Physicochemical Properties of Glyme–Li Salt Complexes as a New Family of Room-temperature Ionic Liquids

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Certain glyme–Li salt complexes, which are composed of equimolar mixtures of a glyme and a Li salt, are liquid under ambient conditions with physicochemical properties such as high thermal stability, wide potential window, high ionic conductivity, and high Li^+ transference number and can be regarded as a new family of room-temperature ionic liquids.

Room-temperature ionic liquids (RTILs), which are liquid at room temperature and composed entirely of ions, have attracted much attention because of their unique properties such as non-flammability, low-volatility, high chemical stability, and high ionic conductivity.[1] RTILs are expected to be applied to electrochemical devices, including electric double-layer capacitors,[2] fuel cells,[3] dye-sensitized solar cells,[4] and lithium ion batteries (LIBs).[5] Most of the RTILs reported to date can be classified as combinations of weakly Lewis-acidic cations and weakly Lewis-basic anions, which leads to ionic dissociation without strong coordination of solvent molecules around each ion. Thus, the most common compositions of RTILs are combinations of onium cations such as imidazolium cations, quaternary ammonium cations, and quaternary phosphonium cations and soft anions such as bis(trifluoromethylsulfonyl)-amide ($TFSA^-$), tetrafluoroborate (BF_4^-), and hexafluorophosphate (PF_6^-). There are few reports of RTILs consisting of strongly Lewis-acidic cations such as Li^+ and Na^+ and strongly Lewis-basic anions such as F^- and Cl^-. Melting points of salts consisting of strongly Lewis-acidic cations and strongly Lewis-basic anions are generally much higher than room temperature, resulting in the formation of ionic crystals at room temperature. So far, we have reported the preparation of lithium ionic liquids consisting of lithium salts of borates having electron-withdrawing groups, to reduce the anionic basicity, and lithium coordinating ether-ligands, to dissociate the lithium cations from the anionic centers.[6] However, possibly due to the strong Lewis acidity of Li^+, the viscosity and ionicity (dissociativity) of the lithium ionic liquids at room temperature are as high as 500 mPa s and as low as 0.1–0.2, respectively, resulting in a low ionic conductivity of 10^{-5} S cm^{-1} at its maximum.

Weakly Lewis-basic anions such as BF_4^- and PF_6^- are prepared by the reactions between Lewis acids (BF_3 and PF_5) and a Lewis base (F^-) by forming coordination bonds. However, the preparation of weakly Lewis-acidic cations for RTILs by the reaction between a Lewis acid and a Lewis base has not been proposed. It is anticipated that weakly Lewis-acidic cations can be prepared by the combination of alkali metal cations (Lewis acid) and suitable ligands (Lewis base).

Ethers are relatively strong Lewis bases, and alkali metal cations are strongly coordinated with ethers. It is well-known that particular molar ratio mixtures of Li salts and oligoethers such as crown ethers, triglyme (G3), and tetraglyme (G4) form complexes. Henderson et al. have conducted a systematic study of glyme–Li salt complexes and reported the crystallographic structures, thermal properties, and electrochemical properties of the complexes.[7] Among the series of glyme–Li salt complexes, they found that [Li(G4)][TFSA] remains in the liquid state at room temperature and exhibits an ionic conductivity of 10^{-3} S cm^{-1}. Our group also reported thermal, transport, and electrochemical properties of equimolar complexes of glyme (G3 or G4)–Li salt complexes (LiTFSA or $LiN(C_2F_4S_2O_4)$).[8] We found that the equimolar complexes of glyme (G3 or G4) and Li salts show unique physicochemical properties similar to those of RTILs, for example, high thermal stability, low volatility, low flammability, and high ionic conductivity. Significantly, a 4 V-class $LiCoO_2$ cathode can be successfully operated in the molten glyme–Li salt complexes;[8] therefore, these complexes are now promising electrolytes for LIBs.

Through the donation of lone pairs of a glyme molecule (Lewis base) to a Li^+ cation (Lewis acid), the weakly Lewis-acidic complex cation [Li(glyme)]$^+$ can be obtained. Due to the formation of the complex, the Lewis acidity of Li^+ is greatly weakened, which can be regarded as an analogous concept to the formation of weakly Lewis-basic anion such as BF_4^- and PF_6^- by the reaction between a Lewis acid and a Lewis base. The combination of a weakly Lewis-acidic complex cation [Li-(glyme)]$^+$ and a weakly Lewis-basic anion leads to ionic dissociation in the fused complex similar to conventional RTILs. Here, we propose glyme–Li salt complexes as a new family of room-temperature ionic liquids. It is anticipated that modification of the chemical structure of the ligand, i.e., glyme in this study, brings about dramatic changes in the physicochemical properties of the glyme–Li salt complexes. So far, the physicochemical properties of conventional RTILs have been tailored by the modification of the chemical structures of cations and/or anions. For example, it has been reported that introducing asymmetric structure into the cation and/or anion of an RTIL is effective in decreasing melting point, glass transition temperature, and viscosity.[9] In this work, asymmetric structure is introduced into the glyme molecules by changing the terminal alkyl group, as shown in Figure 1, and the dependences of physicochemical properties of glyme–Li salt complexes on the chemical structure are investigated.

DSC thermograms (Figure 2) of different glyme (G3 or G4)–LiTFSA complexes show their melting points to be lower than room temperature. In all the DSC curves, no peak due to the melting of pure glymes is observed (see Supporting Information (SI) Table S1),[10] suggesting that no free glyme molecules exist in the equimolar mixtures. It has been reported that the
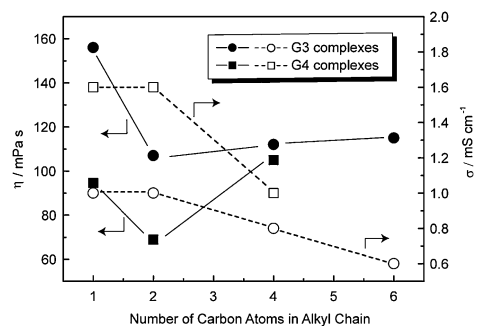
Table 1. Viscosity (η), density (d), molar concentration (M), ionic conductivity (σ), self-diffusion coefficient (D), Li$^+$-transference number (t_+), and $\Lambda_{imp}/\Lambda_{NMR}$ for glyme–lithium salts complexes at 30 °C

| | η /mPa s | d /g cm^{-3} | M /mol dm^{-3} | σ /mS cm^{-1} | Diffusion coefficient/10^{-7} cm^2 s^{-1} | | | t_+ | $\Lambda_{imp}/\Lambda_{NMR}$ |
					D_{sol}	D_{cation}	D_{anion}		
[Li(G3)][TFSA]	156.0	1.46	3.14	1.0	0.84	0.89	0.57	0.61	0.68
[Li(G3Et)][TFSA]	107.0	1.40	2.86	1.0	0.93	0.97	0.70	0.58	0.55
[Li(G3Bu)][TFSA]	112.0	1.34	2.64	0.8	0.94	1.00	0.84	0.54	0.48
[Li(G3Hex)][TFSA]	115.0	1.31	2.44	0.6	0.82	0.86	0.77	0.53	0.41
[Li(G4)][TFSA]	94.6	1.40	2.75	1.6	1.26	1.26	1.22	0.51	0.63
[Li(G4Et)][TFSA]	68.9	1.37	2.62	1.6	1.47	1.55	1.47	0.51	0.54
[Li(G4Bu)][TFSA]	105.0	1.34	2.44	1.0	1.25	1.35	1.31	0.51	0.43
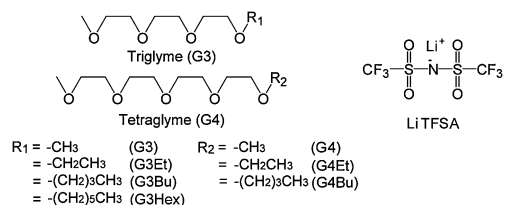
Figure 1. Chemical structures of glymes and LiTFSA.
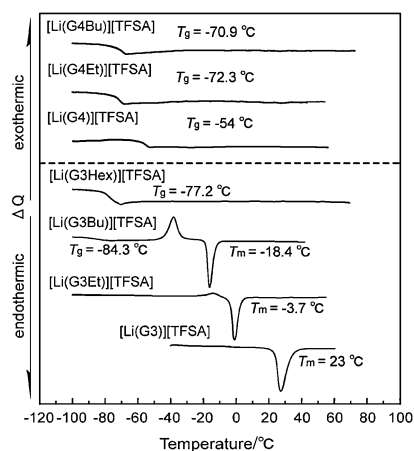
Figure 2. DSC thermograms for glyme–LiTFSA complexes at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

Figure 3. Dependences of viscosity and ionic conductivity on the number of terminal alkyl chain length of glymes in the glyme–Li salt complexes.

equimolar complexes of crown ethers (12-crown-4 (12C4) and 15-crown-5 (15C5)) and LiTFSA are solids at room temperature,[11] although 12C4 and 15C5 have the same number of oxygen atoms as G3 and G4, respectively. The glymes have higher conformational flexibility than the crown ethers, and the flexible structure of glymes may also give rise to conformational freedom in the molten complexes. This leads to an increase in the entropy change of melting (ΔS_m), resulting in a decrease of the melting point ($T_m = \Delta H_m / \Delta S_m$; ΔH_m: the enthalpy change of melting) (SI Table S2).[10] The number of conformers of glyme–LiTFSA can be further increased by the modification of the chemical structure of glyme. As we anticipated, when one of the terminal methyl groups of the glyme is substituted by alkyl groups of various lengths, the melting point and/or glass transition temperature can be reduced.

The thermal stabilities of glyme–Li salt complexes were investigated by thermogravimetric analysis (SI Figures S2 and S3).[10] The pure glymes immediately evaporate at temperatures

higher than 100 °C. However, the mass of each glyme–Li salt complex does not change until 200 °C. The evaporation of glyme from [Li(glyme)][TFSA] started at ca. 200 °C, and the glyme was completely removed from the complex at around 400 °C. At temperatures higher than 400 °C, the decomposition of LiTFSA took place. When the temperature of [Li(glyme)][TFSA] was kept at 100 °C for 1–3 h, almost no mass loss was observed (SI Figures S4 and S5).[10] This confirms that the vapor pressure of [Li(glyme)][TFSA] is negligible at temperatures lower than 100 °C, and the equimolar mixtures behave like an RTIL.

The viscosity, density, molar concentration, and ionic conductivity at 30 °C are summarized in Table 1. The ionic conductivity of glyme–Li salt complexes is in the range of 10^{-4}– 10^{-3} S cm^{-1} at 30 °C, suggesting that the Li salt dissociates in each liquid. Although the viscosity of [Li(glyme)][TFSA] is approximately 10–100 times higher than that of typical organic electrolytes,[12] the ionic conductivity is rather high due to the high ionic concentration of [Li(glyme)][TFSA]. The ionic conductivity of [Li(G4)][TFSA] is higher than that of [Li(G3)][TFSA], which is mainly due to the lower viscosity of [Li(G4)][TFSA]. Figure 3 shows the viscosity and the ionic conductivity of [Li(glyme)][TFSA] molten complexes as a function of terminal alkyl chain length of glyme. The viscosities of the glyme–Li salt complexes pass through a minimum. As the alkyl chain length is increased, the ionic concentration in the liquid is decreased resulting in the relaxation of the Coulombic interaction between ionic species. However, the longer alkyl chains cause larger van der Waals interaction. Consequently, the viscosity exhibits a minimum when the terminal alkyl group is an ethyl group. Despite the viscosity decrease from the methyl- to the ethyl-terminal group, the ionic conductivities of [Li-

(G3Et)][TFSA] and [Li(G4Et)][TFSA] are the same as that of [Li(G3)][TFSA] and [Li(G4)][TFSA], respectively. The concurrent decrease in the ionic concentration caused this result.

The self-diffusion coefficients of the glyme (D_{sol}), Li^+ cation (D_{cation}), and $TFSA^-$ anion (D_{anion}) in glyme–Li salts complexes at 30 °C (Table 1) were measured by pulsed-field gradient spin-echo NMR (PGSE-NMR). For each glyme complex, the self-diffusion coefficients of Li^+ cation and the glyme molecule are the same within experimental error. It should be noted that in conventional organic lithium electrolyte solutions the diffusivity follows the order: solvent > anion > Li^+.[13] This is due to preferential solvation of Li^+ by the solvent, resulting in the largest hydrodynamic volume among the components. The identical values of D_{sol} and D_{cation} in the glyme–Li salt complexes indicate that each Li^+ cation is coordinated by a glyme molecule, and they diffuse together as a complex cation $[Li(glyme)]^+$ in the liquid. The value of Li^+ transference number (t_+) of each glyme–Li salt complex is calculated from the equation $t_+ = D_{cation}/(D_{cation} + D_{anion})$ to be ca. 0.5–0.6. The ionicity ($\Lambda_{imp}/\Lambda_{NMR}$), which has been defined as the ratio of the molar conductivity measured by AC impedance measurements and PGSE-NMR measurements[13,14] and a measure of the dissociativity, is surprisingly high despite the high ionic concentration and ranges from 0.4 to 0.7. The t_+ values close to 0.5 and the high $\Lambda_{imp}/\Lambda_{NMR}$ values are widely observed in common RTILs,[14] which again supports our proposal of the glyme–Li salt complexes as a new family of RTILs.

Cyclic voltammetry (CV) (SI Figure S6)[10] revealed a reversible Li deposition/stripping in each molten complex. To investigate the oxidative stabilities of glyme–Li salt complexes, linear sweep voltammetry was performed using a hermetical two-electrode cell: [Pt plate|[Li(glyme)$_x$][TFSA]|Li metal] (Figure 4). The anodic current due to the oxidation of equimolar complex is not observed in the potential range from 3.0 to 4.7 V vs. Li/Li^+. From the results of CV and LSV, the potential window of equimolar glyme–Li salt complexes is estimated to be 0–4.7 vs. Li/Li^+. It is well known that the oxidation of ether compounds starts from ca. 4 V vs. Li/Li^+. Indeed, anodic current for the [Li(glyme)$_{20}$][TFSA] solution, where a large excess of glyme molecules exists (molar ratio of glyme:LiTFSA = 20:1), increases at ca. 4 V (Figure 4), which is a much lower potential than the anodic limit of [Li(glyme)][TFSA]. The free glyme molecules in [Li(glyme)$_{20}$][TFSA] solutions, which are not involved in the complexation with Li^+, appear to be responsible for the lower oxidation limit. The glyme donates lone pairs to the Li^+ cation resulting in the enhancement of oxidative stability of the ether structure.

In summary, the glyme–Li salt complexes, which are composed of equimolar amounts of a glyme and a Li salt, exhibit high thermal stability, Li^+ ionic conductivity, and high oxidative stability. In this paper, we proposed the utilization of the complex cation, [Li(glyme)], as a component of RTILs. By the complex formation, the Lewis acidity of Li^+ is greatly weakened, and the glyme–Li salt complex can remain in the liquid state and dissociate into ions at room temperature. By the modification of the chemical structure of the glyme molecule, physicochemical properties such as melting point and viscosity of the glyme–Li salt complex change dramatically. In addition to the aforementioned physicochemical properties, the Li^+ transference number and the Li^+ concentration, which are as high as
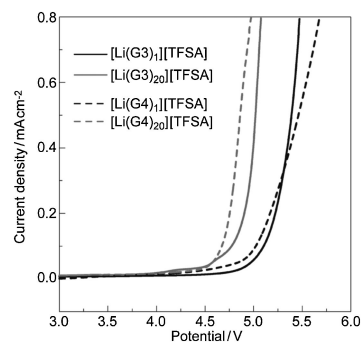

Figure 4. Linear sweep voltammograms of [Pt plate|[Li(glyme)$_x$]-[TFSA]|Li metal] cell at 30 °C. The potential sweep rate is $1 \, mV \, s^{-1}$.

0.5–0.6 and $3 \, mol \, dm^{-3}$, respectively, offer promise for application as a safe electrolyte for lithium secondary batteries.

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