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Structures of $[Li(glyme)]^+$ complexes and their interactions with anions in equimolar mixtures of glymes and Li[TFSA]: Analysis by molecular dynamics simulations

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Molecular dynamics simulations of equimolar mixtures of glymes (triglyme and tetraglyme) and Li[TFSA] (lithium bis(trifluoromethylsulfonyl)amide) show that the glyme chain length affects the coordination geometries of Li^+, which induces the changes of interactions between the $[Li(glyme)]^+$ complex and $[TFSA]^-$ anion and diffusion of ions in the equimolar mixtures.

Room temperature ionic liquids (RTILs) have attracted much attention because of their unique physicochemical properties.[1] RTILs are expected to be applicable to electrolyte for electric double-layer capacitors, fuel cells, dye-sensitized solar cells and lithium-ion batteries.[2] The equimolar mixtures of glymes (oligoethers) and certain Li salts are liquids at room temperature. They have low volatility, high ionic conductivities and high electrochemical stability, which are similar to conventional RTILs.[3] The equimolar mixtures are proposed as a new family of RTILs (solvate ionic liquids).[4] They are studied extensively as new electrolyte candidates for lithium-sulfur (Li-S) batteries owing to the low solubility of reaction intermediates (lithium polysulfides, Li_2S_m).[5]

The triglyme and tetraglyme (Figure 1, G3 and G4) form stable $[Li(glyme)]^+$ complexes in the equimolar mixtures with Li[TFSA].[3g] The solvate ILs are composed of the $[Li(glyme)]^+$ cations and $[TFSA]^-$ anions. The elucidation of the liquid structures of the equimolar mixtures is crucial for understanding the properties of the solvate ionic liquids and for their applications as electrolytes. The structures and stability of the $[Li(glyme)]^+$ complexes and their interactions with anions in the equimolar mixtures play important roles in controlling transport properties of ions and the solubility of Li_2S_m, which are important factors in determining the performance of Li-S batteries.[5] Unfortunately, however, the liquid structures of solvate ionic liquids were hardly studied in contrast to extensive studies on conventional ionic liquids (aprotic and protic ionic liquids). The stable structures of $[Li(G3)]^+$ and $[Li(G4)]^+$ complexes and their interactions with $[TFSA]^-$ anion in the gas phase were studied by ab initio molecular orbital calculations,[6] while the coordination structures of $[Li(glyme)]^+$ complexes in the equimolar mixtures were still unclear. We have carried out molecular dynamics simulations of the equimolar mixtures of glymes (G3 and G4) and Li[TFSA] ([Li(glyme)][TFSA]) to reveal the coordination structures of $[Li(glyme)]^+$ complexes in the mixtures. We have discussed the effects of glyme chain length on the coordination structures of the $[Li(glyme)]^+$ complexes, their interactions with $[TFSA]^-$ anion and diffusion of ions in the mixtures.

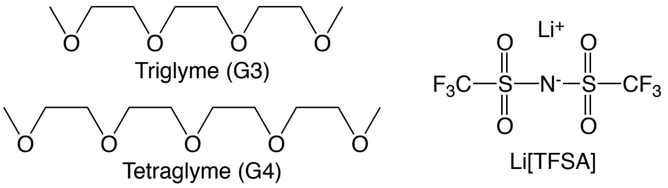


Figure 1. Chemical structures of glymes and Li[TFSA].

MPDyn program[7] was used for the molecular dynamics simulations. Molecular dynamics simulations of the mixtures of 125 glymes and 125 Li[TFSA] were carried out in the NPT ensemble. All the C-H bonds were held rigid using the SHAKE algorithm.[8] Reversible RESPA was used for multiple time step integration of equations of motion of atoms.[9] The time step size for updating interactions in the Ewald reciprocal space was 8 fs, and that for other interactions was 2 fs. Periodic boundary conditions were employed. The nonbonded forces were truncated at 12 Å, while the Coulomb interactions were computed using the Ewald method.[10] Constant-temperature and -pressure conditions (0.1 MPa) were maintained by using the Nosé-Hoover chain thermostat[11] and Andersen barostat.[12] The time constants for the thermostat and barostat are 0.5 and 2.0 ps, respectively. The force field parameters for Li^+ and $[TFSA]^-$ anion were taken from literatures.[13] The parameters for glymes were taken from literature with some modifications based on ab initio calculations.[13d] The force field parameters are summarized in Table 1S in electronic supplementary information. Atom types are shown in Figures 1S and 2S. The mixture of Li-glyme complexs and TFSA anions was used for initial geometries of molecular dynamics simulations. The system was equilibrated from a low-density condition. The density and radial distribution functions of the ionic liquid were evaluated from 12 ns MD trajectories after a 10 ns MD equilibration run at 303 K. The radial distribution functions do not change during the 12ns production run. After a 4 ns equilibration run, a 30 ns production run was made at 403 K to calculate the mean square displacements (MSD) of the ions. The self-diffusion coefficients were determined by calculating the slopes of the MSDs of the ions versus time in the range between 3 and 4 ns.

The density of [Li(G3)][TFSA] and [Li(G4)][TFSA] obtained by the molecular dynamics simulation at 303 K are summarized in Table 1. The calculated density well reproduces the experimental value.[3c] The errors of the calculated density are less than 1 %.

The site-site intermolecular radial distribution functions in the [Li(G3)][TFSA] at 303 K were calculated as shown in Figure 2 (a). The distribution function between the Li^+ and oxygen atoms of G3 and that between the Li^+ and oxygen atoms of $[TFSA]^-$ have the sharp peaks at about 2 Å, indicating the contact of Li^+ with these oxygen atoms in the mixture. The former peak is more than twice as high as that of the latter, which shows that the Li^+ prefers to have contact with oxygen atoms of G3 in the [Li(G3)][TFSA]. The radial distribution functions were calculated with changing temperature from 303K to 403K. The effects of temperature on the calculated radial distribution functions are not large as shown in Figure 3S in electronic supplementary information. The slight broadening of the peaks was observed by the increase of the temperature.

Table 1. Density, self-diffusion coefficient and stabilization energy by the formation of [Li(glyme)][TFSA] complex.

	d^a	$D_{sol}{}^b$	$D_{cation}{}^b$	$D_{anion}{}^b$	$E_{bind}{}^c$
calc					
[Li(G3)][TFSA]	1.43	0.43	0.43	0.24	-82.8
[Li(G4)][TFSA]	1.41	0.78	0.78	0.73	-70.0
exp[d]					
[Li(G3)][TFSA]	1.42	0.77	0.77	0.54	
[Li(G4)][TFSA]	1.40	1.26	1.26	1.22	

[a] Density (303 K) in g cm^{-3}. [b] Self-diffusion coefficient in 10^{-7} cm^2 s^{-1}. Calculated values at 403 K and experimental values at 303 K. [c] Stabilization energy by the formation of [Li(glyme)][TFSA] complex from $[Li(glyme)]^+$ and $[TFSA]^-$. Ref. 6. [d] Ref. 3i.

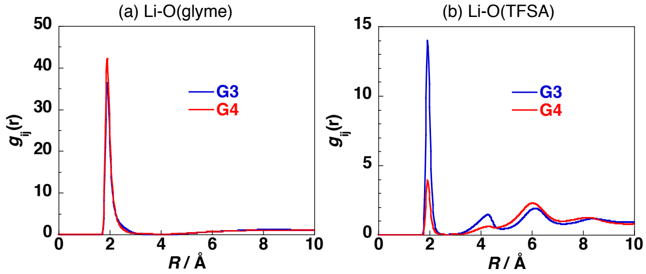


Figure 2. Site-site intermolecular radial distribution functions in the [Li(G3)][TFSA] and [Li(G4)][TFSA] at 303 K. Radial distribution function between the Li^+ and oxygen atoms of the glymes and that between the Li^+ and oxygen atoms of the $[TFSA]^-$ anions.

The site-site intermolecular radial distribution functions in the [Li(G4)][TFSA] at 303 K were calculated as shown in Figure 2 (b). The distribution function between the Li^+ and oxygen atoms of G4 has the sharp peak at about 2 Å, while that between the Li^+ and oxygen atoms of $[TFSA]^-$ has the low peak at about 2 Å. The height of this peak is about one eighth of that of the former peak, which shows that the most of oxygen atoms which have contact with Li^+ in the [Li(G4)][TFSA] are the oxygen atoms of G4. The glyme chain length affects the coordination geometry of Li^+ significantly. Although the effects of temperature on the calculated radial distribution functions are small, the peak of the radial distribution function between the Li^+ and oxygen atoms of G4 decreases and that between Li^+ and oxygen atoms of $[TFSA]^-$ increases slightly by the increase of the temperature as shown in Figure 4S in electronic supplementary information.

The coordination numbers of Li^+ in the [Li(G3)][TFSA] and [Li(G4)][TFSA] are shown in Figure 3. All four oxygen atoms of G3 and one oxygen atom of $[TFSA]^-$ have contact with Li^+ in the [Li(G3)][TFSA]. On the other hand the coordination number of oxygen atoms of G4 is about 4.5 and that of oxygen atoms of $[TFSA]^-$ is 0.5 in the [Li(G4)][TFSA]. The coordination numbers suggest that two coordination geometries of Li^+ exist in the [Li(G4)][TFSA]. One is the geometry, where four oxygen atoms of G4 and an oxygen atom of $[TFSA]^-$ anion have contact with Li^+. Another is the geometry where all five oxygen atoms of G4 and no oxygen atoms of $[TFSA]^-$ anion have contact with Li^+.

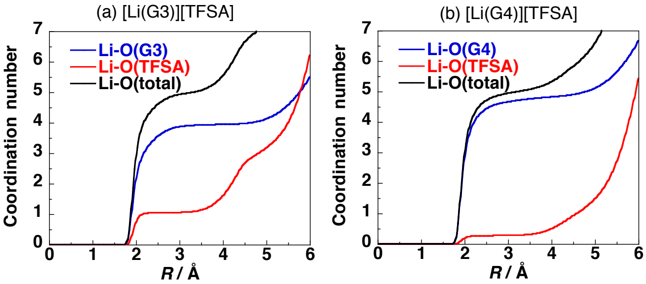
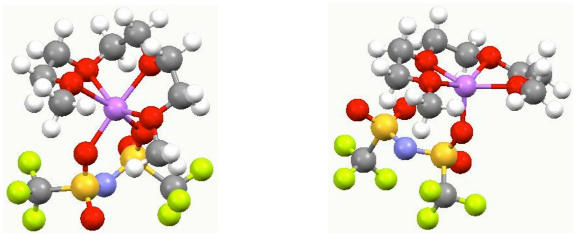


Figure 3. Coordination number of Li^+ in the [Li(G3)][TFSA] and [Li(G4)][TFSA] at 303 K.

The coordination geometry of Li^+ in the equimolar mixture ([Li(G3)][TFSA]) is different from the stable geometry of the [Li(G3)][TFSA] complex in the gas phase obtained by ab initio calculations. Ab initio calculations show that the coordination number of Li^+ is six in the most stable structure of the [Li(G3)][TFSA] complex (Figure 4, 1a).[6] The four oxygen atoms of G3 and two oxygen atoms of $[TFSA]^-$ anion have contact with the Li^+ in 1a. The most stable structure, in which an oxygen atom of $[TFSA]^-$ anion has contact with Li^+, (Figure 4, 1b) is 3.5 kcal/mol less stable. The stabilization energies by the formation of the complex from isolated ions and glyme (E_{form}) calculated for 1a and 1b at the MP2/6-311G**//HF/6-311G** level are -178.4 and -174.9 kcal/mol, respectively.[6] The Li^+ prefers the hexadentate structure in the gas phase, while it prefers the pentadentate structure in the equimolar mixture.

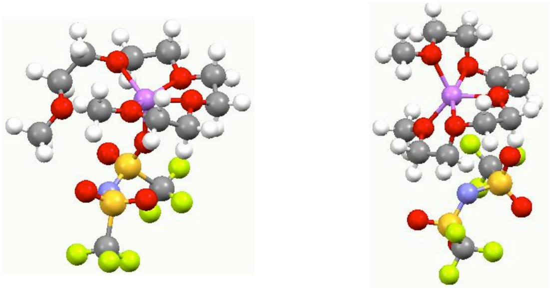


1a -178.4 **1b -174.9**

Figure 4. Stable geometries of the [Li(G3)][TFSA] complex and their stabilization energy by formation of complex obtained by ab initio calculations.

Ab initio calculations show that the coordination number of Li^+ is five in the most stable structure of the [Li(G4)][TFSA] complex (Figure 5, 2a).[6] The four oxygen atoms of G4 and one oxygen atom of $[TFSA]^-$ anion have contact with the Li^+ in 2a. The most stable structure, in which no oxygen atoms of $[TFSA]^-$ anion has contact with Li$^+$, (Figure 5, 2b) is 4.0 kcal/mol less stable. The five oxygen atoms have contact with Li$^+$ in 2b. The E_{form} calculated for 2a and 2b are -177.7 and -173.7 kcal/mol, respectively.[6] Figure 3b shows that both structures exist in the equimolar mixture, although 2b is substantially less stable than 2a in the gas phase.

The coordination numbers of Li$^+$ in the [Li(G3)[TFSA] (Figure 3a) show that a negatively charged oxygen atom of [TFSA]$^-$ anion has contact with the positively charged Li$^+$. This shows that the [TFSA]$^-$ anion interacts with the [Li(G3)]$^+$ cation strongly. On the other hand the coordination number of oxygen atoms of [TFSA]$^-$ is 0.5 in the [Li(G4)][TFSA]. The interaction of the [TFSA]$^-$ anion with the [Li(G4)]$^+$ complex is weaker than that with the [Li(G3)]$^+$. The stabilization energy by the formation of the [Li(glyme)][TFSA] complex from [Li(glyme)]$^+$ and [TFSA]$^-$ obtained by ab initio calculations (E_{bind}) is summarized in Table 1. The calculated E_{bind} values also show that the interaction of [TFSA]$^-$ anion with [Li(G3)]$^+$ is stronger than that with [Li(G4)]$^+$. The E_{bind} calculated for the [Li(G3)][TFSA] and [Li(G4)][TFSA] are -82.8 and -70.0 kcal/mol, respectively.[6] The difference of the coordination geometry affects the magnitude of the interactions.



2a -177.7 **2b -173.7**

Figure 5. Stable geometries of the [Li(G4)][TFSA] complex and their stabilization energy by formation of complex obtained by ab initio calculations.

The self-diffusion coefficients of the ions and glymes in [Li(G3)][TFSA] and [Li(G4)][TFSA] were calculated from the mean square deviations (MSDs) of the ions and glymes as shown in Table 1. The MSDs of ions and glymes in the [Li(G3)][TFSA] and [Li(G4)][TFSA] are shown in Figure 5S. The ratio of self-diffusion coefficients calculated for glyme and Li$^+$ ($D_{\text{sol}}/D_{\text{cation}}$) in the [Li(G3)][TFSA] and [Li(G4)][TFSA] are close to 1.0 as in the cases of experimental self-diffusion coefficients.[3c] The nearly identical self-diffusion coefficients of Li$^+$ and glymes indicate the formation of the stable [Li(glyme)]$^+$ complexes in the mixtures. The self-diffusion coefficients calculated for Li$^+$ and G3 in the [Li(G3)][TFSA] are considerably larger than that for [TFSA]$^-$ (D_{anion}), while the self-diffusion coefficients calculated for Li$^+$ and G4 in the [Li(G4)][TFSA] are close to that for [TFSA]$^-$. The self-diffusion coefficients calculated for ions and glyme in the [Li(G4)][TFSA] are substantially larger than those in [Li(G3)][TFSA]. The self-diffusion coefficients calculated for the ions and glyme in the [Li(G3)][TFSA] and [Li(G4)][TFSA] accurately describe the experimental trend of the self-diffusion coefficients,[3c] although the calculated self-diffusion coefficients were smaller than the experimental values as in the cases of other ionic liquids.[14]

The magnitude of the interaction between cation and anion is one of the important factors controlling the diffusion of ions in ionic liquids.[15] The diffusion of ions becomes slow as the interaction between cation and anion becomes strong. The weaker interaction between the [Li(G4)]$^+$ and [TFSA]$^-$ anion compared with that between the [Li(G3)]$^+$ and [TFSA]$^-$ anion is apparently the cause of the faster diffusion of ions in the [Li(G4)][TFSA] compared with [Li(G3)][TFSA].

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Notes and references

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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14 It is well recognized that the self-diffusion coefficients of ions in ionic liquids obtained by molecular dynamics simulations using commonly used non-polarizable force field are about one order smaller than the experimental values in general. Reference 13c and molecular dynamics simulations by other groups show that the calculated self-diffusion coefficients well reproduce the qualitative trend of the ion dependence of the self-diffusion coefficients, although the absolute values of the calculated self-diffusion coefficients are smaller than experimental ones.

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