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Theoretical Study of Ionic Liquids on the Difference of Melting Points between Tertiary and Quaternary Ammonium Triflates

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The origin of the difference of melting points (T_m) between tertiary and quaternary ammonium triflates has been investigated by ab initio and molecular dynamics simulations. Experimentally, T_m of tertiary ammonium triflates are lower than those of quaternary ammonium triflates. In this work, we used [N_{122H}][TfO] and [N_{1113}][TfO] as typical models of tertiary and quaternary ammonium triflates, and the mutual arrangement of these cation–anion pairs were discussed to elucidate the difference of the melting points of these systems.

Protic ionic liquids (**IL**) such as diethylmethylammonium trifluoromethanesulfonate (triflate) are thought of as a superb electrolyte for nonhumidified intermediate temperature fuel cells.[1] Essential features requisite of fuel cell electrolytes are high ionic conductivities and high electroactivity for hydrogen oxidation and oxygen reduction on the electrode.[2] In addition, wide liquid temperature range and high thermal stability are also required to make more efficient power generation using these protic **IL**s. A series of tertiary (N_{xyzH}) or quaternary (N_{xyzw}) ammonium **IL**s (x, y, z, w stand for the number of carbon atoms in the alkyl side chains) are assumed to be applicable to nonhumidified intermediate temperature fuel cells as electrolytes. The melting points (T_m) for some of these **IL**s are listed in Table 1. Melting points of the **IL**s for which references are not cited in Table 1 were measured in our laboratory using Shimadzu DSC-60 Differential Scanning Calorimetry. We can see the general tendency that the T_m values of tertiary **IL**s are lower than those of quaternary liquids. In this study, we investigated why tertiary ammonium triflate has low T_m compared with quaternary triflate. For this purpose, we selected **IL**s of tertiary ammonium [N_{122H}] and quaternary ammonium [N_{1113}] as cations with the combination of the same triflaste ([TfO]) anion. We evaluated the interaction energy and conformational flexibility of these cation–anion pairs using ab initio and molecular dynamics simulation (**MD** simulation).

Table 1. Melting points (T_m) for a series of tertiary [N_{xyzH}][TfO] and quaternary [N_{xyzw}][TfO]

	T_m/°C
Tertiary ammonium triflate	
[N_{112H}][TfO]	42^1
[N_{122H}][TfO]	-6^1
[N_{114H}][TfO]	-3^b
[N_{123H}][TfO]	-25^b
Quaternary ammonium triflate	
[N_{1222}][TfO]	139^3
[N_{2222}][TfO]	$300^{a,3}$
[N_{1113}][TfO]	198^b

[a]Decomposition temperature. [b]This work.

Ab initio calculation was performed using Gaussian03.[4] To find the energy minimum arrangement of cation–anion pairs (dimer), 3000 initial ion-pair arrangements were generated randomly using a laboratory-made program.[5] These molecular arrangements were first minimized using PM3, then 200 arrangements with lower energy were selected and minimized again at HF/3-21G* level calculation. Again, 20 arrangements with lower energy were optimized at HF/6-31+G* level calculation, and the lowest energy minimum arrangement was obtained. The total energy of this dimer arrangement, E_{dimer}, was evaluated by single point calculation with the correction of basis set superposition error (BSSE). For these **IL** structures, electrical partial charges are calculated by the method of CHelpG.[6]

Energy minimum arrangements of two pairs of cation–anion ions (tetramer) were also obtained by generating 800 initial arrangements of ion pair and minimized similar to dimer optimization. Namely, 100 initial arrangements of ion pair were generated randomly and minimized using PM3, then 30 arrangements with lower energy were selected and minimized again at HF/3-21G* level calculation. Again, 10 arrangements with lower energy were optimized at HF/6-31G* level calculation, and the lowest energy minimum arrangement and its total energy, $E_{tetramer}$, was obtained. In the energy calculation, BSSE was not evaluated because of the limitation of calculation time for the large number of atoms in the tetramer systems.

MD simulation was calculated using program package TINKER[7] with OPLS-AA force field[8] using Lopes' parameter.[9] Partial charges of the molecules were used obtained from ab initio calculation. All simulations were carried out with a system containing 216 ion pairs. At first, structural relaxation was performed at 1000 K for 1000 ps simulation time, and the time step was 1 fs. Ewald's method[10] was employed to handle the long-range Coulombic interaction. Chemical bonds to hydrogen atoms were kept fixed using SHAKE.[11] We equilibrated the system by sufficiently long time simulation at 303 K (*NPT*), then performed 2000 ps simulation for analysis. The simulated errors in density of all **IL**s were within 0.01 g cm^{-3} of experimental values.

The strength of the interaction between a cation–anion ion pair was evaluated as an interaction energy, $\Delta E_{(inte)}$, using eq 1. In this equation, $E_{(ion\ pair)}$ is the single point energy of the ion pair with the correction of BSSE. $E_{(cation\ of\ ion\ pair)}$ and $E_{(anion\ of\ ion\ pair)}$ were the single point energies of cation and anion fractions in the ion-pair arrangement, respectively.

$$\Delta E_{(inte)} = E_{(ion\ pair)} - [E_{(cation\ of\ ion\ pair)} + E_{(anion\ of\ ion\ pair)}] \quad (1)$$

Figure 1 shows the lowest-energy conformations of the cation–anion dimers of tertiary [N_{122H}][TfO] and quaternary [N_{1113}][TfO]. The obtained energy values of E_{dimer} are also

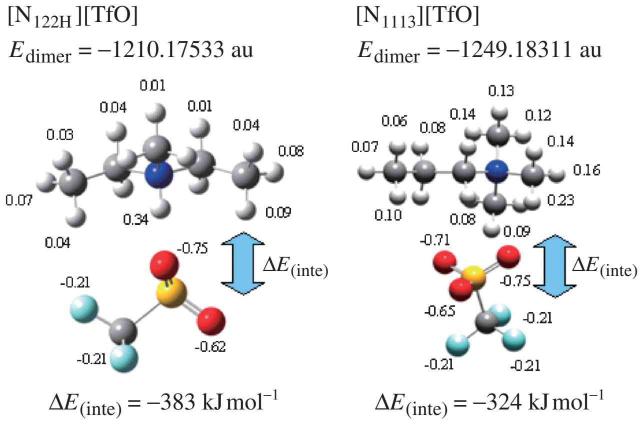

Figure 1. Optimized structures of cation–anion ion pairs (dimer) of $[N_{122H}][TfO]$ and $[N_{1113}][TfO]$ calculated by Gaussian03 with HF/6-31+G*. The total energies of E_{dimer} are shown in the figure. Interaction energies between cation and anion pair $\Delta E_{(inte)}$ and the partial charges of these dimers are also shown in the figure.

shown in the figure. From these conformations, $\Delta E_{(inte)}$ of $[N_{122H}][TfO]$ and $[N_{1113}][TfO]$ were calculated to be -383 and -324 kJ mol^{-1}, respectively. That is, the ionic interaction between the ion pair of $[N_{122H}][TfO]$ is stronger than that of $[N_{1113}][TfO]$. From a thermodynamics point of view, strong interaction generally increases the T_m. Therefore, we may imagine that T_m of the tertiary **IL**s will have higher values than those of quaternary compounds. However, tertiary **IL**s show generally lower T_m values than those for quaternary **IL**s.

To investigate the cation–anion interactions in the **IL**s more in detail, we next used tetramer models of **IL**s (two pairs of cation–anion ions) for $[N_{122H}][TfO]$ and $[N_{1113}][TfO]$ systems. The energy minimum arrangements of these two tetramer systems and the obtained energy values of $E_{tetramer}$ are shown in Figure 2. To calculate the interaction energy between cation–anion pairs included in these tetramer systems, we extract 4 ion-pair arrangements for each system and calculated the interaction energy between them using eq 1. The obtained values of the interaction energies $\Delta E_{(inte)}$ are also shown in Figure 2. We can see that the interaction energies between cation–anion ion pairs included in the $[N_{1113}][TfO]$ system were similar with each other with the values of -318 to -320 kJ mol^{-1}. These values are also similar to that obtained for the dimer of $[N_{1113}][TfO]$ in Figure 1. On the other hand, the interaction energies of the $[N_{122H}][TfO]$ system show two types of interactions. One has the interaction energy of -380 to -381 kJ mol^{-1}, and the other has -299 kJ mol^{-1}. The stronger interaction was the same as that obtained in the dimer system of $[N_{122H}][TfO]$ which works between N–H proton of the ammonium cation and TfO anion. On the other hand, the weak interaction works between alkyl chains of the ammonium cation and [TfO] anion. This interaction is found to be smaller than that of $[N_{1113}][TfO]$ by about 20 kJ mol^{-1}.

We elucidated the reason that the $[N_{122H}][TfO]$ system has two types of interactions by calculating the partial charge distribution on the atoms of these cation–anion pairs. The obtained values of the partial charges for dimer molecules are shown in Figure 1 with the results obtained for $[N_{1113}][TfO]$. It was found that tertiary **IL** has a large positive charge of 0.34 on N–H proton, while the positive charges of the remaining alkyl chain protons of $[N_{122H}][TfO]$ show small values, which is because of the strong localization of the positive charge on the N–H proton. This charge distribution would cause the decrement of the interaction which works between the alkyl side chains of $[N_{122H}]$ and [TfO]. This weak interaction of $[N_{122H}][TfO]$ may decrease the T_m of $[N_{122H}][TfO]$ more than that of $[N_{1113}][TfO]$. On the other hand, the positive charge of $[N_{1113}]$ is uniformly distributed; therefore, the interaction between cation and anion pairs for $[N_{1113}][TfO]$ does not show any large dependence on the arrangement of these pairs. The uniformity of the interaction of $[N_{1113}][TfO]$ would favor an ordered structure which resists fusion. The tendency of $[N_{1113}][TfO]$ to favor the ordered structure can be elucidated from the radial distribution function (RDF) analysis of the **MD** calculation.

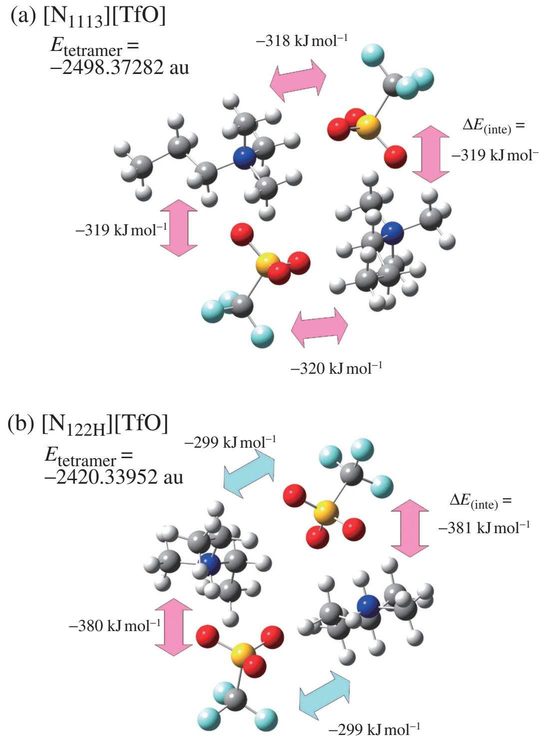

Figure 2. Optimized structures of $[N_{1113}][TfO]$ (a) and $[N_{122H}][TfO]$ (b) tetramers calculated by Gaussian03 with HF/6-31G*. The total energies of $E_{tetramer}$ are shown in the figure. Interaction energy $\Delta E_{(inte)}$ between each cation–anion pair found in these arrangements is also shown in the figure.

The cation–cation RDF between the nitrogen atoms calculated on both ionic liquids of $[N_{122H}][TfO]$ and $[N_{1113}][TfO]$ are shown in Figure 3a. Similarly, cation–anion RDF between the nitrogen–sulfate atoms calculated on $[N_{122H}][TfO]$ and $[N_{1113}][TfO]$ **IL**s are also shown in Figure 3b. In the cation–cation RDF of tertiary $[N_{122H}][TfO]$, it has sharp first peak at around 6 Å but shows no other significant peaks. On the other hand, RDF of quaternary $[N_{1113}][TfO]$ has the first peak at around 6 Å and a second peak at around 10 Å. Moreover, it also shows a third broad peak at around 14 Å. This fact means that the ionic liquid of $[N_{1113}][TfO]$ has somewhat ordered structure, meanwhile the $[N_{122H}][TfO]$ has not.

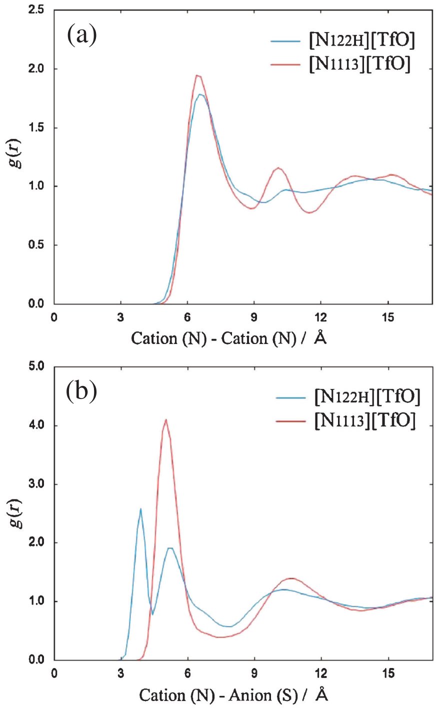

Figure 3. Radial distribution function $g(r)$ between ammonium nitrogen atoms in the cations (a) and between nitrogen–sulfate atoms (b) of [N$_{122H}$][TfO] and [N$_{1113}$][TfO] against their distance which were calculated by MD.

In the cation–anion RDF shown in Figure 3b, tertiary [N$_{122H}$][TfO] has two peaks in the region of 3–6 Å. The first peak located at 4 Å, corresponds to the distance obtained in Figure 2b between the nitrogen of [N$_{122H}$] cation and sulfate of [TfO] anion in the strongly interacting pair. On the other hand, the distance of the second peak at 5 Å corresponds to that obtained between the nitrogen of [N$_{122H}$] cation and sulfate of [TfO] anion of the weakly interacting pair in Figure 2b. These peaks clearly indicate that the two interactions, which were found in [N$_{122H}$] tetramer conformation, exist in the **IL** of [N$_{122H}$][TfO]. Moreover, the shape of the RDF after 6 Å is somewhat distorted, which would be caused by the coexistence of the two types of interactions. The distortion of the cation–anion structure would affect to the whole structure of the [N$_{122H}$][TfO] **IL** to prevent the construction of ordered structure. This can be seen in the cation–cation RDF in Figure 3a, which shows the disordered structure in the [N$_{122H}$][TfO] **IL**.

On the other hand, cation–anion RDF of [N$_{1113}$][TfO] **IL** has single first peak at around 5 Å which corresponds to the distance between the nitrogen of [N$_{1113}$] cation and sulfate of [TfO] anion found in the tetramer conformation in Figure 2a. The second peak appeared at around 10 Å. The profile of these peaks indicates an ordered structure of the [N$_{1113}$][TfO] **IL**. This cation–anion ordered structure would also induce the ordered structure in the cation–cation arrangement as was shown in Figure 3a.

In conclusion, although the relationship between the existence of the two types of interactions and the melting points is still unclear, the analysis of the interaction energy between the cation and anion pairs in dimer and tetramer clusters suggests that the variation of the interaction pattern would be an important factor to determine the difference of the melting points between the tertiary and quaternary ammonium triflates. That is, [N$_{122H}$] has two types of interaction between the cation–anion pair. The weaker interaction of [N$_{122H}$][TfO] is smaller than that of [N$_{1113}$][TfO]. The presence of these two types of interaction would disturb the structure of the ionic liquid of [N$_{122H}$][TfO]. On the other hand, [N$_{1113}$][TfO] consists of uniformly delocalized cation charge which favors ordered structure over the [N$_{122H}$][TfO]. We showed here the possibility that this would be a factor that T_m of [N$_{122H}$][TfO] is lower than that of [N$_{1113}$][TfO]. More detail study will be performed using a series of tertiary and quaternary **IL** molecules in the future.

[N$_{xyzH}$][TfO] were prepared by mixing amine (N$_{xyz}$) and trifluoromethanesulfonic acid (TfOH) in a N_2-filled glove box. [N$_{xyzw}$][TfO] were prepared from corresponding ammonium chlorides according to procedures reported in the literature.[12–15]

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