica, SiO_2 supplied from Nippon Aerosil was used as solid phase after drying under vacuum at 130 °C for 20 h. Solid-liquid coexisting samples were prepared under Ar atmosphere. PC (Kishida Chemical Co., Lithium Battery Grade) and distilled DME was used in the resonance shear and surface force measurement described later.

2.2 Density measurement

Densities of liquid sample were measured using DMA 5000M with oscillating U-tube sensor (Anton Paar). We obtained vibrational frequencies and converted to densities.

2.3 Ionic conductivity measurements

The ionic conductivities were measured by AC impedance measurement using a precision LCR meter (4284A and 4285A of Agilent Technology, USA) with a self-made electrochemical cell which has 12.67 cm^{-1} of cell constant. The cell was calibrated by using a 0.01 mol L^{-1} KCl aqueous solution at 25 °C.

2.4 ^1H NMR spectroscopy

^1H NMR spectra were obtained by a Varian INOVA 400 NMR spectrometer with 9.39 T magnet and 5mmSW probe (Varian, Inc.). To avoid mixing sample with deuterated solvent, the coaxial NMR tube (Wilmad-LabGlass CO. Inc., 516-cc-5) was used and deuterium oxide (Euriso-Top) was filled in outer tube. The ^1H NMR chemical shifts were determined using second order external standard of deionized double distilled water, as tetramethylsilane was first order standard of 0 ppm. All experiments were performed at 25 °C. The quantitative analyses of ^1H NMR spectra (^1H qNMR) was carried out following previous study.³³ ^1H qNMR was defined as following equation;

$$\frac{N_x}{N_{\text{ref}}} = T \times 10^{\frac{Rg_{\text{ref}} - Rg_x}{20}} \times \frac{Ns_{\text{ref}}}{Ns_x} \times \frac{I_x}{I_{\text{ref}}}$$

where N is the concentration of the chemical species that gives the NMR signal, Rg is the receiver gain of the NMR spectrometer, Ns is the number of FID scans, and I is the integrated intensity of the NMR signal. The subscripts “ref” and “x” represent the external standard solution and the sample solution, respectively. T is a specific constant for the measuring condition such as NMR sample tube, NMR equipment, and so on. It is almost unity when a similar NMR sample tube and the same NMR equipment are used for observation.

2.5 ^1H relaxation measurement

The spin-spin relaxation time (T_2) in ^1H NMR was obtained by relaxation time measuring equipment Acorn area (XiGo Nanotools) which have 0.3 T magnet. The solid/liquid coexisting samples were put into 5 mm diameter glass NMR tube. We used the CPMG method.³⁴ T_2 of all intramolecular nuclear were averaged as single relaxation in this method. All experiments were performed at 25 °C.

2.6 Surface forces apparatus-based resonance shear measurement

Surface forces measurement and resonance shear measurement (RSM) were carried out in a similar manner to those of previous studies. The sufficiently thin and smooth quartz glass sheets were used as silica substrate following the procedure reported by Horn et al.³⁵⁻³⁷ The root mean square and the peak to valley roughness of the silica surfaces was 0.29 ± 0.11 nm and 2.5 ± 0.8 nm, as reported in previous study.³⁵ After deposition of silver on the backside, the silica sheets were glued onto cylindrical quartz lenses (radius of curvature, R , of ca. 20 mm) and mounted in crossed-cylinder configuration in the surface force apparatus (SFA). The surface distance between the substrates (D) was determined by fringes of equal chromatic order (FECO) analysis.^{38,39} Before injecting the sample, the state where the upper and lower surfaces are in contact is regarded as the zero point of the distance. About 20 μ L liquid samples were injected between the two silica sheets using micro-syringe and surface forces were measured as a function of D while bringing the surfaces closer together using pulse motor. RSM was performed using a home-built resonance shear system combined with SFA shown as Fig. 5-1. The system was composed of an upper surface unit hung by a pair of vertical leaf springs and a lower surface unit mounted on the horizontal leaf spring of the SFA. The upper unit was connected to a four-sectored piezo tube and oscillated laterally with sinusoidal input voltage (U_{in}) at various angular frequencies, ω . The deflection of the upper unit detected by a capacitance probe was output voltage (U_{out}). The relationship between amplitude ratio, U_{out}/U_{in} and variation of ω recorded for various values of D represents the viscosity and friction of confined liquid. In the measurement of mixture samples containing DME, we quickly measured U_{out}/U_{in} at the fixed frequency at the resonance peak for avoiding effects of DME evaporation while putting the DME with

filter paper in the measuring chamber to make a DME atmosphere. We obtained $U_{\text{out}}/U_{\text{in}}$ with various D as soon as possible and employed surface force measurement before and after the $U_{\text{out}}/U_{\text{in}}$ measurement, confirming the measurement error of D due to the evaporation was within ca. 10 nm. All measurements were conducted at 25 °C.

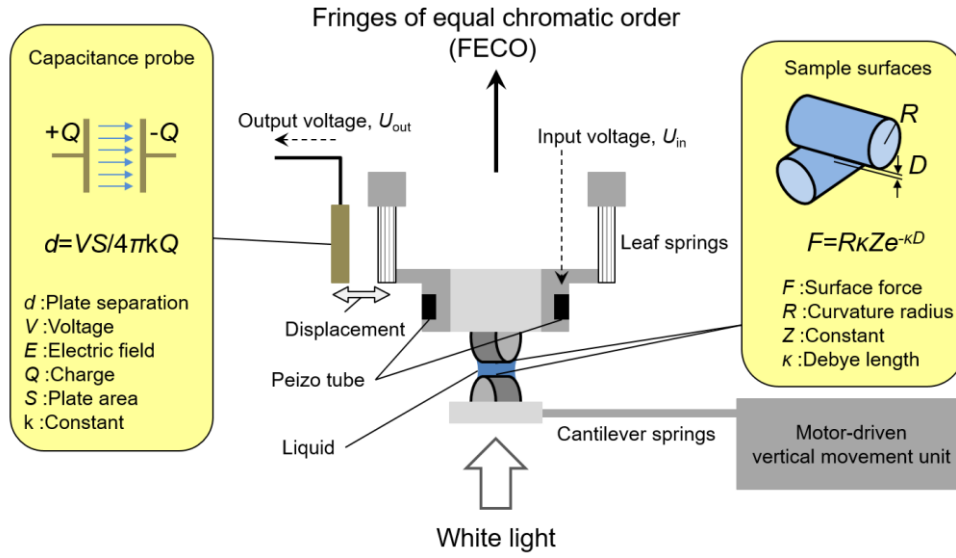


Fig. 5-1. Schematic representation of experimental setups of resonance shear measurement (RSM).

In addition to the above experiments using the silica surfaces of the quartz glass sheets, we carried out RSM immersing the entire upper and lower surfaces in a liquid sample of about 30 mL to avoid DME evaporation effects completely by using sputtered silica surfaces. The sputtered silica surfaces were prepared without glue by the deposition of silica on cylindrical discs.⁴⁰ The apparatus with container for immersion are represented schematically in Fig. 5-2.

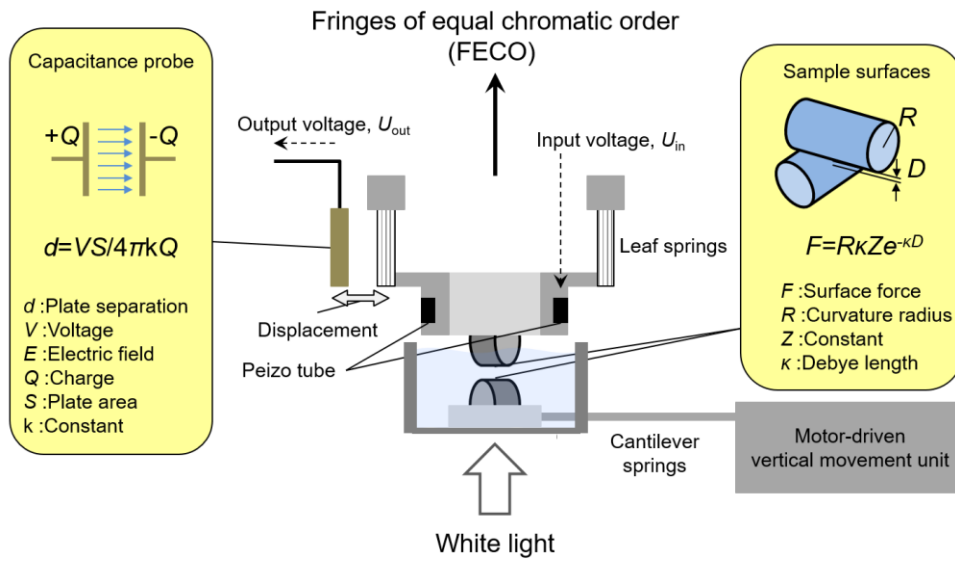


Fig. 5-2. Schematic representation of experimental setups of resonance shear measurement (RSM) with container for immersion.

3. Result and discussion

3.1 Electrical conductivities of $\text{SiO}_2/1 \text{ mol L}^{-1} \text{ LiClO}_4$ PC-DME solution coexisting system

Fig. 5-3 represents variations of the electrical conductivities with the solvent composition for $\text{SiO}_2/1 \text{ mol L}^{-1} \text{ LiClO}_4$ PC-DME solution coexisting system at 25 °C. As is well known, bulk liquid system of $1 \text{ mol L}^{-1} \text{ LiClO}_4$ PC-DME solution showed higher conductivity than $1 \text{ mol L}^{-1} \text{ LiClO}_4$ PC solution. However, the composition of the maximum conductivity shifted toward lower DME mole fraction with the addition of the solid phase. This trend was the same as our previous work using $\alpha\text{-Al}_2\text{O}_3$.²⁰ Additionally, the decrease in electrical conductivity due to the addition of SiO_2 was greater in PC-DME mixed solvent system, which is expected to have higher conductivity, than in the PC single solvent system. As indicated in previous studies, preferential self-assembly of either solvent molecule on the coexisting solid surfaces could occur. Therefore, the solvation structure and the conduction mechanism might be different between single solvent system and PC-DME binary solvent system in solid/liquid interfaces.

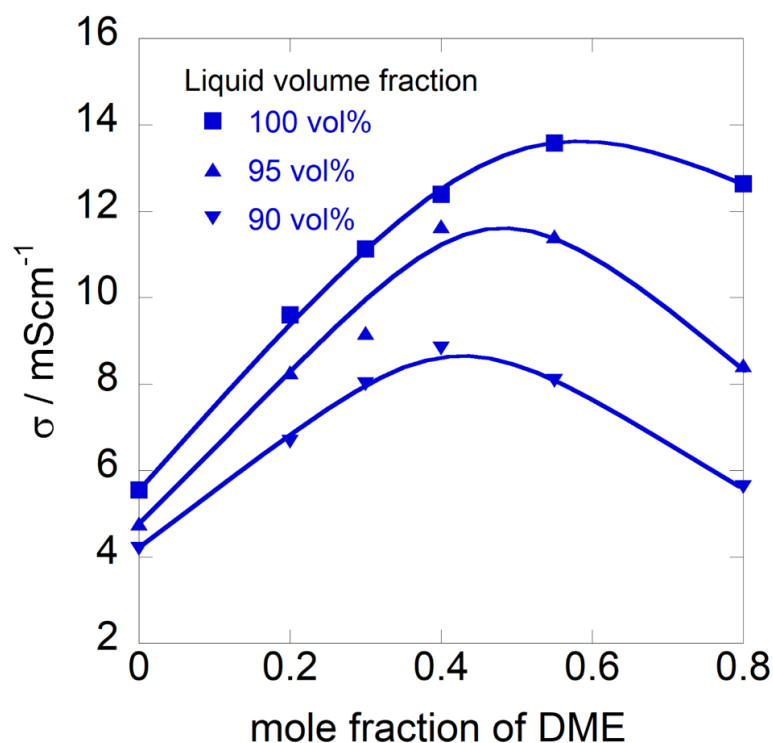


Fig. 5-3. Variations of the electrical conductivities with the solvent composition temperature dependences of conductivities for $\text{SiO}_2/1\text{mol L}^{-1} \text{LiClO}_4$ PC-DME solution coexisting system at 25 °C

3.2 Solvent mobility of $\text{SiO}_2/1 \text{ mol L}^{-1} \text{LiClO}_4$ in PC-DME observed with ^1H -NMR

^1H NMR provides various information of solvent molecules which were influenced by coexisting solid phase. First, in order to investigate the behavior of the solvent molecules, solid/liquid coexisting system in the absence of salt will be described. Fig. 5-4(a) represents ^1H NMR spectra of $\text{SiO}_2/\text{PC-DME}$. Peaks corresponding to each ^1H nuclei of PC and DME were observed. In bulk PC-DME, one doublet (1.88 ppm), two triplets (4.50 ppm and 5.03 ppm) and one sextet (5.34 ppm) were assigned to methyl

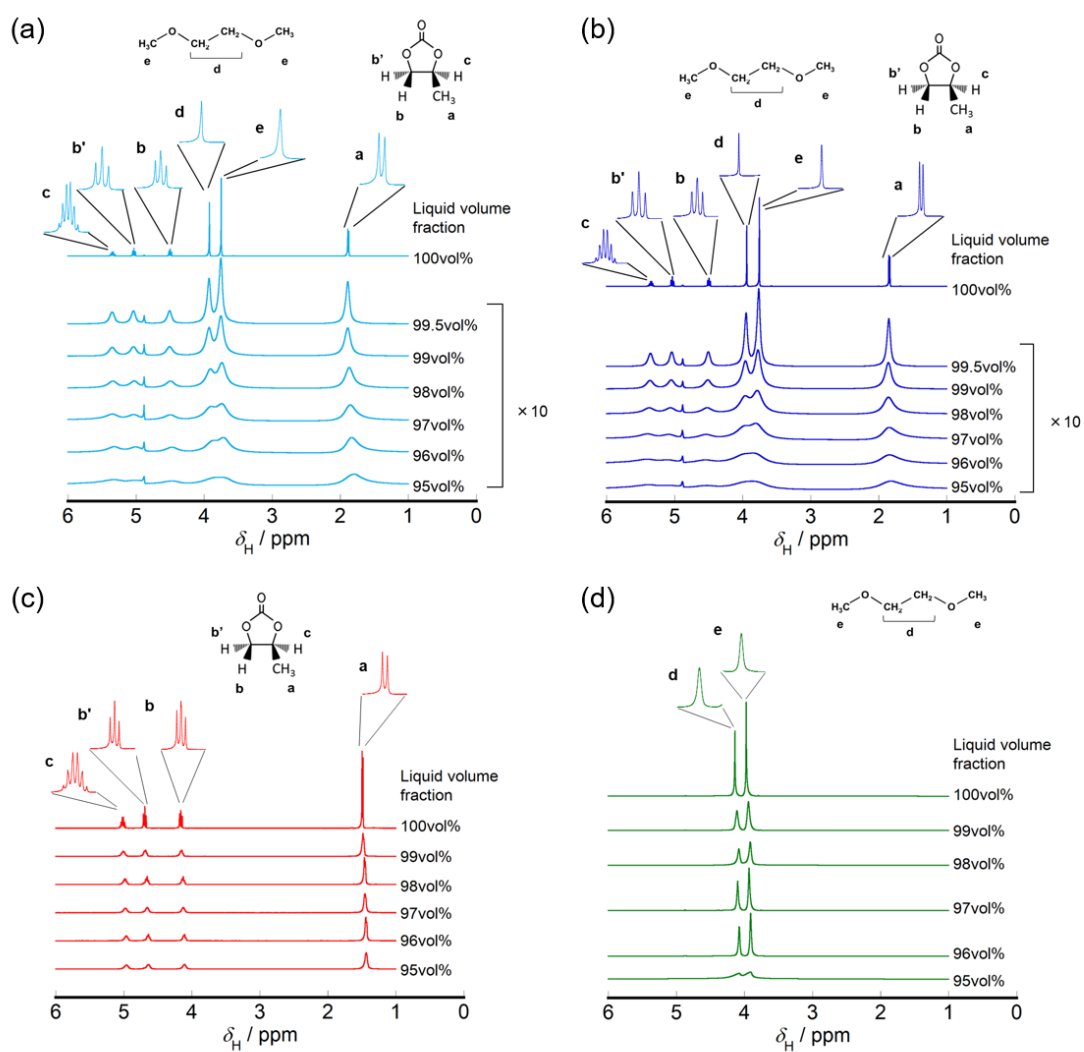


Fig. 5-4. ^1H NMR spectra of solid/liquid coexisting system with variable liquid volume fraction; (a) $\text{SiO}_2/\text{PC-DME}$, (b) $\text{SiO}_2/1 \text{ mol L}^{-1} \text{ PC-DME}$ solution, (c) $\text{SiO}_2/1 \text{ mol L}^{-1} \text{ PC}$ solution and (d) $\text{SiO}_2/0.5 \text{ mol L}^{-1} \text{ DME}$ solution.

group, methylene group and methine group of PC molecule, and two singlets (3.75 ppm and 3.92 ppm) was attributed to distal methyl groups and methylene groups of DME molecule. The small peak around 4.88 ppm was derived from ^1H of H_2O contained in D_2O in the outer tube. NMR peaks of bulk solution were sharp. It is due to the fast chemical exchange of nuclei. However, solid/liquid coexisting system showed broad and weak NMR signals, suggesting molecules are restricted by solid surfaces and decrease their mobility. Depending on liquid volume fraction, changes in chemical shift were confirmed. Secondly, ^1H NMR spectra of solid/liquid coexisting sample based on 1 mol L^{-1} LiClO_4 PC-DME solution was shown as Fig. 5-4(b). The similar result as the system without LiClO_4 was obtained. Moreover, ^1H NMR spectra of $\text{SiO}_2/1 \text{ mol L}^{-1}$ LiClO_4 PC solution and $\text{SiO}_2/0.5 \text{ mol L}^{-1}$ LiClO_4 DME solution were recorded as Fig. 5-4(c) and 5-4(d) for the purposes of comparison of the binary solvent system with the single solvent system. Here, salt concentration of the DME solution was 0.5 mol/L^{-1} due to the constraint of saturation. Comparing Fig. 5-4(b), 5-4(c) and 5-4(d), it was confirmed that the decrease of the peaks and the broadenings due to the addition of the solid phase were small in the single solvent system. These results will be discussed again later. The liquid volume fraction dependences of chemical shift of each peak spectra were shown in Fig. 5-5. The values of chemical shift of the splitting peaks were obtained from the center of gravity of the peaks. In SiO_2/PC coexisting system, the peaks corresponding to the methyl group of PC, which is referred as “a” in Fig. 5-4, shifted to higher magnetic field with decrease of liquid volume fraction. These results indicate the increase of the electron densities of PC molecules in the vicinity of silica surfaces. It seemed to be due to the interaction between PC molecules and negatively charged surface functional groups on silica surfaces. Comparing bulk PC and 1 mol L^{-1}

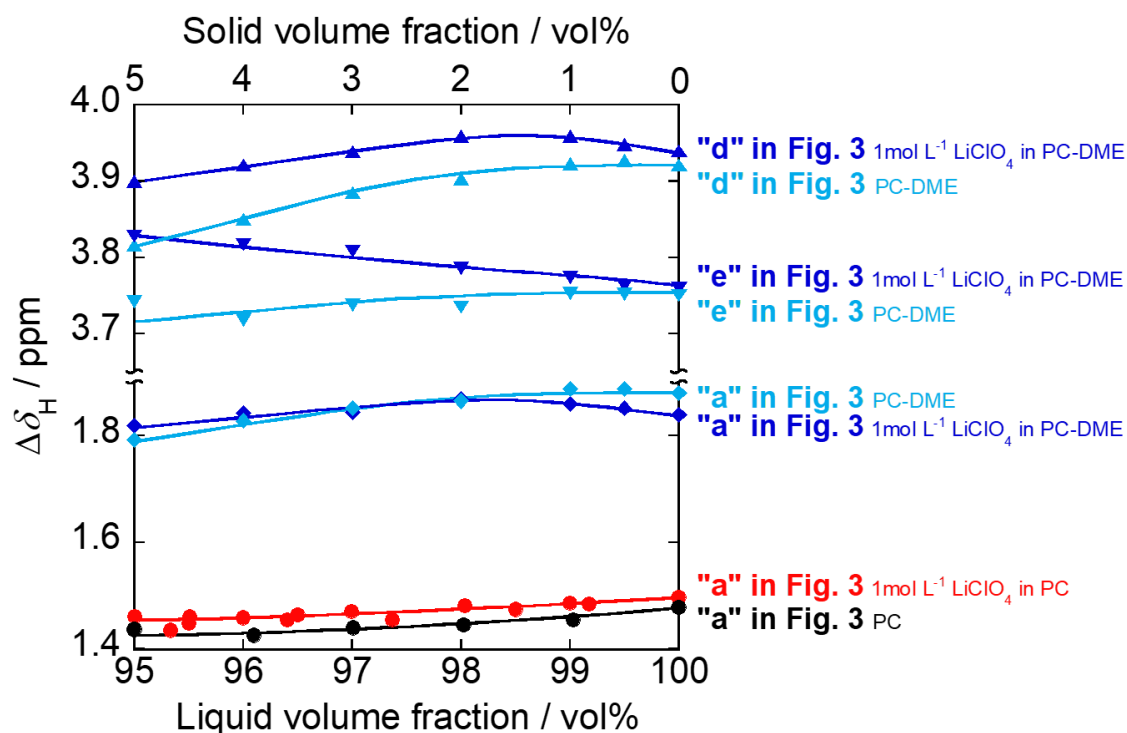


Fig. 5-5. Liquid content dependences of chemical shift for ^1H NMR spectra.

LiClO₄ PC solution, lower magnetic field shifts were confirmed suggesting the decrease in the electron density around the hydrogen nucleus of the PC; this indicates the solvation of Li⁺ by PC through the carbonyl group. In the solid/liquid coexisting system, the higher magnetic field shift with the addition of the solid phase was confirmed regardless of presence/absence of LiClO₄. However, the peak of PC in PC-DME mixture without LiClO₄ hardly changed up to about 1% of solid phase volume fraction, but showed lower magnetic field shift at higher volume fractions. It indicates that PC did not adsorb on the solid phase if the rate of solid phase addition is small, and becomes adsorbed on the solid phase if the volume fraction becomes more than a certain level. Comparing bulk PC-DME and 1 mol L⁻¹ LiClO₄ PC-DME solution, the peak of

PC appeared at higher magnetic field with the addition of LiClO_4 . These peaks showed higher magnetic field shift depending on liquid content while the magnitude relationship of these peaks was switched as shown in the figure. In other words, the electron densities of PC increase with increasing solid phase fraction. From these, it is suggested that PC does not contribute to Li^+ solvation in bulk solution, but as coexisting solid phase increases, it participates in the solvation and also interacts with solid. Additionally, a slight increase up to about 1% of the solid phase volume fraction is considered to be due to Li^+ solvation. The difference in electron density of PC in bulk PC-DME and bulk $1 \text{ mol L}^{-1} \text{ LiClO}_4$ PC-DME solution seems to be the influence from anion. On the other hand, two peaks corresponding to DME in PC-DME, which are referred as “d” and “e” in Fig. 5-4, showed higher magnetic field shift with increase in solid volume fraction, clearly indicating interaction with coexisting solid surfaces. In $1 \text{ mol L}^{-1} \text{ LiClO}_4$ PC-DME solution based system, the methylene groups behaved like the methyl group of PC in binary solvent electrolyte solution, and the distal methyl groups showed lower magnetic field shift with the addition of the solid phase. Although these behaviors are currently under consideration, multiple effects such as competitively interaction of DME and PC with solid surface, desolvation of DME, solvation of PC and effects of ionic species are assumed to affect complicatedly. These results suggested that coexisting solid surfaces affect solvation structure of dissolving ionic species and the solvation structure in the solid/liquid interface does not necessarily agree with it in the bulk solution, while many researchers have studied the preferential solvation of PC and DME with Li^+ .⁴¹⁻⁴⁶

Because integrated intensities of ^1H NMR spectra is proportional to the number of nuclei contributing to that signal, ^1H NMR gives invaluable quantitative information.

Then, we carried out quantitative analyses with ^1H qNMR to confirm influences of solid surfaces on liquid molecules. The relationship between liquid volume fraction and the results of ^1H qNMR for PC and DME were shown in Fig 5-6(a) and 5-6(b), indicating without and with LiClO_4 system, respectively. The vertical axis was calculated as integrated peak intensity of solid/liquid coexisting sample divided by integrated peak intensity of bulk liquid. It represents detection ratio of each molecule in the liquid phase. The broken line in the figures represent the volume fraction-adjusted value of detected amount of PC and DME. In Fig. 5-6(a), the detected amount of PC was lower than the broken line. The differences between measured values and expected values indicate an amount of molecules restricted by solid surfaces. However, in PC-DME mixture system, the detection ratio of PC increased with decreasing liquid volume fraction and DME got much smaller conversely. It suggests that the mobility of DME molecules were highly and preferentially restricted by coexisting SiO_2 surfaces compared with PC. On the other hand, the reason why the detected amount of PC in binary solvent system increased more than bulk can be that PC concentration apparently increased in the region away from solid surfaces as a result of DME preferentially interacting with the solid phase. Therefore, DME concentration increase in the vicinity of the solid surfaces and the liquid structure is supposed to become heterogeneous. From Fig. 5-6(b), the detection ratio of PC and DME indicated a similar tendency regardless of presence/absence of LiClO_4 .

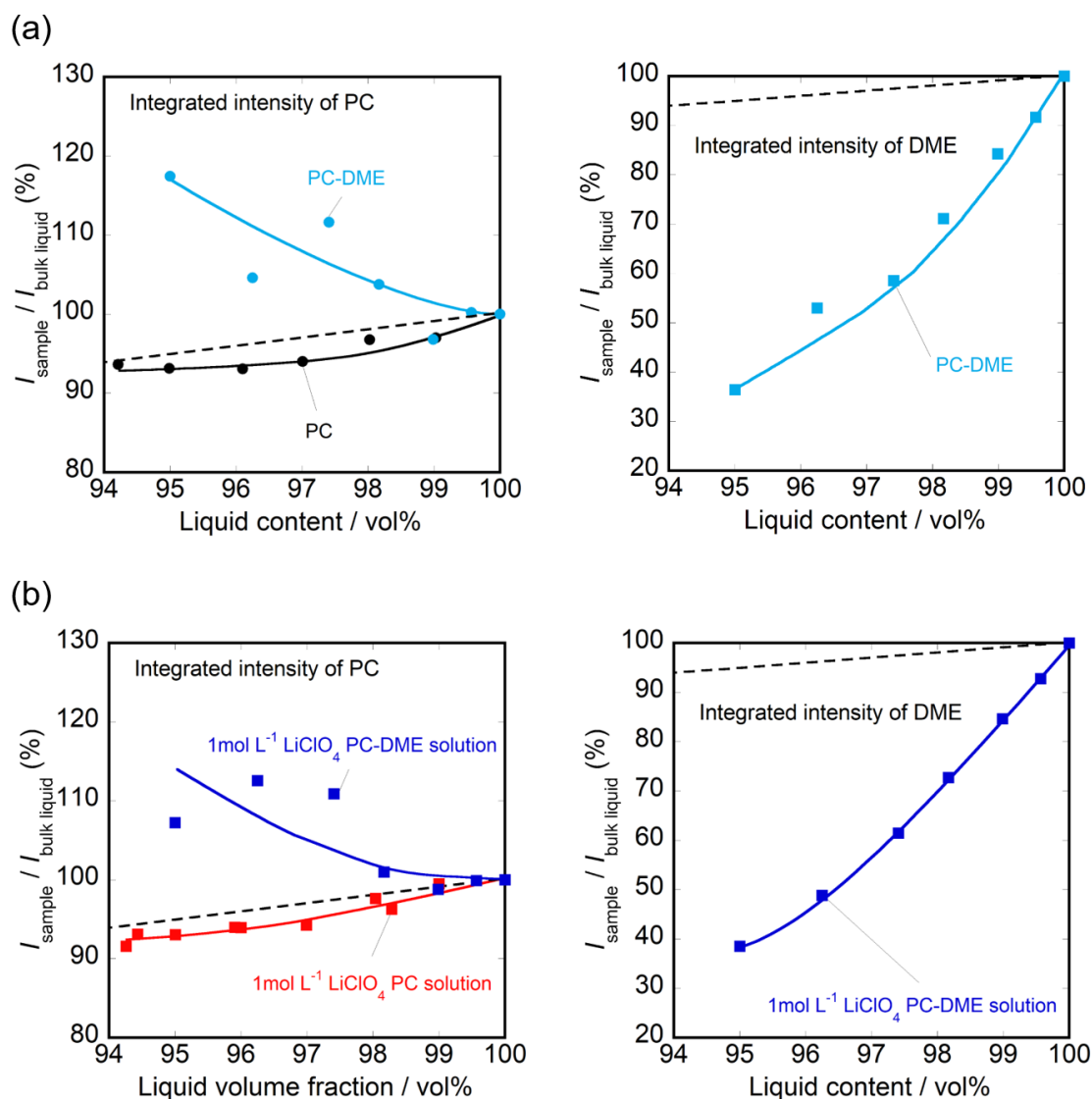


Fig. 5-6. Liquid volume fraction dependences of the detection ratios for PC and DME. The $I_{\text{sample}}/I_{\text{bulk soln.}}$ was calculated as integrated peak intensity of solid/liquid coexisting sample (I_{sample}) divided by integrated peak intensity of bulk solution ($I_{\text{bulk soln.}}$); (a) SiO₂/PC (black) and SiO₂/PC-DME (light blue), (b) SiO₂/1mol L⁻¹ PC solution (red) and SiO₂/1mol L⁻¹ PC-DME solution (blue). The broken lines show the volume fraction-adjusted value of expected amount of PC and DME.

The broadened ^1H NMR signals of solid/liquid coexisting system as shown in Fig. 5-4 suggests the coexisting solid phase affect the dynamic property of solvent molecules. The line width of the ^1H NMR signals corresponds to the spin–spin relaxation time (T_2). In addition, we proposed the spatial model that liquid particles are monodispersed as hexagonal close-packed as mentioned in previous study.⁴⁷ Consequently, we use the parameter called “apparent average thickness” for nanoparticle dispersion system. This parameter replaces volume fraction with the overall liquid layer distance and has a dimension of length. Fig. 5-7 represents the apparent average thickness dependences of T_2 for $\text{SiO}_2/1 \text{ mol L}^{-1} \text{ LiClO}_4 \text{ PC}$ solution system and $\text{SiO}_2/1 \text{ mol L}^{-1} \text{ LiClO}_4 \text{ PC-DME}$ solution system. T_2 of the binary solvent system decreased remarkably and became lower than that of PC based single solvent system under ca. 30 nm of apparent average thickness, although the binary solvent system shows higher mobility in the bulk solutions. This result indicates adding DME to PC based solution does not show any improvement in conductivity in the vicinity of the solid surfaces.

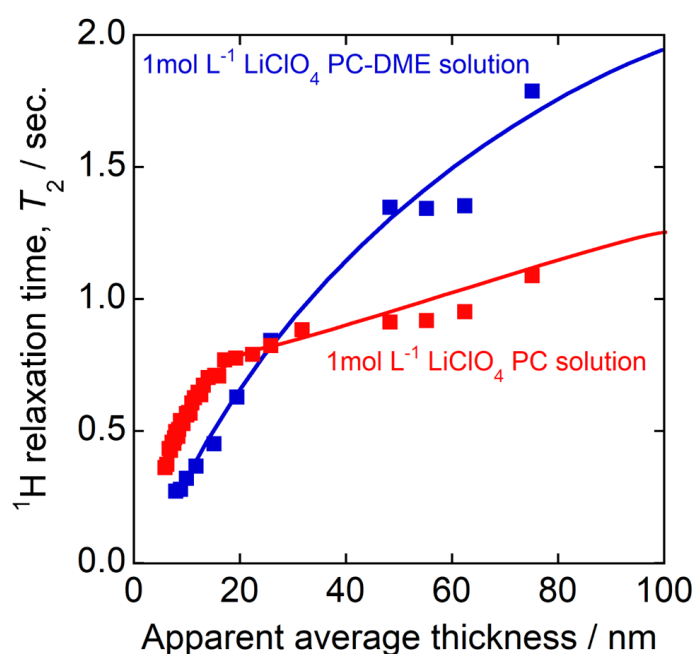


Fig. 5-7. Apparent average thickness dependences of T_2 .

Fig. 5-8 indicates apparent average thickness dependences of T_2 normalized by that of bulk values. Fig. 5-8(a) and Fig. 5-8(b) represents the results of without and with LiClO_4 salt, respectively. Although T_2 of the single solvent system composed of PC or DME decreased around 10nm drastically, the binary solvent system was affected by the solid surfaces from anomalously long distance. It was consistent with the difference in line width change depending liquid volume fraction as shown in Fig. 5-4. Therefore, the inversion of the mobility in Fig. 5-7 was not inherent in PC or DME themselves, but was due to mixing PC and DME. It is more obvious when examining the changes with respect to the addition amount of DME. Fig. 5-9(a) and Fig. 5-9(b) indicates the DME mole fraction dependences of T_2 without and with LiClO_4 salt, respectively. The binary system significantly reduced the mobility even with the addition of 1% SiO_2 . In bulk PC-DME binary system shown as Fig. 5-9(a), it was confirmed that T_2 increased by addition of DME, but there was no such effect on solid/liquid coexisting system. T_2 was an almost constant value. The same trend was obtained in solution system shown as Fig. 5-9(b), but the influence of DME was relatively small compared with the system without salt.

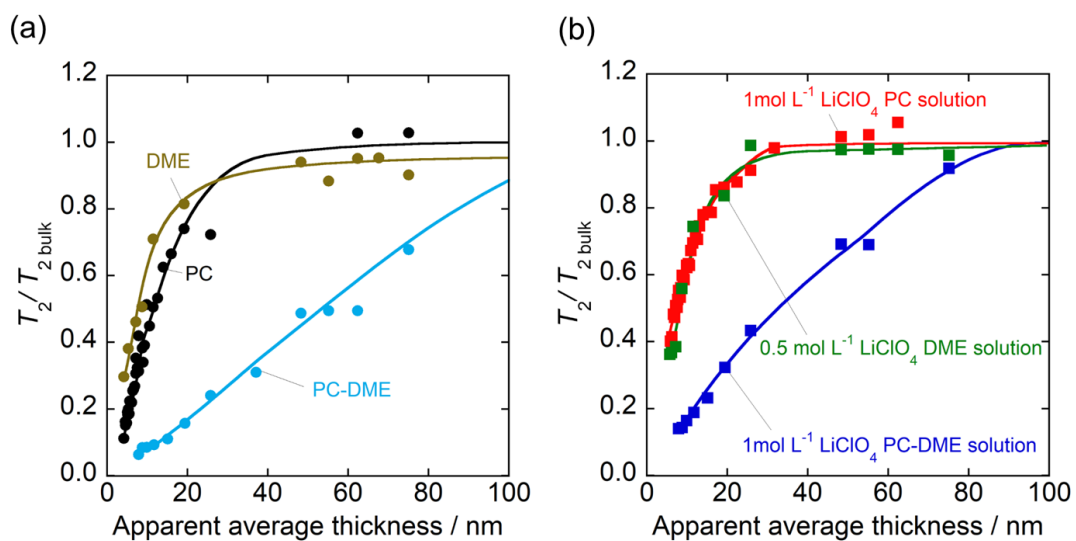


Fig. 5-8. Apparent average thickness dependences of T_2 normalized using $T_{2\text{ bulk}}$ for (a) without and (b) with salt.

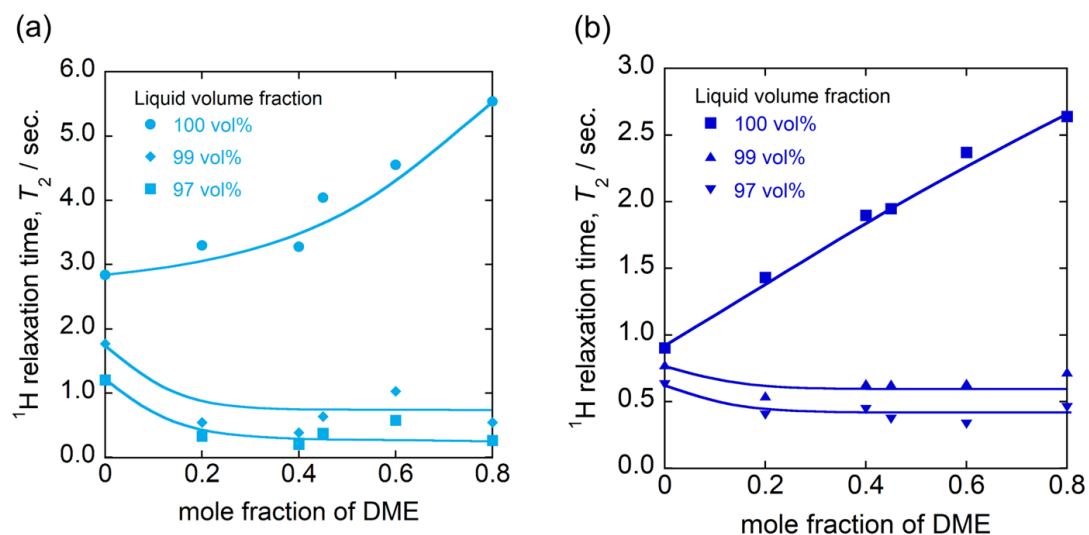


Fig. 5-9. Mole fraction dependences of T_2 of (a) SiO₂/PC_{1-x}DME_x and (b) SiO₂/1 mol L⁻¹ LiClO₄ in PC_{1-x}DME_x.

3.3 Relationships between dynamic properties and salt concentration of single solvent system

At the metal oxide solid surface, accumulation of ionic species occurs due to the influence of surface charges. Since the viscosity increases with increasing salt concentration, mobility in the vicinity of the solid surface is considered to be greatly affected.⁴⁸ Therefore, the effect of salt concentration on dynamic properties was observed. From the concentration dependence of liquid density, we calculated the volume subtraction of PC in the same way as the previous report.⁴⁷ Fig. 5-10 represents volume increment by adding one mole of PC to one mole of LiClO₄ salt. The volume increment was 85.1 ml mol⁻¹ in the infinite dilute solution at 25 °C and decreased under about 11 PC molecules per one salt. This decrease is known as electrostriction caused by ionic species.⁴⁹ Consequently, all PC molecule in the solution above 1 mol L⁻¹ of LiClO₄ concentration was supposed to be spatially affected by Li⁺. Fig. 5-11 shows the relationships between the apparent average thickness and T_2 of SiO₂/PC and SiO₂/LiClO₄ PC solution. We considered concentrated non-aqueous solutions as hydrate melt analogies because non-aqueous solvent molecules such as propylene carbonate have large molecular volume compared with water, and numerical ratio of solvent molecules per salt in concentrated solution becomes similar to inorganic hydrate melts. Therefore, we regarded the number of solvent molecules in the PC solution as a pseudo solvation number, and represented the solution concentration by LiClO₄· n PC like hydrate melts; n means number of PC molecules per one LiClO₄ salt. SiO₂/PC decreased T_2 with decrease of the apparent average thickness. In addition, SiO₂/LiClO₄· n PC system exhibited lower T_2 values as n decreased. Therefore, PC

molecules reduced its mobility by not only ionic interaction but also coexisting solid surfaces. $\text{LiClO}_4 \cdot 3.4\text{PC}$ showed subtle volume fraction dependences. While the surface charges of SiO_2 cause concentration gradients of ionic species and polar solvents, the gradient in $\text{LiClO}_4 \cdot 3.4\text{PC}$ is considered to be smaller than $\text{LiClO}_4 \cdot 11\text{PC}$. Thus, the effect of local viscosity in the interfacial liquid layer on T_2 of $\text{LiClO}_4 \cdot 3.4\text{PC}$ was relatively smaller than $\text{LiClO}_4 \cdot 11\text{PC}$ and PC.

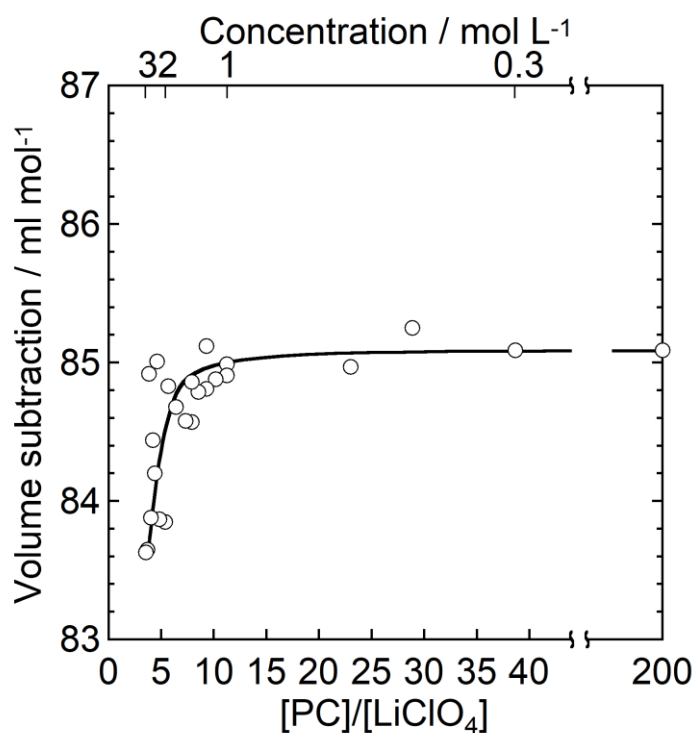


Fig. 5-9. Dependence of volume subtraction on number of PC molecules per one LiClO_4 salt at 25 °C.

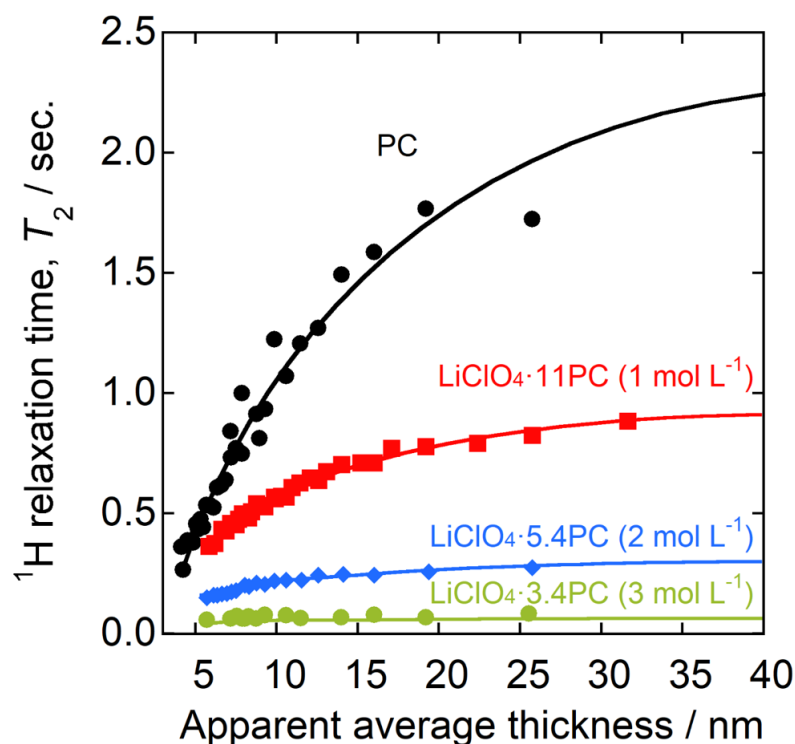


Fig. 5-10. Apparent average thickness dependences of T_2 for $\text{SiO}_2/\text{LiClO}_4 \cdot n\text{PC}$.

Although the relationship between apparent average thickness and T_2 suggested that SiO_2 solid surfaces affect the mobility of liquid molecules, T_2 values include the contribution from molecules far away from the solid surfaces. In order to discuss the thickness of the liquid layer on solid surface in more detail, we observed the shear viscosity of liquid sample confined between silica surfaces using RSM. The resonance curves of $\text{LiClO}_4 \cdot 11\text{PC}$ were shown as Fig. 5-12 at various surface separation, D , between SiO_2 surfaces prepared by quartz glass sheets. The curves for the separation in air (AS) and solid contact (SC) are also plotted as references. In the presence of $\text{LiClO}_4 \cdot 11\text{PC}$, the resonance curve at $D = 137$ nm showed the peak at a resonance frequency $\omega_{\text{res}} = 195 \text{ rad s}^{-1}$, the same frequency as the AS peak. The representative

resonance peak amplitude decreased with the decreasing D from 19 to 11 nm, although the resonance frequencies did not change with the decreasing D from 137 to 8.8 nm, suggesting the existence of interfacial liquid structuring. The resonance peak amplitude almost disappeared at $D = 5.7$ nm. This indicated that the viscosity of the confined liquid sharply increased due to liquid structuring under confinement at $D \leq 11$ nm. At $3.8 \text{ nm} \leq D \leq 5.7$ nm, the resonance curves shifted toward higher frequencies with the decreasing D , while the peak amplitude remained low. These low resonance amplitudes indicated that the viscosity of the confined liquid further increased and friction between the surfaces was low. At $D \leq 3.8$ nm, the ω_{res} values were same as that of the SC peak while the resonance amplitude increased with decreasing D . This increase of resonance amplitude indicates that the upper and lower units vibrate together. These results indicate that the viscosity of the confined liquid increased due to liquid structuring when the surface separation decreased into the nanometer range. To discuss the distance at which the viscosity of the confined liquid started to increase, we plotted the resonance peak amplitude, $U_{\text{out}}/U_{\text{in}}$ at ω_{res} , normalized with that of the AS peak at various D as shown in Fig. 5-13. The vertical axis is the energy loss compared with the AS peak due to the viscoelasticity of confined liquid, thus normalized $U_{\text{out}}/U_{\text{in}} = 1$ means no energy loss like separation in air and the values in long distances reflects the bulk viscosity. As shown in Fig. 5-13, the normalized $U_{\text{out}}/U_{\text{in}}$ at ω_{res} of PC sharply decreased at ca. 10 nm, indicating an increase in local shear viscosity due to the interfacial restricted layer. The thickness of the interfacial liquid layer is seemed to be hardly affected by the salt concentration, because there were little differences in the distances at which normalized $U_{\text{out}}/U_{\text{in}}$ decreased sharply among different concentration.

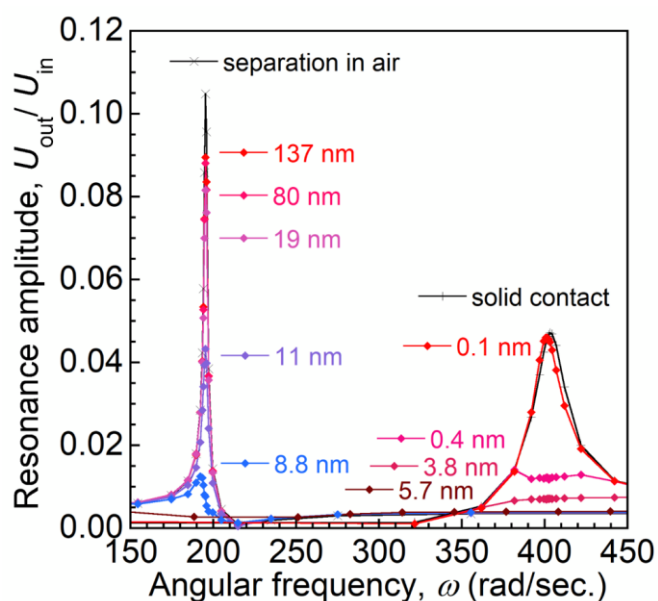


Fig. 5-12. Resonance curves of $\text{LiClO}_4 \cdot 11\text{PC}$ confined between silica surfaces at various surface separations. Two reference states curves for the separation in air and solid contact are also plotted.

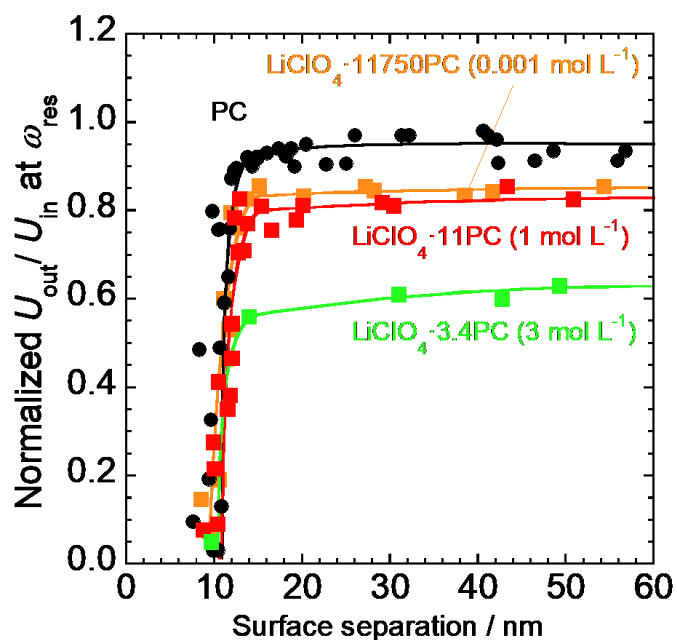


Fig. 5-13. Normalized resonance amplitude of $\text{LiClO}_4 \cdot n\text{PC}$ confined between silica surfaces as a function of surface separation.

The surface separation dependence of surface forces between silica surface is shown in Fig. 5-14(a). A repulsive force was observed in any samples below ca. 10 nm. This agreed with the result of RSM. Fig. 5-14(b) is the semi-logarithmic plot of 0.001 mol L⁻¹ LiClO₄ PC solution. Since the decay length obtained from the slope of the semi-logarithmic plot shown by the broken line in the figure is almost the same order as Debye length of 9.0 nm at 0.001 mol L⁻¹ LiClO₄ PC solution, the observed repulsive force was suggested to be due to the electric double layer repulsive force between the silica surfaces in the dilute solution.

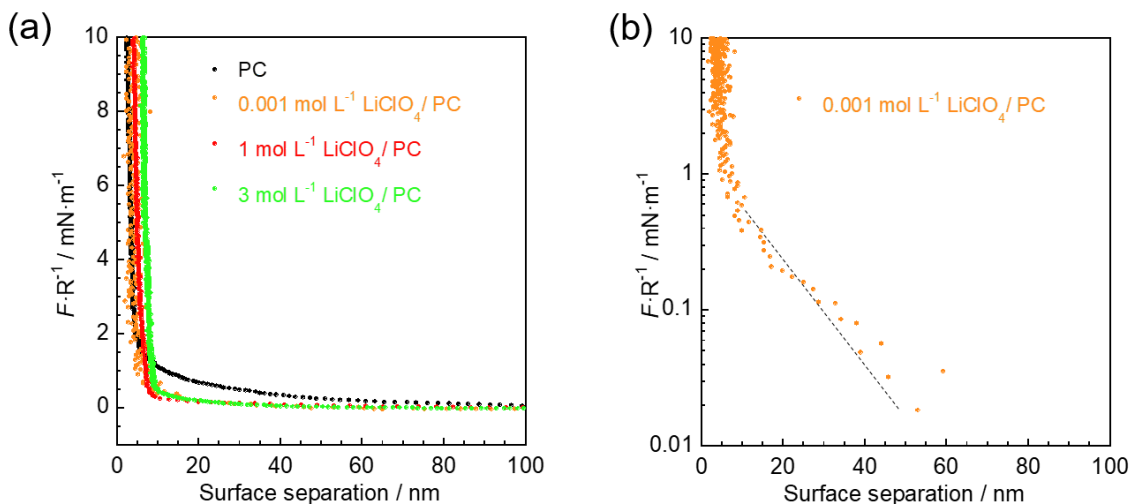


Fig. 5-14. Normal forces of LiClO₄-nPC normalized by radius of curvature, F/R as a function of surface separation between silica surfaces on approaching; (a) linear plot, (b) semi-logarithmic plot of 1mol L⁻¹ PC solution.

3.4 Local viscosity of PC-DME binary solvent system

Fig. 5-15 shows normalized $U_{\text{out}}/U_{\text{in}}$ at ω_{res} of PC-DME binary solvent system observed at various surface separation, D , between SiO₂ surfaces of quartz glass. The

measured values fluctuated greatly due to difficulties in measurement as mentioned in experimental section, but the trend was able to be grasped by repeating the measurement many times. The normalized $U_{\text{out}}/U_{\text{in}}$ of PC-DME gradually decreased below ca. 60 nm, suggesting the binary solvent system has longer interfacial liquid layer than PC. It should be noted that D is the distance between the vertically symmetrical silica surfaces and different from the apparent average thickness, however, the results of RMS was consistent with ^1H NMR relaxation measurement shown as Fig. 5-8. As mentioned by quantitative ^1H NMR, DME was preferentially affected by SiO_2 surfaces compared with PC in the binary solvent system. Therefore, DME seems to be highly restricted and heterogeneously condensed nearby the SiO_2 surfaces. The anomalous long-range interfacial liquid structure observed in the Fig. 5-8 and Fig. 5-15 might be attributed to the heterogeneity near the solid surfaces, and have a marked influence on macroscopic liquid dynamics. The distance at which normalized $U_{\text{out}}/U_{\text{in}}$ of 1 mol L $^{-1}$ LiClO_4 PC-DME solution gradually decrease was ca. 30 nm. It was thinner than PC-DME. This suggests the solvation of LiClO_4 hinders the interaction between the solid surface and solvent molecules, especially DME. This result correlates with that the DME composition dependence shown in Fig. 5-9(b) was smaller than Fig. 5-9(a).

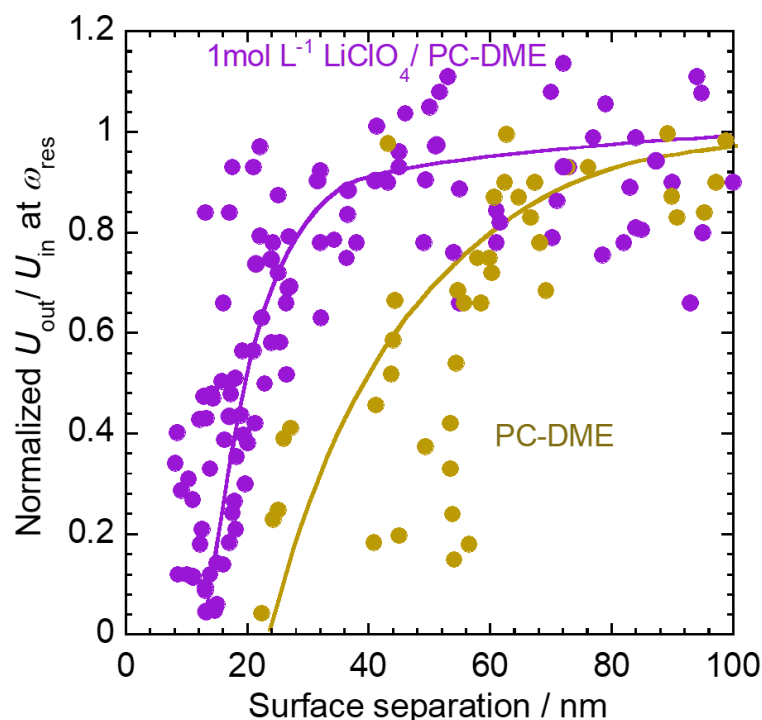


Fig. 5-15. Normalized resonance amplitude of PC-DME binary system confined between silica surfaces as a function of surface separation obtained using SiO₂ surfaces of quartz glass.

In order to measure the dependence of local shear viscosity on surface separation without the influence of DME volatilization, we carried out RSM immersing the entire upper and lower surfaces using liquid container for immersion and sputtered silica surfaces which use no epoxy resin. Since the sputtered silica surfaces are intrinsically soft compared with the quartz glass surfaces, the zero point of the distance changes as it is pushed in, as shown in Fig. 5-16, but if there is a significant difference of several tens nm order between samples, it can be discriminated. In addition, compared with the results using the quartz glass surfaces, it can be seen that the measurement was stably performed without influence of DME volatilization during three measurement times.

Fig. 5-17 is the result of normalized $U_{\text{out}}/U_{\text{in}}$ at ω_{res} observed using liquid container for immersion and sputtered silica surfaces. It is clearly shown that PC-DME has an increased interfacial liquid layer thickness compared with PC and DME. Here, it is considered that the reduction rate of the start of falling of the normalized $U_{\text{out}}/U_{\text{in}}$ at ω_{res} is lower than that of the quartz glass surfaces because the accuracy of the smoothness of the sputtered surface is lower. However, it clearly indicates that mixing increased the interface liquid layer thickness. The normalized $U_{\text{out}}/U_{\text{in}}$ at ω_{res} at the separated position in the figure does not reflect the bulk viscosity. This is probably because the entire unit is immersed, and the dynamics parameters around the unit are greatly different from those in which the sample is not inserted. As shown in Fig. 5-18, the resonance curve after immersing shows that both ω_{res} and amplitude change. Based on the results of the sputtered silica surfaces, we can eliminate the fluctuation due to DME volatilization from the result of using the quartz glass surfaces shown in Fig. 5-14, and then obtain Fig. 5-19. As Fig. 5-19 is in good agreement with Fig 5-14, it was confirmed that the trend grasped with quartz glass is reasonable. Recently, Hsu et al. reported that electrostatic properties of silica surfaces was affected by “viscoelectric immobile layer” which is related to the electric double layer and polarization of solvent molecules.⁵⁰ We revealed that the interfacial liquid structure between silica surfaces and binary solvent electrolyte solution is more complicated.

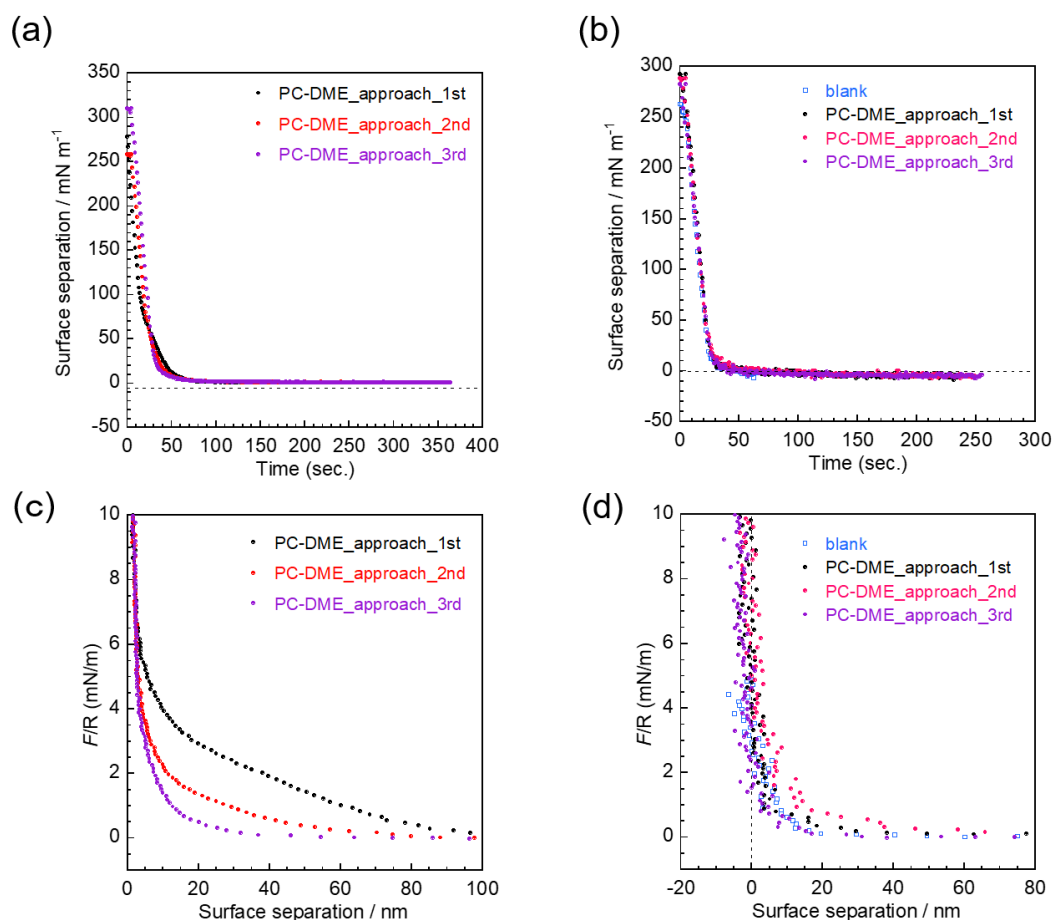


Fig. 5-16. Time dependence of surface separation of PC-DME on approaching at 1000 pulse min⁻¹; (a) obtained using SiO₂ surfaces of quartz glass and (b) obtained using sputtered silica surfaces and liquid container for immersion. Each measurement was repeated three times. Normal forces of PC-DME normalized by radius of curvature, F/R as a function of surface separation (c) which was converted from (a) and (d) from (b).

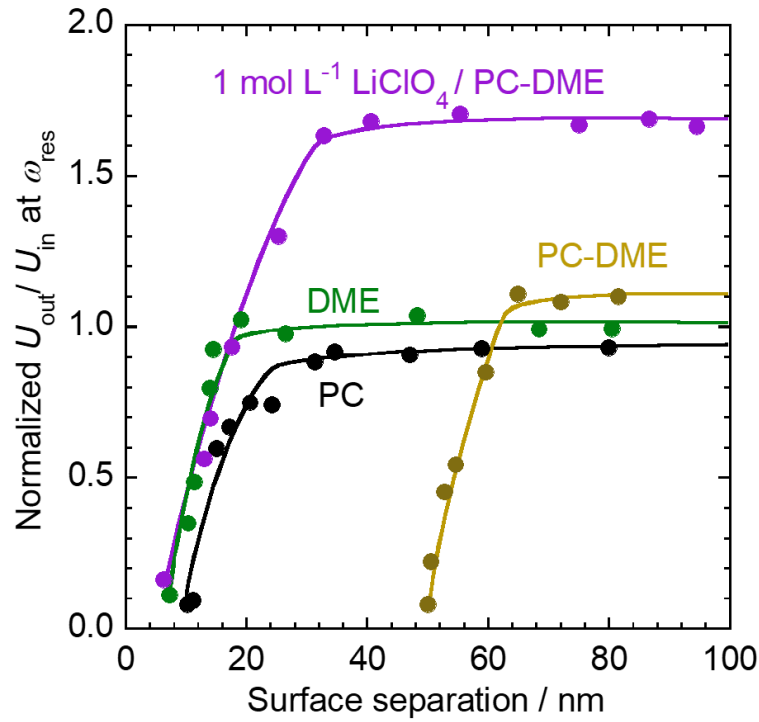


Fig. 5-17. Normalized resonance amplitude as a function of surface separation, D , obtained using sputtered silica surfaces and liquid container for immersion.

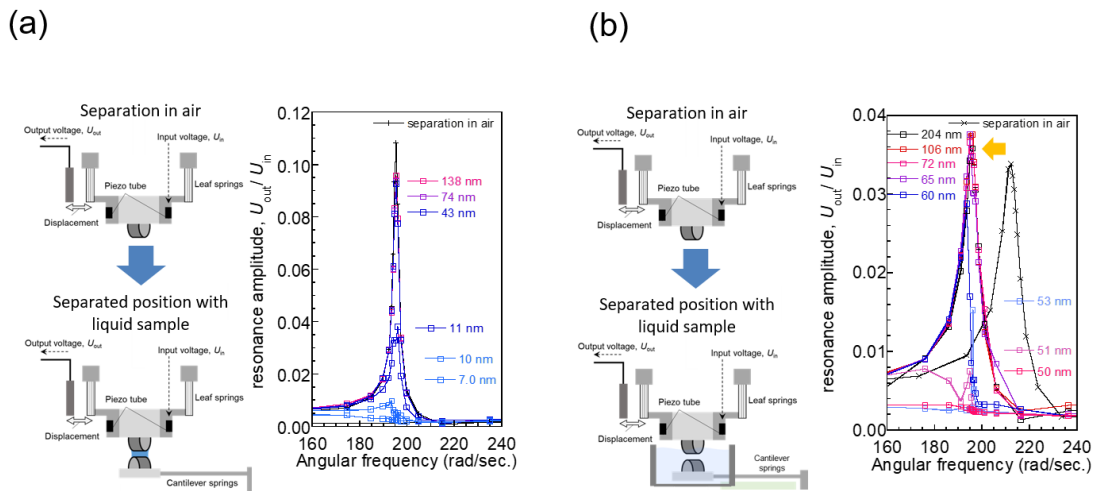


Fig. 5-18 Schematics and resonance curves of (a) PC obtained using SiO_2 surfaces of quartz glass and (b) PC-DME obtained using sputtered silica surfaces and liquid container for immersion.

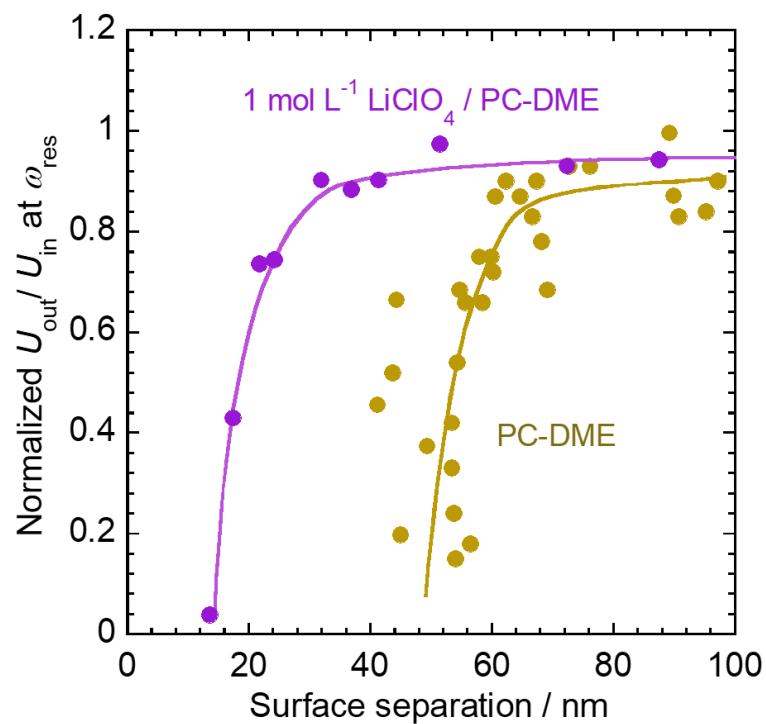


Fig. 5-19 Normalized resonance amplitude of PC-DME binary system confined between silica surfaces as a function of surface separation, D , obtained using SiO_2 surfaces of quartz glass.

Conclusion

The liquid behavior of nanoconfined non-aqueous system based on PC and PC-DME mixed solvent were observed. The DME mole fraction dependence of conductivities for 1 mol L⁻¹ LiClO₄ PC-DME solution was affected by coexisting solid phase, indicating the conduction behavior is different between single solvent system and PC-DME binary solvent system in solid/liquid interfaces. ¹H NMR relaxation measurements clearly showed differences in behavior between single solvent systems and binary solvent systems. The chemical shifts obtained from ¹H-NMR confirmed that the solvation structure changed in the solid/liquid coexisting system compared with bulk solution state. ¹H qNMR revealed that DME molecules in PC-DME binary system preferentially interacts with coexisting SiO₂ surfaces. Therefore, the liquid structure seems to be heterogeneous as a result that DME is condensed in the vicinity of the solid surfaces and PC concentration apparently increased in the region away from the solid surfaces. We measured the length of the interfacial liquid layer by RSM based on SFA. RSM reveals that 1 mol L⁻¹ LiClO₄ PC-DME solution exhibited increase of local viscosity about 30 nm of the surface distance, while that of 1 mol L⁻¹ LiClO₄ PC solution was about 10 nm, and ionic concentration has little effect on the thickness of the interfacial liquid layer. It was consistent with the result of ¹H NMR relaxation measurement. From the above, the addition of DME, which is expected to improve the conductivities of PC based solution for LIBs, turned out to be counterproductive in nanoconfined liquid system, and single solvent system is superior in terms of solvent mobility. Therefore, unexpected property changes could occur when using mixed solvents in heterogeneous condensed dispersion system.

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Summary

In the present work, the properties of the condensed electrolyte liquid system and condensed dispersion systems were studied with various measuring methods. The results were summarized as follows.

In Chapter 1, the properties of binary amide anion-based ionic liquid; $\text{TMPAFSA}_x\text{TFSA}_{1-x}$ were investigated. From DSC measurements, $\text{TMPAFSA}_x\text{TFSA}_{1-x}$ showed the binary phase diagram which had the eutectic point at the mole fraction of $x = 0.33$, and suggested the polymorphism. Thus, we carried out XRD measurements using temperature controlling unit to investigate the polymorphism. Comparing each XRD pattern with the simple statistical method, polymorphic behaviors due to the intramolecular rotation of amide anion were confirmed. The eutectic composition showed relatively good reproducibility in XRD patterns. This result seemed to be consistent with the composition dependences of heat of fusion and of ideal glass transition temperature determined from VTF equation, T_0 . Additionally, we studied the binary cation containing lithium ion and binary anion based system. The phase transition temperature of the binary anion system was lower than single anion system. In the binary cation and binary anion system, Raman spectra suggested lithium ion interacts more preferentially with TFSA^- than with FSA^- .

In Section 1 of Chapter 2, the dynamic properties of metal oxide nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$ system were discussed within wide salt concentration range from dilute to concentrated solution. Numerical ratio of water molecules per one salt and apparent average thickness were employed to describe the liquid behavior in the vicinity of solid surface. The H_2O - ZnSO_4 system showed phase diagram which have

eutectic composition at $n = 19$. The volume increment of water molecules derived from density measurement represented that one ZnSO_4 had influence on ca. 40 water molecules due to the electrostriction of ZnSO_4 . From ^1H relaxation of metal oxide nanoparticles/ $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$, water molecules in aqueous solution was affected by not only ionic interaction but also coexisting solid surface, although $\gamma\text{-Al}_2\text{O}_3$ exhibited stronger effect than SiO_2 . This difference between SiO_2 and $\gamma\text{-Al}_2\text{O}_3$ might be due to the surface potential of each solid particles depending on pH of liquid phase. Raman spectroscopy suggested that ion pairing tendencies were enhanced in vicinal area of SiO_2 surfaces.

In Section 2 of Chapter 2, dynamic properties and solvation structure of dissolving species in hydrate melt influenced by coexisting solid phase were investigated. The depolarization ratio of polarized Raman spectroscopy suggested distortions of $\nu_1\text{-SO}_4^{2-}$ and $\nu_1\text{-}[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ occurred in the vicinity of solid surfaces. The fraction of contact ion pair, α increased with decrease of apparent average thickness especially in $\gamma\text{-Al}_2\text{O}_3$ coexisting system. Influence of $\gamma\text{-Al}_2\text{O}_3$ are stronger than SiO_2 . The peak deconvolution using three-Gaussian fits indicated that ionic species and metal oxide solid surfaces affected OH stretching vibrational modes of H_2O in different wavenumber.

In Chapter 3, dynamics of nanoconfined LiClO_4 non-aqueous electrolyte systems based on PC and PC-DME were observed. Temperature dependences of conductivities for $\text{SiO}_2/1 \text{ mol L}^{-1} \text{ LiClO}_4$ in PC-DME showed VTF behavior which indicates decrease of free volume necessary for molecular movements, although $\text{SiO}_2/1 \text{ mol L}^{-1} \text{ LiClO}_4$ in PC exhibited Arrhenius type behavior. The chemical shifts obtained from ^1H -NMR confirmed that the molecules to be solvated changed in the solid/liquid coexisting system. ^1H qNMR revealed that DME molecules in PC-DME binary solvent electrolyte

preferentially interacts with coexisting SiO_2 . The liquid structure becomes heterogeneous as a result that DME is condensed in the vicinity of the solid surface and PC concentration apparently increased in the region away from the solid surfaces. RSM reveals that $1 \text{ mol L}^{-1} \text{ LiClO}_4$ PC-DME exhibited anomalously long-range interfacial liquid structure about 40nm, while that of $1 \text{ mol L}^{-1} \text{ LiClO}_4$ PC was 10nm and ionic concentration has little effect on the thickness of the interfacial liquid layer. It was consistent with the result of ^1H NMR relaxation measurement. It is the first time in our laboratory to measure the thickness of the interfacial liquid layer directly. The interfacial liquid layer thickness measured by RSM became almost the same order as the apparent average thickness at which liquid property change from bulk. It shows the effectiveness of the parameter based on a simple spatial model: apparent average thickness.

Based on the above, the ionic condensed system consisted of binary anion showed dramatically change in phase transition behavior compared with the ionic liquids composed by single anion. This is due to the competitive interaction with cation between two different anions which have different bulkiness and mobility. The condensed system of ion in condensed dispersion system showed the liquid layer of several tens nm exists in the vicinity of metal oxide solid surfaces. We revealed that the ion and metal oxide solid surfaces interact competitively with water molecules in the layer, and the way of influence on solvent molecules are different between them. The solid surfaces affect liquid properties heterogeneously. The condensed dispersion system based on binary solvent electrolyte, which was consisted of molecules with high dielectric permittivity and high donor number, exhibited anomalous long-range interfacial layer. The addition of DME, which is expected to improve the conductivities

of PC based solution, can turn out to show higher hindrance in ionic transport. We believe the above knowledge will contribute to the highly condensed system for next generation industry.

Publication list

Thermophysical Properties of Binary Aliphatic Quaternary Ammonium Ionic Liquids: TMPAFSA_xTFSA_{1-x}

Minoru Mizuhata, Nobuaki Kunikata, and Shigehito Deki

ECS Transaction, **25(39)**, 3, (2010).

Thermophysical Properties of Binary Amide Anion-Based Ionic Liquids; TMPAFSA_xTFSA_{1-x}

Nobuaki Kunikata, Kengo Tomioka, Hideshi Maki, and Minoru Mizuhata

Electrochemistry, **86(2)**, 92 (2018).

Properties of Concentrated Aqueous Electrolyte Solution in a Vicinal Region of Coexisting Solid Surface

Nobuaki Kunikata, Masaki Matsui, Hideshi Maki, and Minoru Mizuhata

ECS Transaction, **80(10)**, 1459, (2017).

Influence of coexisting metal oxide powder on spectroscopic properties of Zinc-based hydrate melt

Nobuaki Kunikata, Masaki Matsui, Hideshi Maki, and Minoru Mizuhata

in preparing (I am carrying out the final confirmation with co-author to submit to the

Journal of Physical Chemistry C in February.)

Dynamics of Non-aqueous LiClO₄ Electrolyte Nanoconfined by Silica Surfaces

Nobuaki Kunikata, Marie Takemoto, Motohiro Kasuya, Kazue Kurihara, Hideshi
Maki, and Minoru Mizuhata

*in preparing (I am carrying out the final confirmation with co-author to submit to the
Journal of Colloid and Interface Science in February.)*

Related publication

**In Situ Synthesis of a Supramolecular Hydrogelator at an Oil/Water Interface for
Stabilization and Stimuli-Induced Fusion of Microdroplets**

Yuki Nishida, Akiko Tanaka, Shota Yamamoto, Yudai Tominaga, Nobuaki Kunikata,
Minoru Mizuhata, and Tatsuo Maruyama

Angew. Chem. Int. Ed., **56**, 9410 (2017).

Presentation list

[1] Physico-chemical Properties for the Binary Ionic Liquids of TFSI-FSI

N. Kunikata, M. Mizuhata, S. Deki

The 3rd Workshop of Electrochemical Society of Kansai in 2008

[2] Physico-chemical Properties for the Binary Ionic Liquids of TFSA-FSA

M. Mizuhata, N. Kunikata, S. Deki

The 76th Spring Meeting of the Electrochemical Society Japan

**[3] Thermophysical and Structural Properties of Binary Ionic Liquids consisting of
TMPAFSA_xTFSA_{1-x}**

N. Kunikata, M. Mizuhata

The 53th Meeting of the Material Tailoring Society

**[4] Thermophysical Properties of Binary Aliphatic Quaternary Ammonium Ionic
Liquids : TMPAFSA_xTFSA_{1-x}(II)**

M. Mizuhata, N. Kunikata, S. Deki

216th ECS Meeting

**[5] Thermophysical Properties of Binary Aliphatic Quaternary Ammonium Ionic
Liquids : TMPAFSA_xTFSA_{1-x}**

M. Mizuhata, N. Kunikata, S. Deki

The 41th Symposium on Molten Salt Chemistry

[6] Physicochemical Properties for the Binary Ionic Liquids of TFSA-FSA (II)

N. Kunikata, M. Mizuhata

The 3rd Workshop of Electrochemical Society of Kansai in 2009

[7] Structure and functionalizing of ionic liquid in hetero phase systems

M. Mizuhata, N. Kunikata, K. Tomioka, T. Minowa, M. Maekawa, S. Deki

文部科学省科研費特定領域研究「イオン液体の科学」 2009 年度第 2 回全体会議

[8] Thermophysical Properties of Ionic Liquids Consisting of Amide Anions

N. Kunikata, M. Mizuhata

The 47th Symposium on Molten Salt Chemistry

[9] Properties of Concentrated Aqueous Electrolyte Solution Coexisting with Silica Nano Particle

N. Kunikata, H. Maki, M. Mizuhata

The 5th JACI/GSC Symposium

[10] Properties of Concentrated Aqueous Electrolyte Solution Coexisting with Silica Nano Particle

N. Kunikata, H. Maki, M. Mizuhata

The 76th Meeting of the Material Tailoring Society

[11] Properties of Concentrated Aqueous Electrolyte Solution Coexisting with Silica Nano Particle

N. Kunikata, H. Maki, M. Mizuhata

NGRC (Nucleation & Growth Research Conference) – International Workshop of

Electrochemical/Materials Processing for Renewable Energy –

[12] Properties of water molecule in hetero-phase coexisting system based on ZnSO₄ hydrate melt

N. Kunikata, H. Maki, M. Mizuhata

The 48th Symposium on Molten Salt Chemistry

[13] Behavior of water molecule in hetero-phase coexisting system based on

aqueous concentrated solution

N. Kunikata, H. Maki, M. Mizuhata

The 3rd Workshop of Electrochemical Society of Kansai in 2016

[14] Properties of water molecule in hetero-phase coexisting system based on aqueous concentrated solution and silica nanoparticles

N. Kunikata, M. Masaki, H. Maki, M. Mizuhata

The 84th Spring Meeting of the Electrochemical Society Japan

[15] Properties of ZnSO₄ hydrate melts coexisting with nanosilica powder

N. Kunikata, H. Maki, M. Mizuhata

The 77th Meeting of the Material Tailoring Society

[16] Influence of solid phase on structure of electrolyte in metal oxide powder/aqueous ZnSO₄ solution coexisting system

N. Kunikata, M. Masaki, H. Maki, M. Mizuhata

The 68th Divisional Meeting on Colloid and Interface Chemistry,

The Chemical Society of Japan

[17] Changes of solvation and intramolecular interaction in ZnSO₄-H₂O system coexisting with metal oxide nanoparticle

N. Kunikata, M. Masaki, H. Maki, M. Mizuhata

The Autumn Meeting of the Electrochemical Society of Japan

[18] Properties of Concentrated Aqueous Electrolyte Solution in a Vicinal Region of Coexisting Solid Surface

N. Kunikata, M. Masaki, H. Maki, M. Mizuhata

232nd ECS Meeting

[19] Influence of coexisting metal oxide powder on Raman properties of Zinc-based

hydrate melt

N. Kunikata, M. Masaki, H. Maki, M. Mizuhata

The 49th Symposium on Molten Salt Chemistry

[20] Influence of coexisting metal oxide powder on intermolecular interaction of Zinc-based hydrate melt

N. Kunikata, M. Masaki, H. Maki, M. Mizuhata

The 3rd Workshop of Electrochemical Society of Kansai in 2017

[21] Influence of coexisting metal oxide powder on spectroscopic properties of Zinc-based hydrate melt

N. Kunikata, M. Masaki, H. Maki, M. Mizuhata

The 85th Spring Meeting of the Electrochemical Society Japan

[22] Properties and interfacial behavior of condensed liquid system based on hydrate melt and ionic liquid

N. Kunikata

The 2nd Workshop of Electrochemical Society of Kansai in 2018

[23] Interfacial Behavior of Concentrated Solution in the Vicinity of Coexisting Metal Oxide

N. Kunikata, M. Takemoto, M. Kasuya, K. Kurihara, H. Maki, M. Mizuhata

2nd Bilateral Kobe-Kiel Workshop

[24] Hetero-phase coexisting effect in metal oxide powder/electrolyte solution dispersion system

N. Kunikata, M. Takemoto, M. Kasuya, H. Maki, M. Matsui, K. Kurihara,

M. Mizuhata

The workshop held in department of science

[25] Dynamic Properties of Non-aqueous Binary Solvent Electrolyte Solution in the Vicinity of Silica Surfaces

N. Kunikata, M. Takemoto, M. Kasuya, H. Maki, M. Matsui, K. Kurihara,

M. Mizuhata

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