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Accounts

Functional Design of Ionic Liquids

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Ionic liquids, molten salts at temperatures lower than 100 °C, preferably below room temperature, are unique liquids having very different characteristics from ordinary molecular liquids. Since these ionic liquids are prepared by coupling relatively large organic ions, there are many chances to create novel functionalities by changing structure of component ions. To develop such novel and functional ionic liquids, we first developed a facile preparation method, i.e., neutralization of tertiary amines with organic acids. By this convenient method, we prepared hundreds of salts having low melting points. We, then, tried to prepare ionic salts containing small ions such as lithium cation, proton, or chloride anion. Because small ions received stronger electrostatic force due to higher surface charge density, which results in the formation of salts with higher melting points, case must be taken. Ionic liquids containing halogen-free salts are another interesting subject to challenge from the viewpoint of environmentally friendly materials. Heteroaromatic rings such as azolates gave excellent ionic liquids having very low viscosity by coupling with suitable cations. Amino acids have also been used as anions to prepare salts with low melting points or amorphous glasses. They are helpful to analyze the relationship between ion structure and characteristics of the salts. Zwitterions, in which both cation and anion were tethered with a covalent bond, were prepared to function as ionic liquids. These ions should not migrate under a potential gradient and should be an excellent ion conductive matrix for added ions. Tethering of ions caused the T_m to be high, and the zwitterions with melting points around room temperature have not been synthesized yet. However, lots of solid zwitterions became liquids by adding suitable solid salts or acid such as lithium bis(trifluoromethanesulfonyl)imide. In this mixture, lithium cations had a transport number higher than 0.5, meaning that the lithium cations are the major mobile ions in the mixture. Some of the functionality is achieved by dimension control, such as polymerization of ions, and so on. Other functional modifications and design of ionic liquids are also mentioned.

Introduction

Ionic liquids, which are room temperature molten salts, have gained in interest because of their unique properties. The science of molten salts has been important research area for nuclear science and electrochemistry; however, they have been studied at relatively high temperatures, so-called "high-temperature melts or molten salts." Also, low-temperature melts have long history, but they are not stable in air. Therefore, the applications are limited. In 1992, air- and water-stable molten salts were reported.[1] 1-Ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]) has a melting point of 15 °C. The report gained little attention when it was published. However, the numbers of papers on the stable ionic liquids increased exponentially after 2000. More than 1000 papers related to the ionic liquids were published in 2004, and the number of papers is still increasing. The initial stage of the development of ionic liquids was briefly summarized with personal aspects by Wilkes.[2] This explosive increase in interest on the ionic liquids is attributable to the possibility of these charming materials.

Ionic liquids have been developed primarily for use as solvents in chemical reactions. There are lots of papers and several reviews on the basic study of these ionic liquids as reaction solvents.[3–8] It is noteworthy that several chemical reactions occur in ionic liquids, but, at the same time, there are only a few types of ionic liquids have been studied. Enzymatic inverse reactions in ionic liquids have been studied, and several hydrolytic enzymes have been developed as catalysts for the inverse reactions in water-free ionic liquids.[9] Related to the bio-related reactions in ionic liquids, an increasing number of studies on the solubilization of bio-derived materials as well as proteins have been published. The development of ionic liquids as solvent substitutes for water in biological fields will meet a big success in science and technology. The bio-related studies in ionic liquids will be summarized in the near future. Solubilization of gas molecules is another interesting subject for ionic liquids, and some ionic liquids have been used as gas absorbents. It is known that carbon dioxide has the highest solubility compared to other gas molecules.[10] As well, they have been used for both gas separation and concentration. Ionic liquids have been specifically designed to have an affinity for certain gas.[11] The combination of ionic liquids with supercritical fluids has the potential to general processes for reaction, separation, transport, etc. It is important to understand

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the structure–property relationship for many ionic liquids.

On the other hand, since ionic liquids are composed of only ions, they should be able to act as substituents for electrolyte solutions. Ionic liquids are non-volatile, which is a great advantage over electrolyte solutions and important for the preparation of safe energy devices such as batteries, capacitors, etc. In addition to these applications, there are many other interesting uses for ionic liquids. Because the characteristics of ionic liquids are different from these of ordinary molecular liquids, like water and organic solvents, and atomic liquids, like mercury, new fields of technology have opened up. In spite of the rapid increase in the number of publications, only a few kinds of ionic liquids have been used. In order to understand the structure–property relationship of ionic liquids, a variety of ionic liquids is needed. Synthetic chemistry has the potential to accelerate the evolution of ionic liquids from simple non-volatile liquids to functional liquids. In this accounts, the design and evaluation of several functional ionic liquids are mentioned.

Initial Stage of Liquidization of Salts with the Aid of Polyether Chains

Polyethers, simple polymer structure, have been used in a wide variety of fields from industrial aspects to pharmaceutical field[12] because of their biphasic characteristics, i.e., they are both hydrophilic and hydrophobic. Similar to water, polyethers especially poly(ethylene oxide)s (PEOs) coordinate to cations through ion–dipole interactions. This complex formation led to the design of ion conductive polymers,[13] and thousands of papers have been published on PEO-based ion conductive polymers. Since there are a few reviews and books on PEO-materials,[14–17] I do not want to mention them in detail here. However, the following PEO-derivatives should be mentioned due to their applications as functional ion conductive polymers. In 1993, Dr. Kaori Ito and I discussed the preparation of functional PEO derivatives having cation conductive characteristics. We designed PEO chains having charge unit(s) on the chain end(s), called polyether/salt hybrids.[18–33] The properties of this hybrid varied dramatically depending on the ion structure at the chain end, PEO chain length, etc. Especially, the average molecular weight of PEO is a key parameter governing the phase of the hybrids.[19] PEO molecular weight dependence on the melting point of a PEO/salt hybrid is almost the same regardless of terminal salt structures. Figure 1 shows the phase change of PEOs having sulfonate salt structure on both chain ends.[24] The hybrid is a crystal-like solid when shorter PEO chains are used (left-hand side of Fig. 1). It was also solid when longer PEO chain was hybridized with salt unit (right-hand side of Fig. 1) because it resembles a pure but long PEO chain. Interestingly, hybrids composed of a medium size PEO chain, around 500–1000 in molecular weight, was liquid (Fig. 1, center). The biggest factor to influence the phase of the PEO/salt hybrid is the average molecular weight of the PEO chains. The molecular weight range of PEO to give a liquid hybrid slightly depended on the salt structure. The structure–property relationship of these polyether/salt hybrids was first studied by Dr. Kaori Ito. We have prepared PEO hybrids having carboxylate,[18,19] sulfonate,[19,20] benzenesulfonate,[22] sulfonamide,[20,23] and so on. A wide variety of polyether/salt hybrids have been studied by Dr. Yoichi Tominaga. A few derivatives of the hybrids having anion(s) on the PEO chain are shown in Fig. 2. All of the hybrids are cation conductive materials, but they have different characteristics. Because several hybrids have been prepared with cationic charges on the PEO chain end and different structures, it is possible to study in detail the relationship between structure and property. Even PEO/salt hybrid polymers (**1d**) and their networks have been prepared.[31,32] Use of poly(propylene oxide) (PPO) instead of PEO was effective in lowering the T_g in a series of hybrids. However, the ionic conductivity of these PPO/salt hybrids was not as high as expected. This was attributed to the lower polarity of the PPO than PEO. Dr. Tomonobu Mizumo has attempted to improve the characteristics of the PPO/salt hybrids, which are presented elsewhere, but they strongly depend on the shape of the hybrid. Several kinds of cationic units have been attached to PEO chains,[25,27] and there are basically three different types of hybrids: cation-tethered PEO, anion-tethered PEO, and their mixture. Based on Figs. 2 and 3, there is a variety of ion conductive derivatives and/or matrices. Hybridization with PEO enables us to prepare liquid salts from any kind of organic salt. Even dialkylviologens were liqui-

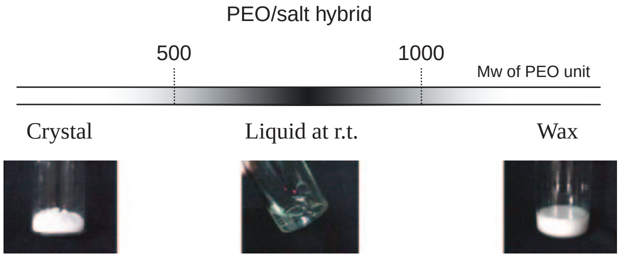


Fig. 1. PEO molecular weight dependence of melting point of PEO/salt hybrid (Scheme).

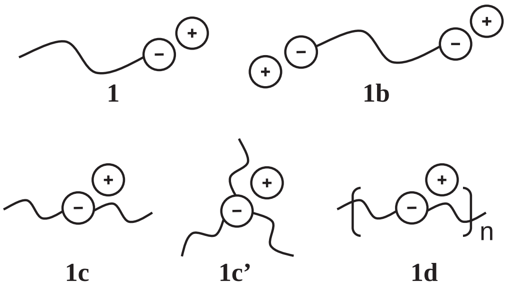


Fig. 2. Some examples of cation conductive PEO/salt hybrids (Scheme).

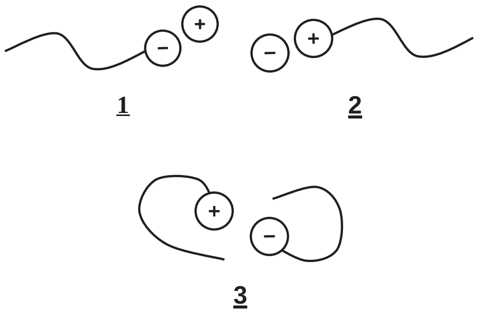


Fig. 3. Classification of PEO/salt hybrids.

dized by this method (like **2** in Fig. 3).[21]

In Fig. 3 (**3**), imidazolium cation and sulfonamide anion were individually tethered to the PEO chain end to form PEO/salt hybrid with lower glass transition temperatures (T_g).[27,34] In the early 1990's, some imidazolium-type ionic liquids were reported to have low melting point, and although we read the papers on these ionic liquids, we insisted on using PEO chains for the preparation of ion conductive matrices. Nevertheless, imidazolium-type ionic liquids are interesting, and we have slightly changed our starting molecules from PEO derivatives to imidazolium salts with low T_m, which were called room temperature molten salts at that time. Then, in 1996, Dr. Kaori Ito and Mr. Yoshikazu Nakai introduced the imidazolium cation and sulfonate anion to form an ionic liquid at the end of PEO chains expecting low T_g and high ionic conductivity after mixing these PEO/salt hybrids, Fig. 3 (**3**). However, we were able to prepare a matrix having a low T_g, and small ions were shown to migrate not in the PEO domains but in the ionic liquid phase. The results prompted us to develop ion conductive polymers based not only on polyethers but also on ionic liquids. Details will also be mentioned elsewhere.

For any (organic) salt, it is possible to make a liquid salt by forming hybrids with PEO chains. The PEO/salt hybrids were initially single ion conductors. A cation conductive hybrid can be prepared by the hybridizing of PEO chain with anionic site. In these anion-bound PEO chains, there are free counter cations, and these cations can migrate in the PEO matrix. The ionic conductivity of these PEO/salt hybrids is the function of their structure. Especially, terminal salt structure is important because of the degree of dissociation directly influences the number of mobile ions. Figure 4 shows Arrhenius plots of the ionic conductivity of a series of PEO/salt hybrids having different terminal salt units.[20] A hybrid that has a highly dissociable salt unit at the terminal has a higher ionic conductivity, and the radius of the alkali metal cations in the same hybrid had an effect on the ionic conductivity.[19] Interestingly, the larger alkali metal cations migrate faster in the hybrid, which is similar to the mixture of salts and linear PEOs.[35] This is attributed to the degree of ion–dipole interactions. Larger cations have lower surface charge density, and accordingly, they received weaker coordination force from ether oxygen units.[35] A small increase in the degree of dissociation for larger cations also contributed to the increase in the ionic conductivity. In addition, the PEO chain length affected the bulk viscosity, in other words, diffusion coefficient of counter ions. The PEO structure affects the conductivity of the ions, and these have been a few reports on how to improve the ionic conductivity.[20] The development of PEO based ion conductive polymers will be reviewed in the near future. Study on the PEO chains considerably influenced to my later studies on the ionic liquids. As mentioned above, the characteristics of air stable ionic liquids are quite attractive, and this material has been extensively studied in our laboratory.

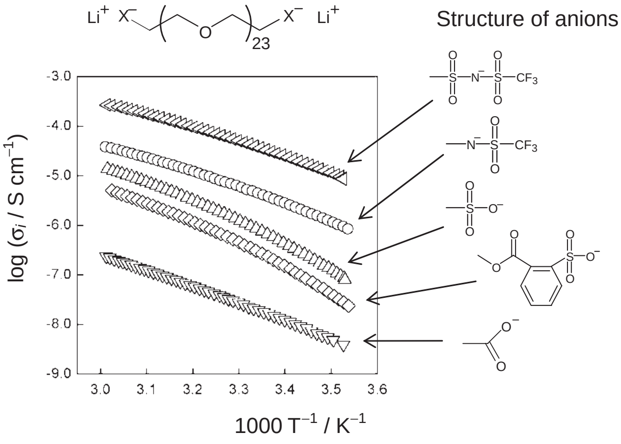


Fig. 4. Arrhenius plots of the ionic conductivity for a series of cation conductive PEO/salt hybrids.

Key Factors to Lower Melting Point of Salts

The major interaction forces in crystalline salts are electrostatic, and they are much stronger than other secondary binding forces. Thus, electrostatic forces have a big effect on the physical and thermal characteristics of the salts. To suppress the crystallization of ions, certain aspects of the ion structure must be considered. Most important is the size of ions. Since the electrostatic forces are a function of the surface charge density of the ions, larger ions generally receive weaker electrostatic forces. This tendency is easily seen by comparing the T_m of alkali metal chloride salts, i.e., NaCl ($T_m = 801\,°C$), KCl (770 °C), and CsCl (645 °C). However, the structure of organic ions is not simple, and the surface charge density is not a simple function of the formal weight. Table 1 shows the melting points of a few representative salts. The melting point of tetrapropylammonium chloride ($(Pr)_4NCl$) is 241 °C which cannot be explained simply by the ion size. Thus, we must also consider the shape of the ions. There are many studies on the thermal properties of organic salts, and suitable structures of ions were proposed in order to prepare excellent ionic liquids. Planar ions, such as imidazolium cation, are suitable for lowering the T_m. For example, 1-ethyl-3-methylimidazolium chloride ([emim][Cl]) melts at 87 °C, and [emim][Cl] has been categorized as an ionic liquid in Europe and US. The anions are also important for lowering the T_m. [emim][nitrate] and [emim][BF_4] had a T_m of 38 and 15 °C, respectively, and [emim][BF_4] has been categorized as an ionic liquid in Japan. The general definition of "ionic liquids" in Japan is "molten salts at room temperature." Further attempts to lower T_m were carried out by using larger anions such as TFSI anion (see

Table 1. Melting Point of Some Salts

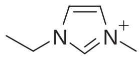
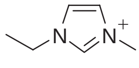
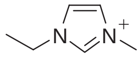
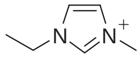
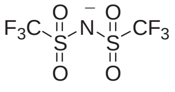
Cation	Anion	T_m/°C
Na^+	Cl^-	801
Cs^+	Cl^-	645
$(Pr)_4N^+$	Cl^-	241
	Cl^-	87
	NO_3^-	38
	BF_4^-	15
		−3

Table 1). The T_m of [emim][TFSI] is surprisingly low with values reported between −3 and −15 °C probably depending on the contaminants including water. It is noteworthy that this is a liquid salt near the freezing temperature of water. There are now several ionic liquids having a T_m below zero degrees.

In addition, conformational rotation of alkyl chains on the ions might be the third factor for lowering the T_m of the corresponding salts. Accordingly, ions having relatively longer alkyl chains form salts with low T_m or amorphous salts showing only glass transition temperature (T_g), e.g., a few imidazolium salts. Many ionic surfactants are potential candidates for the preparation of ionic liquids. Although the introduction of alkyl chains onto the ions is an easy way to prepare these molten salts, that generally have rather high viscosities. Such viscous ionic liquids are needed for some research fields such as tribology.

Since there are a few steric factors that suppress crystallization, a combination of these factors may afford new ionic liquids. It should be emphasized here that there are millions of different ions and their combinations are limitless, and the number of known ionic liquids is probably less than two thousand, which means there is still a chance to discover new ionic liquids. Mixing different salts is another strategy to achieve a lower T_m, and these salts are known as eutectic salts. Basic physicochemical data is important for preparing eutectic salts. Degree of dissociation of the salt unit is also important, and there are a few strategies to lower the T_m. Some of them have produced salts with very low dissociation constants in the bulk, and these salts have low T_m or T_g. However, they are gradually becoming rather organic in nature. In the near future, a protocol based on ion structure will be developed for preparing excellent ionic liquids.

Properties of Typical Ionic Liquids

Ionic liquids are defined as salts having a T_m lower than 100 °C in both Europe and the U.S.A. As mentioned above, the definition of "ionic liquids" is much stricter in Japan than other countries, i.e., they should be salts with T_m lower than room temperature (around 25 °C). For example, [emim][BF_4], mentioned in the Introduction, has a T_m of 15 °C. The properties of ionic liquids are considerably different from those of molecular liquids. The most interesting feature of the ionic liquids is the lack of vapor pressure. Since ionic liquids are composed of only ions, it takes a considerable amount of energy to vaporize the ion. The energy is easily estimated to be larger than the electrostatic forces for the ions to exist as ion pairs. However, ions are considerably stabilized by a pseudo-lattice which minimizes the lattice energy of the salts similar to ionic crystals. Accordingly, the vaporization force is much larger than the electrostatic force between a cation and an anion. This extraordinarily large stabilization is the reason for thermal stability of ionic liquids. This accounts for such properties as no-vapor pressure at temperatures up to 400 °C and non-flammability. Since even ionic liquids ignite after decomposition, the word "non-flammability" is not suitable to express characteristics of the ionic liquids. It is therefore better to use "flame-retardancy" or "high flame resistance." Anyways, the ionic liquids are stable over a wide temperature range with negligibly small vapor pressure, Fig. 5. During the preparation of this manuscript, Prof. Seddon and his international collaborators reported that "many" ionic liquids can be distilled under high vacuum.[36] For example, a series of [dialkylimidazolium]-[TFSI] salts were distilled at 300 °C under high vacuum (800–500 Pa). Prof. Seddon commented at the 231st American Chemical Society Meeting in Atlanta (March 2006) that ionic liquids in vapor phase might not be ion pairs but aggregate ions. We should also consider the volatility with respect to the nature of ionic liquids, i.e., there are different mechanisms expected for protic ionic liquids and aprotic ones as Prof. Seddon mentioned in his recent Nature paper.[36] In the case of protic ionic liquids, they are distillable because they are in an equilibrium state between salt and an acid/base pair.[37] Although a detailed discussion will be reported soon, there are several discussions concerning the volatility of ionic liquids.[38] There are not many common characteristics of ionic liquids but lots of exceptions. At the same time, it is important to understand that there is no "ideal ionic liquid" having all of unique characteristics that have been frequently written in many papers such as low melting point, high decomposition temperature, low viscosity, high polarity, high density, non-flammability, high ionic conductivity, etc. These papers should be noted but not followed blindly. Basic researches will uncover the true properties of ionic liquids.

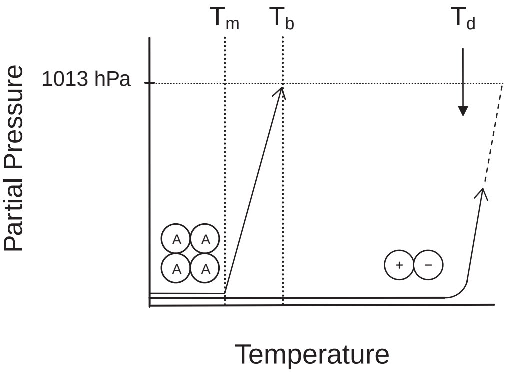


Fig. 5. Relationship between the temperature and vapor pressure of a molecular liquid (expressed as A) and that of ionic liquid (scheme).

The viscosity of an ionic liquid is remarkably low from the viewpoint of the strong electrostatic interaction forces among ions. Since component ions are surrounded by the oppositely charged ions, the motion of component ions is basically restricted. Although these ions are stabilized, the viscosity strongly depends on the structure of the component ions, and only a few ionic liquids have very low viscosity. The relationship between the component ion structure and the viscosity is not fully understood, probably because there are several parameters, such as shape of ions, charge density, contribution of other interaction forces, conformational change of alkyl chain, etc, involved.

Ionic conductivity of ionic liquids is equal to the number of ions times their mobility. Since ionic liquids are composed of only ions, the number of ions per volume is larger than that for ordinary salt solution. However, the number is not as large as expected from the fact that ionic liquids contain no solvent molecules due to relatively large formula weight. Mobility

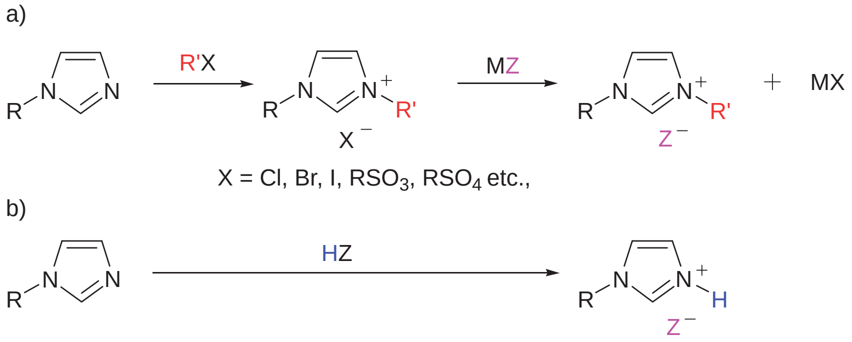


Fig. 6. Two different preparation routes for ionic liquids: (a) quaternization of tertiary amines followed by anion exchange, (b) neutralization of amines.

of the component ions in the ionic liquids reflects the viscosity, and considering these two characteristics, ionic liquids are expected to have high ionic conductivity. There are several ionic liquids having ionic conductivity higher than 10^{-2} S cm^{-1}. Ion conductive and non-volatile liquids could replace electrolyte solutions, especially in energy conversion devices such as batteries, capacitors, etc. However, every device requires different characteristics from the ionic liquids; the known ionic liquids cannot be used immediately for these devices. For example, a lithium ion battery requires an electrolyte solution in which lithium cations are preferentially transported.

It should be noted here that the ionic liquids are promising liquids; there are still a few steps to optimize the characteristics to satisfy current requirements. In addition, there is no ideal ionic liquid to satisfy all the requirements such as stability up to 450 °C, electrochemical stability in a wide potential range (so-called wide potential window), low viscosity, high ionic conductivity, and target ion transport. Furthermore, toxicity, purity, price, etc. must also be considered. It is important to match the required characteristics to the ionic liquids through structural design.

Preparation of Model Salts by Neutralization

Preparation of ionic liquids looks easy but is practically rather difficult. Quaternized ammonium salts are generally prepared by the reaction of tertiary amines with alkyl halides. The formed quaternized cations accompanied halide anions as counter ions. Small ions, like chloride or bromide anions, are not good anions for the preparation of ionic liquids with low T_m. Accordingly, substitution of the anions with suitable ones should be required for excellent ionic liquids (Fig. 6a). The complete anion substitution of organic salts is not so easy, and small amount of contaminant ions remain in the target salts. Hydrophobic salts are rather easy to purify by simple washing with water because generated salts as by-products are water-soluble. Water-soluble ionic liquids therefore need specific purification methods. This purification process can be skipped by improving the synthesis route. For example, methyl- (or ethyl-) esters or organic acids are directly reacted with tertiary amines to form quaternized salts having desired anions derived from acid esters.[39] For this reaction, it is very easy to form salts, but the number of acid esters is limited and problematic when several ionic liquids with variety of anions are required. However, there are several different acid esters reported to be effective for the preparation of ionic liquids.

We have proposed a very simple method to synthesize model salts. Neutralization of tertiary amines with suitable acids gave salts composed of protonated ammonium cations and corresponding acid anions (see Fig. 6b).[40] The preparation is easy, just mixing these two components equimolarly. Generally, the amine and acid were separately dissolved in ethyl alcohol. The solutions were slowly mixed and stirred. Slightly the solution was concentrated by evaporation and dehydrated diethyl ether was added. The two layers and precipitates were separated and washed with the proper solvents (depended on the salt species). The salts were then dried in vacuum for 2 days at 60 °C. Nothing was generated as by-products, and pure salts were prepared and purified by drying while heating. Most of the generated salts were stable and excess molecular components were removed by vacuum drying if needed.

Table 2 shows the characteristics of some of the neutralized salts prepared by the equimolar mixing of tertiary amines and HBF_4. For example, T_m of 1-methylimidazole neutralized with HBF_4 was 36.9 °C. Some of the amines are new candidates for preparing ionic liquids. For example, 2-methyl-1-pyrroline and 1-methylpyrazole were neutralized with HBF_4 to give salts with T_m at 17.1 and −5.9 °C, respectively.[40] It is interesting to compare the T_m of amines before and after protonation. The difference in melting points between the molecules and the salts is quite remarkable. For example, butane and sodium chloride have almost the same formula weight of 60. The melting points of butane and sodium chloride are −138.5 °C and about 800 °C, respectively. The big difference (above 900 °C) is attributed to the interaction forces among the components. Namely, the electrostatic forces are much stronger than any other interaction force such as hydrogen bonding, van der Waals force, and so on. Accordingly, amines should show much higher T_m after salt formation. Interestingly, the increase in T_m (<150 °C) is not so large when the amines were neutralized with HBF_4.[41] Quite possibly, a more suitable acid is needed. In particular, neutralized 1-ethyl-2-phenylindole and 1,2-dimethylindole had lower T_m values.

Neutralization is very easy and is therefore a potential method for preparing model salts. Among the many neutralized salts prepared by the method as mentioned above, some amines are excellent candidates, and thus, ionic liquids should be prepared by the quaternization of these selected amines. There are a few excellent anions for the preparation of ionic

Table 2. Properties of Starting Tertiary Amines and Their Salts Neutralized with HBF_4

Starting amines	Before neutralization		After neutralization with HBF_4			
	T_g/°C	T_m/°C	T_g/°C	T_m/°C	σ_i[a)]/mS cm^{-1}	η[a)]/cP
1-Methylimidazole	—	−14	—	37		
1-Ethylimidazole			−87	—		41
1,2-Dimethylimidazole			−97	—		100
1-Ethyl-2-methylimidazole			−88	—		67
1-Benzyl-2-ethylimidazole			−43	—		
1-Methylpyrrolidine	—	−95	—	−32	16	46
2-Methyl-1-pyrroline	−133	—	−94	17	16	38
1-Methylpyrazole	−125	−44	−109	−6	35	
1-Ethyl-2-phenylindole	8	86	−74	30	16	
1,2-Dimethylindole	—	56	−75	25	11	

a) 25 °C.

liquids, and their acids can be used to neutralize the selected amines.[42] It should be easier to prepare ionic liquids by this method and the probability is much higher than that for random coupling of cations and anions.

Polarity of ionic liquids is quite important when selecting them for specific applications, and there are several methods to measure the polarity. Since it is theoretically impossible to measure the dielectric constants of conductive materials, polarity should be evaluated by other methods. The most convenient method is spectroscopy. Especially, solvatochromism of some dye molecules is used most in this field.[43] The polarity of most ionic liquids has been estimated by this solvatochromism of dye molecules such as Reichardt dye.[44] These dye molecules cannot be used with neutralized amines, because all these dyes are bleached by protons in the system. This means that these neutralized amines are "protic ionic liquids." To evaluate the polarity of these protic ionic liquids, models of ionic liquids or ionic liquids containing active protons, we analyzed several different dye molecules to find suitable and durable one in such a condition. After evaluating lots of dye molecules, Nile red was found to be suitable for such salts having dissociable protons.[45] It should be noted here that the polarity measurement by the solvatochromism depends on the dye molecules, and therefore, a few dye molecules should be used to analyze the polarity, proton-donating ability, proton-accepting ability, and so on. It is rather dangerous to estimate the polarity of ionic liquids with only one dye molecule.

Liquidization of Small Ions

According to physical chemistry, electrostatic interaction forces can be lowered by lowering the surface charge density, i.e., increasing the corresponding ion radius. In other words, small ions, such as lithium cation (Li^+), proton (H^+), and chloride anion (Cl^-), form salts or acids with relatively higher melting points than those for salts with other larger ions. However, these small ions are inevitably important for a variety of applications such as lithium (ion) batteries, fuel cells, and polar solvents. In above-mentioned systems, fast ion transport or low viscosity is strongly required. However, the increase in electrostatic interaction makes it difficult. For example, in the case of Li^+ transport systems, it is easy to imagine adding lithium salts to some low-viscous ionic liquids expecting fast migration of Li^+ in the mixture. It is important to confirm the difference between ionic liquids and molecular solvents. Namely, in ordinary molecular solutions containing salts, there are only two major ion species: cation and anion that are generated from the added salt. In contrast, in the ionic liquids, there are component ions of the ionic liquids as well as ions generated from the added salts. For example, if a lithium salt is added into imidazolium-type ionic liquid, both imidazolium cation and Li^+ behave as "cations" in the salt/ionic liquid mixture. It is, therefore, impossible to transport Li^+ selectively in ordinary salt/ionic liquid mixture under potential gradient. Furthermore, the solubility of inorganic salts in ionic liquids is generally not very high, and addition of the lithium salt induces an increase in viscosity, an elevation of the melting point, and phase separation. Therefore, it is necessary to prepare ionic liquids inherently containing small ions that are transported selectively. Again, electrostatic interaction forces become stronger when the corresponding ion radius is reduced. So, how can we prepare ionic liquids containing some small ions such as Li^+ and H^+?

There are a few strategies to lower the T_m of salts having small ions as component ions. A convenient one is the preparation of PEO/salt hybrids. As already mentioned above, PEO/sulfonate hybrids are liquid when PEOs with average molecular weights of 500–1000 were used.[19] PEO-tethering is relatively easy, and not only cations but also anions can be liquidized by selecting suitable PEO-tethered anion and cation, respectively. However, the hybrids are very viscous. PEO chains are inherently viscous, and the ion–dipole interaction between alkali metal cations and ether oxygens further increased the viscosity. Relatively lower decomposition temperature of PEO derivatives (<250 °C) is another drawback for liquidizing small ions. The ether bond is not strong, and so, PEO chain modification is effective only under limited conditions.

We have tried to synthesize ionic liquids with small ions. However, coupling of Li^+, for example, and a monovalent anion leads salts with relatively high T_m. As seen in Fig. 7, Dr. Wataru Ogihara then proposed to couple a divalent anion and a monovalent cation like imidazolium cation together with Li^+. It is difficult to form an ionic liquid with multivalent ions because of their very strong electrostatic attractive force, and it was actually quite difficult to find suitable organic cations for this purpose. However, 1-ethylimidazolium lithium sulfate (see Fig. 7)[46] afforded a liquid salt. Although the salts were

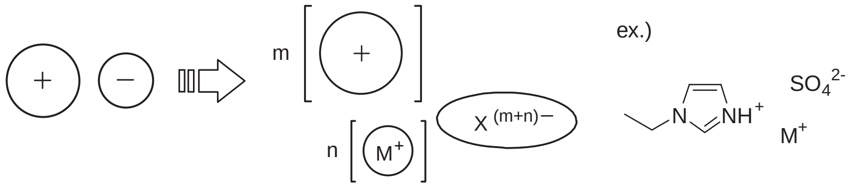


Fig. 7. Development of ionic liquids from those composed of monovalent ions to those of multivalent ions. Typical example is protonated ethylimidazolium sulfate.

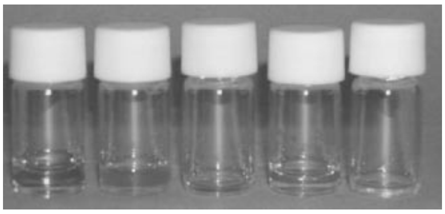
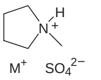


Fig. 8. Ionic liquids containing alkali metal ions; ([eHim/M][SO_4]). From left to right; M = H, Li, Na, K, and Cs.

Table 3. Properties of Ionic Liquids Containing Several Small Inorganic Cations

	EImMSO4		MPyMSO4	
	T_g/°C	$\sigma_i$$^{a)}$/mS cm^{-1}	T_g/°C	$\sigma_i$$^{a)}$/mS cm^{-1}
M = H	−75	0.236	−96	1.46
Li	−60	0.054	−78	1.69
Na	−68	0.180	−82	1.74
K	−67	0.174	−85	1.93
Rb	−55	0.030	−85	1.32
Cs	−59	0.059	−84	2.10

a) 25 °C.

liquid, the bulk viscosity was obviously high due to strong electrostatic forces. Preparation of liquid salts was possible using the combination of ethylimidazolium cation and hydrogensulfate for not only Li^+ but also Na^+, K^+, Rb^+, Cs^+, and even H^+, Fig. 8. Typical properties of [ethylimidazolium]-[alkali metal hydrogensulfate] ([eHim/M][SO_4]) are summarized in Table 3. The ionic conductivity of these salts was around 10^{-4} S cm^{-1} at room temperature. Their viscosity was not low enough, but they showed moderate ionic conductivity which is reflected by their low glass transition temperature (T_g), Table 3.

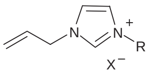
There are however several other possibilities for obtaining less viscous ionic liquids containing small ions because there are limitless combinations of organic ions. In spite of the tremendous number of cation candidates, there are only small numbers of cations that afford liquid salts of this kind, Fig. 7. Improvement in both T_g and ionic conductivity occurred when 1-methylpyrrolidinium cation was used instead of imidazolium cation.[47] This strongly suggests that thermally stable lithium ion conductive liquid will be prepared in the near future. A similar organic cation was used to prepare a liquid proton transport system. The proton-conductive liquids with wide liquidus temperature range can be used as thermally stable electrolytes for fuel cells.

These results opened some possibilities to apply ionic liquids as electrolyte solution substituents for not only lithium ion batteries but also fuel cells. Since the proton conduction in fuel cells being vigorously explored has depended on hydrated polymer membranes, performance is not guarantied at temperatures higher than 120 °C. Due to the vaporization of water molecules at high temperature, the driving conditions are limited, and a thermally stable proton conductive matrix is being required. Proton conductive ionic liquids should be useable. The solution viscosity of this ionic liquid must be reduced in order to improve the conductivity. The bulk viscosity of all these ethylimidazolium alkali metal hydrogensulfates ([eHim/M][SO_4]) was above 1000 cP at room temperature. Further searches for suitable cations led to the protonated *N*-methylpyrrolidinium (mHPy) cation. By using the mHPy cation, bulk viscosity of the corresponding salts was lowered, for example, the viscosity of [mHPy/Li] [SO_4] was 854 cP at 45 °C. As expected, the ionic conductivity of [mHPy/Li] [SO_4] was higher than that of [eHim/Li][SO_4]. Introduction of these small cation conductive ionic liquids into polymer films will be mentioned later.

Liquidization of small anions especially chloride anion, is important for developing ionic liquids that act as polar solvents. As mentioned later, 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) is a potential polar ionic liquid.[48] Although T_m of [bmim][Cl] (around 40 °C) is lower than that of [emim]-[Cl], [bmim][Cl] is still a solid at room temperature and it must be heated before using as a solvent. Dr. Noriyoshi Matsumi and Dr. Tomonobu Mizumo synthesized very low-viscosity ionic liquids[49] through the development of functional ionic liquids. 1,3-Diallylimidazolium chloride ([aaim][Cl]; Fig. 9) melts at 21.5 °C and has a viscosity of 1200 cP at 25 °C. This allylimidazolium cation effectively lowers the solution viscosity of the chloride salt.[49] As seen in Table 4, a series of imidazolium cations having allyl group(s) have very low viscosity. For example, 1,3-diallylimidazolium TFSI ([aaim][TFSI]) has a bulk viscosity of 31 cP at 25 °C. The effect of allyl group is outstanding and neither propyl nor propargyl groups caused a low viscosity for the corresponding salts. 1,3-Dipropargylimidazolium bromide has a T_m of 142 °C.[49] These data clearly show that conformational rotation of allyl group effectively suppresses the crystallization of the corresponding imidazolium salts. 1-Allyl-3-methylimidazolium halides and 1,3-diallylimidazolium bromide have already been reported.[50,51] The authors, however, simply mentioned that some of these salts

Fig. 9. Structure of 1,3-diallylimidazolium chloride ([aaim]-[Cl]).

Table 4. Thermal and Electrochemical Properties of a Series of 1-Allylimidazolium Type Ionic Liquids

		T_g /°C	T_m /°C	σ_ia) /mS cm^{-1}	ηa) /cP
R	X^-				
$CH_2=CH–CH_2–$	Cl^-	−68.3	21.5	0.58	1198
$CH_3–$	Br^-	−65.5	53.1	1.55	852
$CH_3CH_2–$	Br^-	−69.0	—	1.05	723
$CH_3CH_2CH_2–$	Br^-	−67.0	29.5	0.48	1665
$CH_2=CH–CH_2–$	Br^-	−67.9	—	0.74	827
$CH_2=CH–CH_2–$	I^-	−72.1	—	1.21	
$CH_2=CH–CH_2–$	$TFSI^-$	−91.6	—	2.48	31

a) 25 °C.

were obtained as a liquid. The other halide anions have also been used to prepare liquid salts by combining with the 1,3-diallylimidazolium cation. Introduction of only one allyl group is effective, and other derivatives, such as 1-allyl-3-alkylimidazolium cations, are also effective.

Halogen-Free Ionic Liquids

For the preparation of ionic liquids with low viscosity, most of the anions include a halogen, especially fluorine. The electron-withdrawing effect of fluorine atoms onto the anionic structure is useful for delocalizing the anionic charge. By comparing the T_m of a salt with ordinary anion to that with fluorinated anion, the electron-withdrawing effect is obvious when the fluorine atoms were located near the anionic charge to attract the electrons. In spite of this electron-withdrawing effect of halogen atoms, there are some requirements to prepare ionic liquids without the aid of these halogen atoms due to non-favorable effect in combustion process or other treatments. It is easy to prepare halogen free salts; however, their properties are generally not so attractive. It is therefore important to look for better anions.

Some ionic liquids have been prepared without the aid of halogen atoms. The first report of one such ionic liquid involved the preparation of methylamine nitrate by Walden.[52] A few of the halogen-free salts with a low T_m have been prepared with nitrate, carboxylate, sulfonate, etc. It should be mentioned here that the degree of dissociation of the corresponding salts is important because the dissociation degree influenced the polarity, viscosity, diffusion coefficient, ionic conductivity, etc.

One interesting approach for the halogen-free ionic liquids is the use of azolates.[53] Some heteroaromatic rings can be used as acids and be coupled with suitable cations like imidazolium cations. Dr. Masahiro Yoshizawa and Dr. Wataru Ogihara synthesized some imidazolium azolates.[53] The basic characteristics of two representative salts are shown in Table 5. It is interesting that triazole and tetrazole act as acids to afford suitable anions for low-temperature ionic liquids. Salts obtained in this experiment showed very low viscosity, Table 5. Their viscosity is almost equivalent to that of [emim][TFSI]. Furthermore, since triazole and tetrazole are explosive compounds, the ionic liquids are expected to be a type of energetic fluid, and Rogers et al. have researched ways to stabilize the azolates.[54]

Table 5. Properties of Azolate Type Ionic Liquids

	Anion	T_g/°C	T_d/°C	ηa)/cP	σ_ia)/mS cm^{-1}
EMImTri		−76	207	60	1.47
EMImTet		−89	—b)	43	8.68

a) 25 °C. b) Not measured.

Amino Acid Ionic Liquids

As mentioned above, there are many kinds of anions that can be used to form ionic liquids without the aid of the electron-withdrawing properties of halogens, and carboxylates were useable depending on the cation structure. Mr. Kenta Fukumoto and Dr. Masahiro Yoshizawa used amino acids because they have a common unit structure and variety of side chains. These characteristics are quite useful to analyze the effect of anion structure on the properties of the corresponding salts. Similarly, amino groups in all of these amino acids can be chemically modified. Similarly, amino acids can be used as cations, and in that case, both side chains and the carboxylic acid group should be useful to introduce functionality. They are also less expensive and bio-related materials.

Preparation of amino acid ionic liquids (AAILs) is not difficult.[55] 1-Methylimidazole was quaternized with ethyl bromide to prepare 1-ethyl-3-methylimidazolium bromide. The bromide anion of the salt was exchanged with hydroxide by passing an aqueous solution of the salt through a column filled with anion exchange resins (Amberlite). Since 1-ethyl-3-methylimidazolium hydroxide ([emim]OH) was not stable when it was concentrated, a dilute aqueous solution of [emim]OH was slowly poured into an aqueous solution of corresponding amino acid. After gentle stirring for several hours, the water was removed under reduced pressure at 50 °C. The amino acids did not appear to racemize upon heating, and they seemed to be stable at around 100 °C. We are preparing manuscript on the thermal racemization of amino acids after forming ionic liquids with some cations. After removing precipitated free amino acid by washing with acetonitrile/methanol mixed solvent, the resulting liquids were dried in vacuo for 2 days at 80 °C. AAILs were all viscous liquids at room temperature having only a glass transition temperature (T_g). The lowest T_g (−65 °C) was seen for [emim][Gly]. On the other hand, the T_g of the salts of aspargic acid and glutamic acid was 5 and 6 °C, respectively. These data clearly show that addition of some functional groups (to interact with each other through hydrogen bonding) increased the T_g of the salts. This will be discussed in the next paragraph. The T_g strongly affects the ionic conductivity when ions migrate through the matrix. The ion conductive matrix that has this kind of T_g dependent behavior is classified as a coupled system.[55] Semi-empirically, there is a good relation between ionic conductivity at constant temperature and T_g of the matrix. The matrix having a lower T_g has higher ionic conductivity at the same temperature. As seen in Fig. 10, the ionic conductivity of most of AAILs fit this relation; however, there were a few exceptions.[55] These exceptions include the

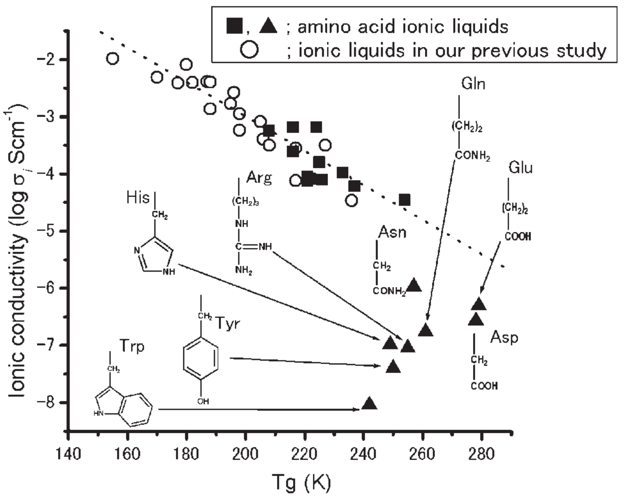


Fig. 10. Relationship between the glass transition temperature and ionic conductivity at 50 °C for general ionic liquids and a series of amino acid ionic liquids.

imidazolium salts of triptophan, tyrosine, histidine, arginine, etc. These salts have a much lower ionic conductivity than the expected value from the T_g. Detailed discussion will be reported soon.

The ionic conductivity of ionic liquids was mainly governed by their T_g, and those having low T_g generally have higher ionic conductivity at constant temperature. For the [emim] cation the trend in T_g for the amino acids is as follows: -47 °C ([emim][Lys]) $<$ -12 °C ([emim][Gln]) $<$ $+6$ °C ([emim][Glu]). The presence of a functional group usually induces extra interactions between the ions and results in an increase in T_g. If a hydroxy group is introduced onto [emim][Ala] ($T_\mathrm{g} = -57$ °C) to form [emim][Ser], the T_g value increased about 8 °C. Furthermore, the carboxylate group in [emim][Asp], caused the T_g value to increase more than 60 °C. The increases are due to hydrogen bonding and other interactions. Introduction of some functional groups always induces additional interaction among ions resulting in an increase in T_g. Because many factors affect the ionic liquids made with amino acids, it is difficult to design functional ionic liquids with the desired physicochemical characteristics. However, ionic liquids with component ions that have chiral centers are of great interests for electrochemistry and especially for electroorganic synthesis. Amino acid ionic liquids can be used in a wide variety of fields, e.g., they should be biologically friendly materials.

Other cations can be used in preparing amino acid ionic liquids. Tetraalkylphosphonium cations are one class of cations, and relatively less viscous ionic liquids are obtained by coupling the amino acids with tetraalkylphosphonium cations.[56] For example, tetrabutylphosphonium alaninate ([TBP][Ala]) was obtained as liquid, and it had a lower glass transition temperature (T_g) than that of [emim][Ala]. We have examined physicochemical characteristics of the other 19 natural amino acids. The salts of the amino acids that were prepared by neutralization with [TBP][OH] were liquids at room temperature. One more advantage of the use of tetraalkylphosphonium cations is the excellent stability of tetraalkylphosphonium hydroxide ([TBP][OH]) in an aqueous solution. Different from other hydroxides, [TBP][OH] is quite stable and readily forms salts simply by mixing equimolar amount of acids. However, TBP salts have relatively high melting points when [TBP][OH] was mixed with organic acids. Amino acid salts had exceptional properties when neutralized with this base. The thermal stability of [TBP][amino acid] was generally better than that of [emim][amino acid]. In particular, the decomposition temperature of [emim][amino acid] was around 220 °C, while that of several [TBP][amino acid] was above 300 °C. Additionally, the viscosity of [TBP][amino acid] was lower than that of [emim][amino acid]. Most of these amino acid anions contain functional groups, such as amino-, carboxyl-, hydroxy-groups, alkyl chain, and so on. There are many chances to modify these ionic liquids with regards to specific applications because of functional groups.

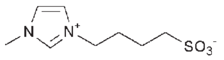
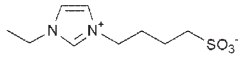
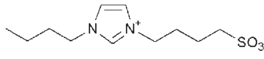
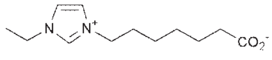
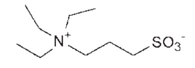
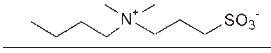
Zwitterions

One of advantages of ordinary ionic liquids is large diffusion coefficient of the ions. However, the migration of these component ions is a serious drawback when they were used as electrolyte solutions. For example, lithium (ion) batteries require migration of lithium cations in the electrolyte solution. In some cases, useful ions are only desired to be transported; however, the component ions of ionic liquids that were used as solvents were also mobile. The component ions should not be mobile under a potential gradient, and it seemed impossible to inhibit migration of the ions. We discussed how to inhibit the migration of component ions in the bulk, and Dr. Masahiro Yoshizawa et al. proposed a simple and excellent idea, namely, tethering of both cation and anion.

Both cation and anion were tethered by covalent bond to prepare so-called zwitterions. These are unique salts showing little migration under potential gradient because they have a zero net charge. The liquid zwitterions at room temperature may open a wide range of applications in electrochemistry fields, because they can be used as solvent without diffusion under DC polarization. We have prepared lots of zwitterions having alkylimidazolium cation structure.[57–62] Table 6 summarizes some physicochemical characteristics of these zwitterions. However, tethering cation with anion resulted a considerable elevation of the melting point (and T_g).

Generally, the T_m was on average about 120 °C higher after tethering both ions. It is therefore very difficult to design liquid zwitterions from even excellent ionic liquids such as [emim]-

Table 6. Thermal Properties of Various Zwitterions

Zwitterions	abb.	T_g[a)]	T_m[a)]	T_d[a)]
	mim-4S	20	206	308
	eim-4S	14	175	305
	bim-4S	13	158	324
	eim-6C	3	144	218
	$\mathrm{N_{222}}$-3S	—	—	294
	$\mathrm{N_{411}}$-3S	—	—	276

a) Temperature in °C.

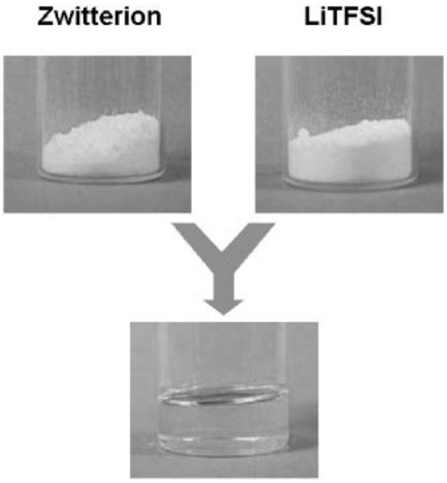


Fig. 11. Equimolar mixture of solid zwitterion and crystalline LiTFSI was obtained as liquid salts.

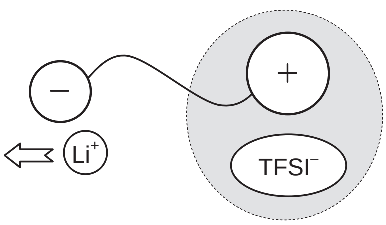


Fig. 12. Equimolar mixture of solid zwitterion and solid LiTFSI is an ionic liquid composed of TFSI anion and organic cation having anionic charged tail. This mixture is a kind of task-specific ionic liquid.

[TFSI]. However, we found liquidization of these zwitterions after mixing with TFSI salts.[59,62] For example, zwitterion bim-4S melts at 158 °C, but when this was mixed with equimolar amount of LiTFSI, the mixture turned amorphous and had a T_g of −20 °C. The mixture is a liquid, Fig. 11. This liquid is viscous although it contained a large amount of lithium cations. This liquidization was due to the interaction between the TFSI anion and the imidazolium (or ammonium) cation of the zwitterions. It is already known that the TFSI anion and imidazolium cation form an excellent pair to become an ionic liquid with a very low T_m or T_g. The ion pair involving the lithium cation and anionic site of the zwitterions should dissociate in the ionic liquid like environment formed by the imidazolium cation and TFSI anion, shown in Fig. 12. The liquid is ion conductive, and its ionic conductivity is around $1.7 \times 10^{-5}\,\mathrm{S\,cm^{-1}}$ at room temperature. The cation transport number (t_+) of the mixture is generally around 0.1–0.3 in salt containing organic polar solvents. The anions are more mobile in solution as well as in polyether type polymer electrolytes due to stronger ion–dipole interactions between the cations and solvent molecules or polymer matrix. However, in the case of the zwitterion/LiTFSI mixture, interaction between imidazolium cation and TFSI anion trapped the anion, and a relatively high cation transport number was observed. The value of t_+ depends on a few parameters such as cation and anion structure of the zwitterion, structure and chain length of spacer between cation and anion, anion species of the added salts, etc. Especially, the characteristics of anion of the zwitterion are quite important for a cation transport liquid through the trapping of anions. Dr. Asako Narita clarified the effect of these three parts, i.e., cation site, spacer, and anion site, on the properties of the corresponding zwitterions.[62] She first determined the most suitable cation structure by comparing several zwitterions containing different cation unit. She found that the ionic liquid-like domain formed by the coupling of *N*-methylpyrrolidinio-sites and TFSI anions could not provide effective ion conductive pathway as *N*-ethylimidazolio-sites did. These results indicate again that cation structures like typical ILs are not always effective for improving ionic conductivity of zwitterion/lithium salt mixtures. At this stage, *N*-ethylimidazolio group was selected as one of the most suitable cation structures for controlling the T_m of pure zwitterions. Although it is possible to prepare zwitterions with a low T_m by introducing long alkyl-chains to cation-sites,[62] the introduction of long alkyl-chains lowers ion density and increases bulk viscosity. Accordingly, *N*-ethylimidazolio group is concluded to be most suitable structure. We also measured the ionic conductivity of the mixture of a series of zwitterions having different spacer chain length with LiTFSI. Except for the case of the zwitterions with the shortest spacer, all mixtures had an ionic conductivity between 1×10^{-5} and $1 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$. However, the T_m of a pure zwitterion can be lowered by increasing the spacer chain length. An equimolar mixture of LiTFSI and zwitterions with spacer length of C_6 showed the highest ionic conductivity in this series. For the electrochemical applications, we concluded that the most suitable spacer-chain length (**n**) of zwitterions is in between 5 and 7. With such a chain length, equimolar mixtures of LiTFSI and zwitterion had high thermal stability and high ionic conductivity. Modifications to the anion structure, particularly imide-anion sites, affected both the T_m value of pure zwitterions and the cation transference number of the equimolar mixture of LiTFSI and zwitterion.[62] Zwitterions are expected to be functional materials for not only ionics but also reaction catalysts and so on. Considerable advancement in ion design will occur for these zwitterions in the near future.

Electrochemical Reactions of Biomolecules in Ionic Liquids

Ionic liquids are excellent reaction matrix for electrochemistry. There are several advantages of the electrochemistry in these matrices, and increasing number of studies on the application of ionic liquids to ionics devices such as lithium ion batteries, capacitors, fuel cells, solar cells, and so on, have been conducted. The ionic liquids must meet certain requirements that depend on the applications. For example, predominant transport of lithium cations as well as high ionic conductivity of the electrolyte matrix is essential for lithium ion battery. Solar cells need iodide transport matrix, and proton conduction is required for fuel cells. Accordingly, suitable ionic liquids should be designed depending on the applications. The large numbers of organic ions make the candidates for designing ionic liquids that support these ionics devices. Some applications of ionic liquids toward devices are summarized elsewhere.[63] There are an increasing number of studies involving electrochemical reactions in ionic liquids. One of unique aspect of electrochemistry in ionic liquids is the shielding effect form the electrostatic interactions due to the extraordinarily large ion density. Suppression and acceleration of electrostatic interaction may affect the kinetics of reactions in the ionic liquids. Currently, there are only small numbers of studies on the shielding effect of electrostatic interaction in ionic liquids; however, this should be changed in the near future.

Bioelectrochemistry in ionic liquids is also an interesting field. It is long believed that bio-derived molecules, especially proteins and enzymes, are only active in water, and they are denatured in organic media. There are two major subjects for the solubilization of biomolecules such as proteins, enzymes, co-factors, etc. One is the design of suitable ionic liquid having high solubilizing ability of target proteins. The other is the modification of proteins with "ionic liquid-phile" molecules. The former subject should be the design of ionic liquids depending on the properties of target proteins. However, it is important to keep their functions after dissolving in ionic liquids. It seems quite difficult to maintain the higher-ordered structure of proteins because of different nature of ionic liquids from that of water. In the ionic liquids, extra contribution or shielding of electrostatic interaction should be taken into account. Accordingly, it is generally believed to be quite difficult to solubilize proteins in ionic liquids without changes in the higher-ordered structure. Some lipases have been used without any chemical modification for catalytic reactions in ionic liquids.[63] Also we have already found that small amount of heme-proteins, such as cytochrome *c* (10^{-4} M), was soluble in some polar ionic liquids such as 1-allyl-3-methylimidazolium chloride. Details will be reported soon. Dr. Kyoko Fujita, while working as a postdoctoral research fellow with Prof. Forsyth and Prof. MacFarlane, however, found that the addition of 10–20 wt % water in an ionic liquid helped stabilize certain proteins, such as cytochrome *c*, and that they were thermally stable for months.[64] Finding or designing new ionic liquids suitable for the electrochemistry of proteins, enzymes, etc. are extremely interesting subjects. The structure of the ions must vary depending on the biomolecules.

The other method to solubilize biomolecules is widely applicable for most proteins. We have been studying poly(ethylene oxide) modification of several proteins to solubilize them into oligomer and polymer matrices.[65–78] Especially, PEO-modified proteins showed extreme thermal stability,[71,76,78,79] and quasi-reversible redox reaction of a few PEO-modified heme proteins was clearly observed in PEO oligomers and polymers. Ms. Natsue Kawahara and Dr. Fumiyo Kurusu observed electron-transfer reactions of heme proteins in PEO oligomers, the research was quite helpful towards applying ionic liquids as solvents for biomaterials. PEO modification is easy, and activated PEOs can react with the amino groups of the proteins in aqueous media to form amide bonds. The PEO-modified proteins were soluble in most ionic liquids, because PEO chains can interact with ions through ion–dipole interaction. PEOs are regarded as "ionic liquid-phile" molecules. Heme proteins were soluble in ionic liquids after PEO modification.[80,81] The thermal stability of the PEO-modified heme proteins in ionic liquids was found to be similar to those of PEO oligomers. The extreme thermal stability is attributed to the lack of water molecules. Most proteins are heat-denatured in aqueous media, because of the vigorous thermal motion of water molecules at high temperature. Both polymers and ionic liquids show much less thermal mobility than water molecules inducing less chance of thermal denaturation even at high temperatures.

Accordingly, any molecule modified with PEO chains should be soluble in most ionic liquids. PEO modification is a rather general method to solubilize biomolecules into ionic liquids with different properties, and it becomes important technology for conducting biochemical reactions in ionic liquids in the near future. PEO chains can also tether functional molecules such as mediators, promoters, catalysts, metal complexes, etc.

Polymerization of Ionic Liquids

There are a few methods to bring about dimension control in ionic liquids. Since ionic liquids are homogeneous or isotropic liquids, a unique domain is formed after dimensional regulation of isotropic ionic liquids. Typical example is the formation of a liquid crystalline phase with the ionic liquids, i.e., the ionic liquid is incorporated into the liquid crystalline phase. We have been collaborating with Prof. Takashi Kato of The University of Tokyo to prepare dimensionally controlled ionic liquids for anisotropic ion conduction.[82–98] A review on this subject has been published elsewhere.[99]

One of the biggest requirements on the ionic liquids is the preparation of films having similar characteristics to ionic liquids. To prepare ionic liquid-containing polymers, Dr. Kaori Ito and I proposed a direct polymerization of ionic liquids.[100] A vinyl group was covalently introduced onto the imidazolium cation ring. 1-Vinylimidazole was quaternized with a series of alkyl halides, and the halide anions were then substituted with certain anions, such as the TFSI anion, to prepare ionic liquid monomers. Introduction of a polymerizable group, such as the vinyl group, onto the imidazolium cation improved the physicochemical properties of the ionic liquid because of more widely spaced π-conjugated orbital. After the polymerization, ionic liquid polymers should have excellent ionic conductivity. However, simple polymerization of these ionic liquid monomers lead very poor ionic conductivity due to a considerable increase in T_g and a reduced number of mobile ions after covalent bonding of the component ions.[100] Figure 13 shows the ionic conductivity of 1-methyl-3-vinylimidazolium TFSI ([mvim][TFSI]) before and after polymerization. The ionic conductivity was about 1000 times lower after polymerization. Although these polymers are not ionic liquids, it is possible to construct an ionic liquid like domain in the polymer matrix. The T_g of the polymerized [mvim][TFSI] was $-75\,^\circ$C. The T_g increased after polymerization, but the T_g of the polymerized ionic liquids was still considerably lower than that of ordinary polyelectrolytes or charged polymers. The low T_g of the polymerized [mvim][TFSI] is attributed to the presence of TFSI anions.[63] This TFSI anion acts as a plasticizer as well as a counter anion.

Polymerization of ionic liquids is however an important method for preparing ion conductive polymer films. These polymers should have film-like the characteristics of ionic liquids. For example, Shen et al. are studying polymerized ionic liquids as films for gas separation.[101] Nakashima and Kawai are studying polymerized ionic liquids as stable matrix for quantum dots,[102] and polymer films having ionic liquid-like

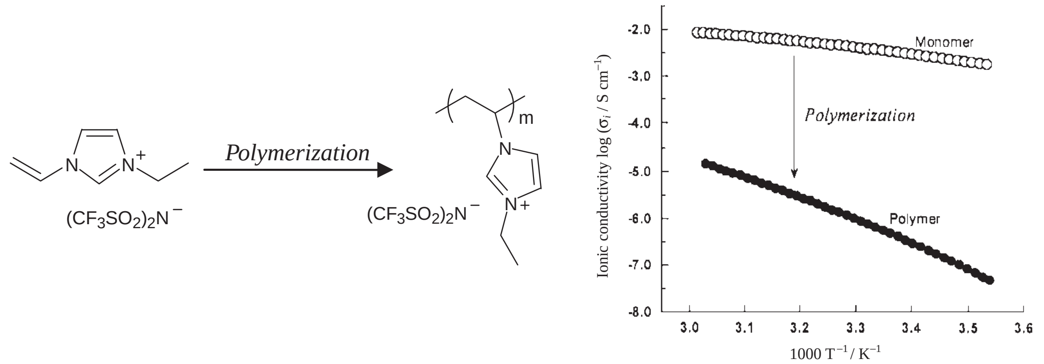
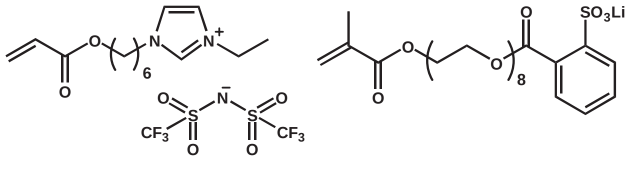


Fig. 13. Arrhenius plots of the ionic conductivity of 1-ethyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide before and after polymerization.



(a) (b)

Fig. 14. Two ionic liquid monomers having different roles; monomer to lower the glass transition temperature (a) and that to generate lithium cations (b).

properties should be quite useful. Requirements for these polymers deeply depend on the purpose of application. In any case, it is important to control physicochemical properties of the polymerized ionic liquids.

For the case of ion conductive polymers, both high ion density and low T_g are required for good performance. To avoid an increase in T_g, we have tried several different chemical modifications such as introduction of flexible spacer group in between polymerizable group and charge site.[103] Copolymerization of ionic liquid monomer and flexible chain containing monomer is also effective to improve selective ion conductive properties. For this, the two monomers shown in Fig. 14 were used to prepare copolymers having tuned characteristics. The copolymerization of two kinds of monomers having different roles makes it possible to tune the properties of ion conductive polymer film or solid.[104,105] In the case of copolymerization of ionic liquid monomer (a) and lithium salt monomer (b), Fig. 14, the conductivity and cation transport number were determained to be the function of copolymer composition. The T_g of (a) was $-80.7\,°C$, and it became $-59.1\,°C$ after homopolymerization. The ionic conductivity of homopolymer of (a) is $1.37 \times 10^{-4}\,S\,cm^{-1}$, and that of homopolymer (b) is below $10^{-9}\,S\,cm^{-1}$ due to higher T_g of $-14\,°C$. The T_g and ionic conductivity of copolymers of (a) and (b) varied in between the value of corresponding homopolymers.[105] Since these characteristics are the function of monomer composition, one can design suitable copolymers for application. At present, it is however quite difficult to improve both the ionic conductivity and cation transport number of these copolymers.

To improve the mechanical properties of ion conductive polymers, the addition of a small amount of a cross-linker is quite effective.[106] The small amount of cross-linker did not affect the ionic conductivity but improved the thermal stability and mechanical properties. There are some cross-linkers used commercially, but we could not find an ionic liquid cross-linker. An ionic liquid having multiple polymerizable groups should be effective to be a cross-linker without lowering the ionic liquid density even after polymerization. Dr. Hiromichi Nakajima synthesized a series of mono- and bi-functional monomers from ionic liquids,[107] and the monomers having two vinyl groups are thermally stable cross-linkers. The network polymers obtained by the radical polymerization of these ionic liquid cross-linkers decomposed above 400 °C. The network polymers prepared by the polymerization of ionic liquid monomers with the ionic liquid cross-linkers had higher decomposition temperatures than that of the polymers with ordinary cross-linkers such as ethylene glycol dimethacrylate.

Ion Conductive Polymer Films

It is also possible to prepare ion conductive polymer films based on the ionic liquid science.[63] Polymer gel electrolytes are most common because they can be prepared easily. The polymer gel electrolytes are prepared by two methods: one is simple absorption of ionic liquids by a polymer matrix, and the other is polymerization of monomers in ionic liquids. In both cases, it is important to design or control the affinity of ionic liquids towards the polymers. Compatibility of these two components is mainly governed by their structure. Polymer gel electrolytes are easily prepare and, therefore, be examined thoroughly. There are many polymers that can be used as scaffolds for polymer gel electrolytes. It is important to design (or control) the affinity (or interaction) between the scaffolds and the ionic liquids.

Biopolymers can also be used for this purpose. There are many biopolymers known as biomass. For example, DNA extracted from animal (mainly fish) eggs or milt can be used as functional materials. The DNA was mixed with ionic liquids to prepare ion conductive biopolymer films. Dr. Naomi Nishimura has been actively examined to prepare ion conductive DNA films, and Dr. Nishimura and I discussed strategies to form an ionic liquid-like environment with a low T_g along with the DNA chains in 1998. After studying the complexation of DNA with a PEO/salt mixture,[108] we prepared an ionic liquid-like domain in the DNA double helix. To us, nucleic acid bases are basically conjugated heterocyclic amines waiting the neutralization by suitable organic acids. These nucleic acid

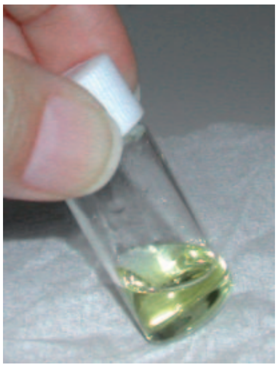


Fig. 15. Cytosine was neutralized with HTFSI to prepare liquidized nucleic acid base [cytH][TFSI].

bases are considered to be excellent candidates to prepare cations with delocalized cationic charge. In 2000, she prepared liquid-state salts of nucleic acid bases. It was a big surprise for me when she brought a liquid of cytosine neutralized with HTFSI. It is an amorphous liquid, and the T_g of [cytH][TFSI] was −30.8 °C. Figure 15 is a picture of liquid [cytH][TFSI]. The reason why she succeeded to prepare ionic liquid from nucleic acid bases is the use of the neutralization method. We tried to quaternize the nucleic acid bases with methylating agents, but it is quite difficult to prepare quaternized ammonium cations from these nucleic acid bases. Since the nucleic acid bases are conjugated hetero aromatic amines, quaternized ammonium salts cannot be obtained by the introduction of a few methyl groups on the nucleic acid bases. Whenever one of amino groups was quaternized, adjacent amino group immediately released a proton due to a conjugated ring. Accordingly, formation of quaternized nucleic acid bases after full alkylation is quite difficult, and the yield should be very low. Therefore, we examined the neutralization of the nucleic acid bases. Because of acidity of these nucleic acids, only adenine and cytosine were expected to be neutralized by the acids. However, care must be taken when trying to neutralize these nucleic acid bases with acids, to avoid degradation of the purine rings. Actually, guanine was degradated by the acid, and only cytosine was protonated stably by the acid to form a liquid salt.

The above method was then extended to DNA to prepare chains that have ionic liquidized nucleic acid bases. Upon addition of organic acids, the DNA chains became cationic.[109] However, stronger acids destroyed the double helix due to the quaternization of nucleic acid bases. The protonated nucleic acid bases cannot interact with each other through hydrogen bonding. Electrostatic repulsion of protonated nucleic acid bases caused cleavage of the double helix.[109] HTFSI is better than other acids, but the neutralized DNA (DNA-TFSI) was not soluble in any solvent. HBF_4 was then used to neutralize the DNA, and protonated DNA chains were obtained as a white powder. The ionic conductivity of the DNA-BF_4 solid was very low, 10^{-9} S cm^{-1}. The low ionic conductivity was due to insufficient ionic liquidized bases on the DNA chains as well as partial decomposition of purine rings. Accordingly, we added [eHim][BF_4] to this DNA-BF_4 salt to enhance the ionic conductivity. The ionic conductivity dramatically improved to reach 1.74×10^{-4} S cm^{-1} at 50 °C by the addition of 23.7 wt % [eHim][BF_4]. More than 40 wt % [eHim][BF_4] was needed to give the equivalent ionic conductivity for native DNA because of the ionic liquidized bases on the DNA chains.[109]

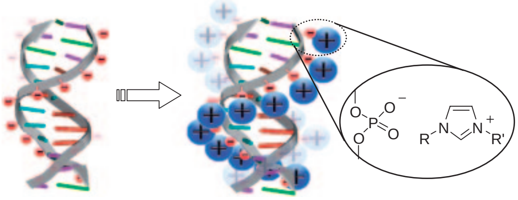


Fig. 16. DNA was mixed with [RR′im][OH] to form ionic liquid sheathed DNA.

We then tried to prepare ionic liquidized DNA chains in which the double helix was intact (Fig. 16).[110] For this purpose, we tried to make salts of phosphate anions on the outside the DNA strands with imidazolium cations. Initially, we tried the coupling of 1-ethyl-3-methylimidazolium cation and phosphoric acid dibutylester (PDE). The PDE was used as a model of phosphate residue outside the DNA strands. The salt [emim][PDE] had no T_m, and the T_g was found to be −73.5 °C. Liquidization of PDE using [emim] suggested that a salt could form on outside the DNA strands. Sodium cations of DNA were exchanged with [emim] via the neutralization of acid type DNA and [emim][OH]. The [emim][DNA] was obtained as a white powder by freeze drying an equimolar aqueous mixture of acid type DNA and [emim][OH]. The ionic conductivity was 10^{-9} S cm^{-1} at room temperature that is due to insufficient density of the phosphate salts around the DNA strands. We then added 11 mol % of [emim][BF_4] to [emim][DNA]. The ionic conductivity improved to 5.4×10^{-6} S cm^{-1} at room temperature. To compare the effect of ionic liquidized phosphate groups, the same amount of [emim][BF_4] was added to native DNA. However, no improvement in the ionic conductivity was found, and an ionic conductivity of less than 10^{-9} S cm^{-1} was detected at room temperature. According to the thermal analysis, the DNA strand and ionic liquid phase were phase separated because a continuous ionic liquid phase around the DNA strands formed.[110] Ionic liquid formation of sulfonate anions around the DNA strand with imidazolium cations is another interesting approach to prepare a successive ion conduction path along the DNA double helix.[110] Although ionic liquid-like ion pairs in the DNA alleys were formed, and the density of the ion pairs was not high enough to provide successive ion conductive path. Addition of 11 mol % of [emim][BF_4] to the repeating unit of phosphate anionic residues improved the ionic conductivity to 5.4×10^{-6} S cm^{-1} at room temperature.[110]

As mentioned above, we tried to prepare ion conductive DNA films. Unfortunately, we still do not have ion conductive DNA chains, but these approaches can be used to prepare polymer electrolyte films from biomass, and they can also be used for other natural polymers such as polysaccharides, polypeptides, and so on.

Conclusion and Future Aspects

Several characteristics and design of functional ionic liquids have been summarized. There are increasing number of studies on the properties of ionic liquids as well as application in a few ionic devices. Although there are many advanced studies, more basic studies are needed. It is without saying that the relationship between structure of component ions and the properties of the ionic liquids is extremely important to design functional as well as high-performance ionic liquids. Since most ionic liquids are composed of organic ions, there are limitless possibilities of ionic liquids. The development of "functional ionic liquids" has just started with the aid of "chemistry." At present, the introduction of functional groups onto ions caused an increase in T_m and/or viscosity of the corresponding ionic liquids. We are currently preparing many salts to obtain new "solutions." Chemistry enables us to play games with new ionic liquids, interesting and important papers based on advanced ionic liquids will be published in the future.

The present account is the summary of research results on the ionic liquids that have been carried out by many students in my laboratory. I would like to thank all of my students and staff for their energetic concern. Most of studies have been supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology. The recent studies have been carried out under the 21st century COE program of Future Nano-Materials.

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