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Criteria for Solvate Ionic Liquids

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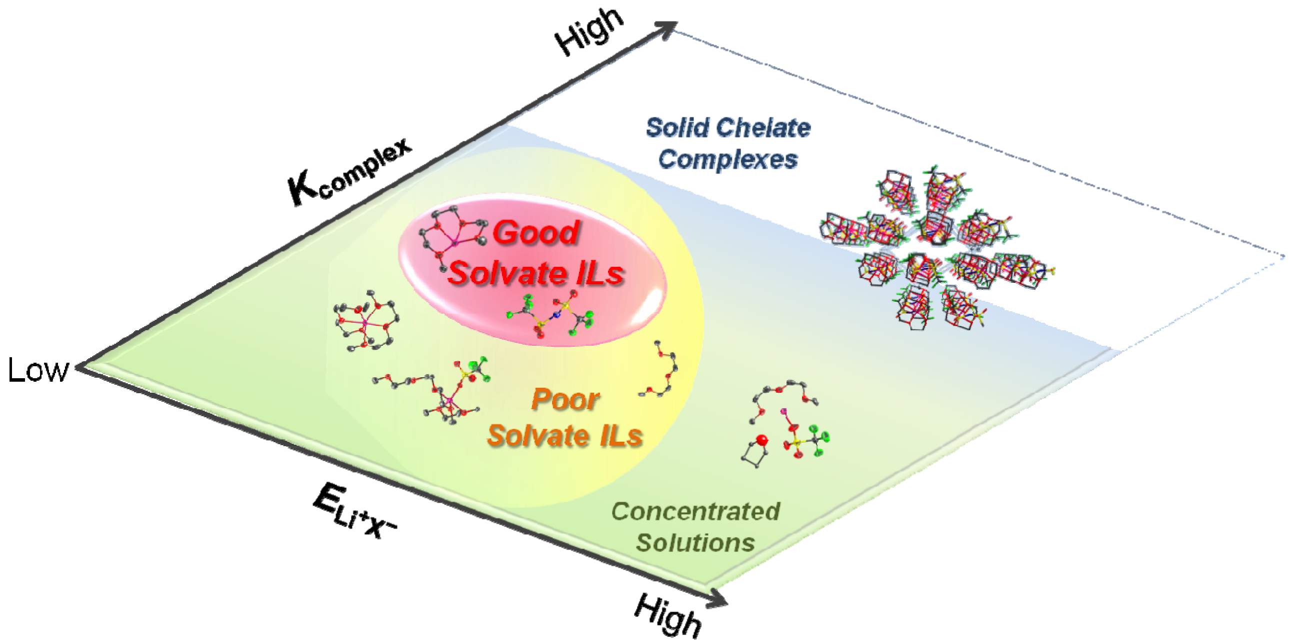
ABSTRACT. Certain concentrated mixtures of salts and solvents are not simply "solutions" anymore, but they may be described as "ionic liquids". In this perspective paper, we describe possible criteria for the new family of ionic liquids: "solvate" ionic liquids. This subclass of ionic liquids was originally proposed by Angell et al. in their recent review, however, their criteria remain to be debated. Concentrated mixtures of lithium salts and organic solvents are useful models for these solvate ionic liquids, and the effects of the salt concentration, types of solvents, and counter anions of the lithium salts on their structure and properties have been explored to enable contrast with traditional solutions, and to help determine whether a given mixture belongs to the solvate ionic liquid or not.

KEYWORDS: solvate ionic liquid, glyme, ligand, lithium salt, Lewis basicity, concentrated electrolyte solution

Table of Contents.



Certain concentrated mixtures of salts and solvents may be described as “solvate” ionic liquid, possible criteria of which are proposed.

1. Introduction.

Understanding the behaviors of concentrated electrolytes has long been an important subject of research on electrolyte solutions.[1-4] In extremely concentrated electrolyte solutions, ion-ion, ion-solvent, and their mutual interactions are very complicated, and therefore there has been little systematic research on such behavior.[4] On the other hand, the importance of highly concentrated electrolytes has become increasingly obvious in recent years, especially when they are applied in high energy-density batteries in which high electrochemical stability, thermal stability, and excellent flame resistance of electrolytes, in addition to high ionic conductivity, play crucial roles.[5-7]

Ionic liquids (ILs) are molten salts having melting points below 100 °C, and this is a well-accepted definition.[8,9] Because of their remarkable properties (*e.g.* negligible vapor pressure, non-flammability, and high ionic conductivity), ILs have attracted much attention as a new class of materials for use as electrolytes in batteries and electrochemical capacitors,[10-12] as well as reusable solvents for organic synthesis and separation.[13, 14] From the standpoint of solution chemistry, these molecular-solvent free ILs can be regarded as an extreme case of an electrolyte, and so much effort has been devoted to understanding the fundamental physicochemical properties of ILs.[15-19] Practical research has also focused on lithium-ion conducting ILs to address today's growing demand for increased safety of lithium secondary batteries. One approach towards this is to design lithium ILs that are lithium salts having melting or glass transition temperatures lower than room temperature.[20, 21]

During our research on lithium ILs, we found that certain equimolar mixtures of oligoethers (glymes) and certain Li salts (LiX, where X is an anion) yielded low melting (or glass-forming) complexes, abbreviated as $[\mathrm{Li(glyme)_1}]\mathrm{X}$.[22, 23] Typically, as the Li salt concentration is increased, the properties of the glyme-Li salt mixtures change in the dilute−intermediate regions (~1.5 $\mathrm{mol \cdot dm^{-3}}$) as seen in typical electrolyte solutions.[2, 3] However, a peculiarity can be seen for the equimolar composition, wherein strong complexation occurs between all the glyme molecules and the $\mathrm{Li^+}$ ions, resulting in $[\mathrm{Li(glyme)_1}]^+$ formation (**Figure 1**). As a result, the glyme-Li salt molten complexes consist of these independent complex $[Li(glyme)_1]^+$ cations and their counter anions, which together form the essence of an IL. In a recent review paper by Angell et al.,[24] four categories of ILs were identified: existing aprotic, protic, inorganic ILs, and novel solvate (or chelate) ILs. The solvate ILs, in which ligand molecules strongly coordinate with the cations and/or anions of salts, thus forming complex ions, could be an important class of ionic liquids, especially for preparing ILs based on metal cations. According to this classification, the low melting glyme-Li salt molten complex can be a prototype for solvate ILs.

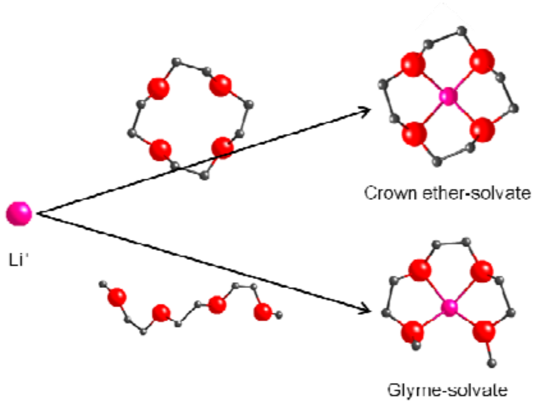
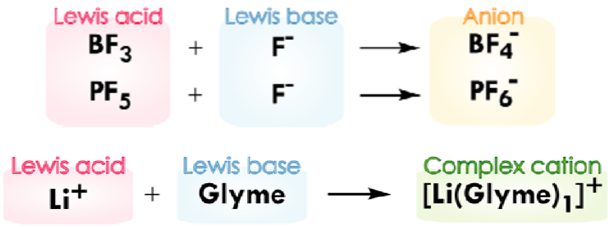


Figure 1. Crown ether- and glyme-based $[Li(ligand)_1]^+$ solvate models.

The basic idea of solvated cations being constituents of ILs was first proposed by Angell, who regarded the hydrated calcium ion as an independent cation in molten hydrates such as $[Ca(H_2O)_4](NO_3)_2$.[25] This concept is akin to that for common complex anions of ILs such as BF_4^-, PF_6^-, and $AlCl_4^-$; these ions are the adducts of a Lewis acid (BF_3, PF_5, and $AlCl_3$) and a Lewis base (F^- and Cl^-) as shown in **Scheme 1**. Similarly, the Li^+ ions and the glymes are a Lewis acid and base, respectively, forming a complex $[Li(glyme)_1]^+$ cation. A difference is seen between them; the glyme complexes are non-covalent ones, whereas the latter complexes like BF_4^- are covalent ones. Mixtures of metal salts and crown-ethers or cryptands are also typical examples of well-defined solvate complex cations,[26-29] as many of these complexes melt at temperatures much higher than room temperature (usually > 100 °C). The coordinating structures in glyme-Li salt 1:1 complexes have also been widely studied as models for poly(ethylene oxide) (PEO)-based polymer electrolytes in crystalline states[30-34] and using *ab initio* calculations.[35, 36] In some cases, these chelate compounds have also been used in electrolyte solutions to increase their solubility in non-polar solvents, and to enhance the dissociation of the Li salts.[37]



Scheme 1. Concept of complex cation in solvate ILs.

As opposed to the abundant expertise available on various ligand-transition metal salt complexes based on coordination chemistry, little is known about the liquid structure and electrolyte properties of bulk solvates in the fused state.[38] Given the similarity between ordinary concentrated solutions and the solvate ILs, a question arises; can a sharp boundary be drawn between them? In other words, such liquids may act as a bridge between ordinary solutions and molecular-solvent free ILs. In this regard, the current criteria applied to the definition of solvate ILs are still somewhat ambiguous, and this motivated us to study factors that divide the concentrated electrolyte solutions into these two liquid states. There is no doubt that the interplay between the ion-ion and ion-solvent interactions is essential in discussing the differences between these two concentrated liquids and their related properties. Because of these factors, we investigate the effects of salt concentration and the respective natures of solvents (ligands) and counter anions on the structures and properties of a series of concentrated solutions of Li salts, and we propose more detailed criteria for characterizing the new family of ILs, solvate ILs.

2. Glyme-lithium salt mixtures.

Because glymes have multiple ether-oxygen atoms with relatively high electron donating ability, they function as multidentate ligands and exhibit strong solvation power towards alkali metal cations.[39] It is well known that the preferable coordination number of the Li^+ ion is usually 4–5 in solution.[40] Thus, triglyme (G3) and tetraglyme (G4) are selected as model ligands because they have four and five coordination sites per molecule, respectively. Herein, we describe typical examples of solvate ILs, the equimolar mixtures of $Li[N(SO_2CF_3)_2]$ (Li[TFSA]) and the glymes, $[Li(G3 \text{ or } G4)_1][TFSA]$, and we show how their behavior is different from that of dilute solutions of Li[TFSA] in glyme solvents.

In **Figure 2**, the deviation of the thermal weight loss temperature (T_d) of the mixtures from those of the pure glymes, ΔT_d, is plotted against the ratio of the number of oxygen atoms to the number of Li^+ ions, $[O]/[Li^+]$, for several mixtures of G3-Li[TFSA] and G4-Li[TFSA]. Each T_d was defined as the 5 % weight loss temperature in the thermogravimetric curves measured at a scan rate of 10 K/min under a nitrogen atmosphere; the weight loss is a consequence of the evaporation of the glymes. The T_d values of the pure G3 and G4 were 104 °C and 134 °C, respectively. Therefore, ΔT_d indicates how the thermal stabilities of the mixtures are improved relative to that of the pure solvent by the addition of Li[TFSA]. In the dilute regions, ΔT_d increases gradually as the molar ratio of Li[TFSA] increases ($[O]/[Li^+]$ decreases). At the equimolar composition, however, ΔT_d rises more significantly, and the thermal stability of the electrolyte is dramatically improved by the complexation. This result suggests that all the glyme molecules were strongly bound to Li^+ ions at the molar ratio of 1:1 to form the complex cation $[Li(glyme)]^+$. The ion-dipole (induced-dipole) interactions between the glymes and the Li^+ ions suppress the evaporation of the glymes, and consequently, a high thermal energy is needed to desolvate the Li^+ ions coordinated with the multidentate glymes. The ΔT_d of $[Li(G3)_1][TFSA]$ ($[O]/[Li^+] = 4$) was slightly higher than that of $[Li(G4)_1][TFSA]$ ($[O]/[Li^+] = 5$), implying that the coordination number of four provides the most thermally stable condition for the glymes to interact with the Li^+ ions. The much lower volatility of the equimolar mixtures was further confirmed by isothermal gravimetric analysis (for detail, see **Figure 5**). At 100 °C, the pure glyme solvents gradually lose weight due to the evaporation. By contrast, the weight loss of $[Li(G3 \text{ or } G4)_1][TFSA]$ is almost negligible at 100 °C even after 3 h.

This outstanding low volatility of $[Li(G3 \text{ or } G4)_1][TFSA]$ indicates an obvious similarity to common ILs.

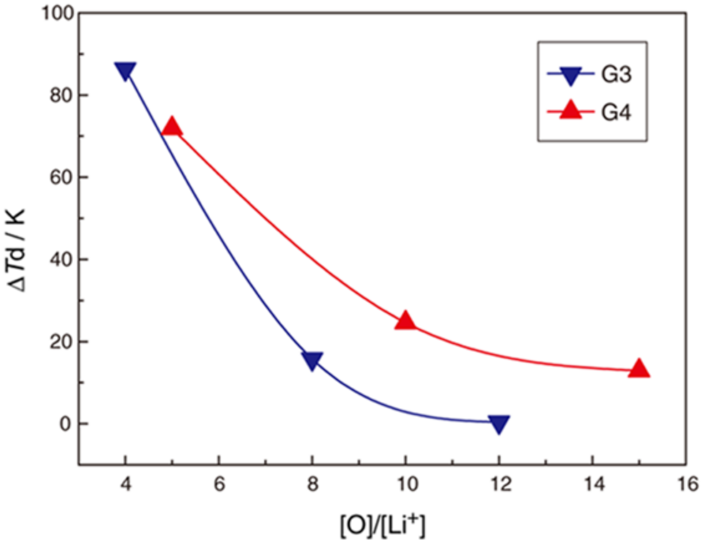


Figure 2. Correlation between thermal stability and [O]/[Li$^+$] of glyme-Li[TFSA] mixtures. The lines in the figure are visual guides only.

By increasing the Li[TFSA] concentration to 1:1 in the glyme-Li[TFSA] ratio, the electrochemical stability of the mixtures was also significantly improved. It is well known that the oxidation of ether compounds starts below *ca*. 4 V vs. Li/Li$^+$.[41, 42] Indeed, the anodic current for the glyme solutions, where a large excess amount of glyme molecules existed (molar ratio of glyme:Li[TFSA] = 20:1), increased at *ca*. 4 V. In contrast, the anodic limits were increased to be *ca.* 5 V for $[Li(G3 \text{ or } G4)_1][TFSA]$.[23] $[Li(G3)_1][TFSA]$ shows a slightly higher anodic limit than that of $[Li(G4)_1][TFSA]$,[23] suggesting again that the coordination number of four is preferable to achieve high electrochemical stability of the glymes, and that G3 is more strongly bound to the Li$^+$ ion than G4.

Due to their low melting points and glass-forming character, crystal structures of $[Li(G3 \text{ or } G4)_1][TFSA]$ have not yet been revealed, while the aforementioned remarkable properties would provide strong evidence for the complexation. Instead, as shown in **Figure 3**, the crystal structure of

$[Li(G3)_1][N(SO_2C_2F_5)_2]$ ($[Li(G3)_1][BETA]$), which is an analog of $[Li(G3)_1][TFSA]$, is available in the literature, and the structure is classified as a contact-ion pair (CIP).[43] All of the oxygen atoms of G3 coordinate to the Li^+ ion forming a 12-crown-4 ether-like coordination geometry,[44] and one oxygen atom from the $[BETA]^-$ anion also participates in the coordination with the Li^+ ion. The coordination structures of $[Li(G3 \text{ or } G4)_1][TFSA]$ were also studied by *ab initio* molecular orbital calculation.[23, 45] In the optimized structures of $[Li(G3)_1][TFSA]$ and $[Li(G4)_1][TFSA]$, the glyme donates lone pairs of oxygen atoms to the Li^+ ion, and the glyme molecule wraps around the Li^+ ion to form a crown ether-like, one-to-one complex cation $[Li(glyme)_1]^+$ (see **Figure 3**). The calculated structure of the $[Li(G3)_1]^+$ complex cation showed good agreement with the cation structure observed in the crystal of $[Li(G3)_1][BETA]$. The chemical nature of the $[TFSA]^-$ anion is very similar to that of the $[BETA]^-$ anion. We speculate that the crystal structure of $[Li(G3)_1][TFSA]$ is also a CIP structure. These results strongly support the hypothesis for the formation of a complex cation $[Li(glyme)_1]^+$ in the equimolar mixture of glyme and Li[TFSA]. In addition, the resemblance of the coordinating structure of the glymes in crystalline $[Li(G3)_1][BETA]$ and liquid $[Li(G3)_1][TFSA]$ was proved by Raman spectroscopy as discussed in a later section.

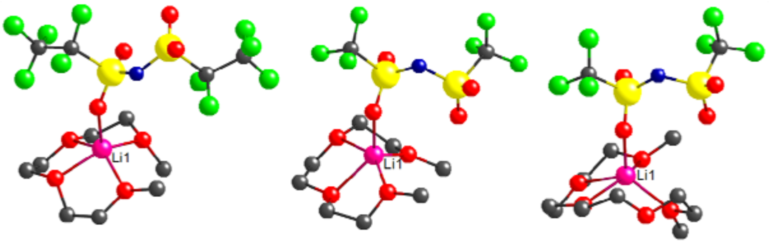


Figure 3. Solvate structures of $[Li(G3)_1][BETA]$ (left), $[Li(G3)_1][TFSA]$ (center) and $[Li(G4)_1][TFSA]$ (right). H atoms are omitted for clarity. Pink, Li; red, O; gray, C; blue, N; yellow, S; green, F.

When Li^+ ions and ligands form long-lived robust complexes, even in the liquid state, they would diffuse together, resulting in the same diffusion coefficients between Li^+ ions and ligands. The concentration dependence of the self-diffusion coefficients for glymes (D_G), anions (D_-), and Li^+ ions

(D_{Li+}) was measured by means of pulsed-field-gradient NMR spectroscopy.[46-48] In the diluted system, the diffusion coefficients are in the order $D_G > D_- > D_{Li+}$, which agrees well with the corresponding order for conventional organic electrolytes.[49, 50] However, with increasing Li[TFSA] concentrations, the difference between D_G and D_{Li+} becomes less pronounced, and consequently, they become identical at the equimolar ratio. This result also supports the hypothesis for the formation of a 1:1 complex in the equimolar binary mixture of the glyme and the Li[TFSA] salt.

As described above, the concentration of Li[TFSA] in the glymes strongly affects the physicochemical properties of the solution. In particular, the equimolar binary mixture of Li[TFSA] and the glymes showed characteristic features, namely, remarkably high thermal and electrochemical stability, and identical diffusion coefficients of the Li^+ ions and the glyme molecules. These phenomena arise from the formation of a stable 1:1 complex. The single-crystal structure analysis of $[Li(G3)_1][BETA]$ complex, having the structural analog of the $[TFSA]^-$ anion, also supports this idea. Because $[Li(G3)_1][TFSA]$ and $[Li(G4)_1][TFSA]$ are in the liquid state at ambient temperature and exhibit negligible vapor pressure under ambient conditions, they satisfy the criteria for common ILs. Therefore, these liquid complexes that are without free (uncoordinating) solvents can be classified as solvate ILs.

The thermal and physicochemical properties of conventional ILs have been tailored by the modification of the chemical structures of cations and/or anions.[51, 52] For example, it has been reported that introducing an asymmetric structure into the cation and/or anion of an IL is effective in decreasing the melting point, glass transition temperature, and viscosity of the mixture.[18, 53] Likewise, it is anticipated that modification of the chemical structure of glyme brings about remarkable changes in the physicochemical properties of the glyme-Li salt complexes. Asymmetric structure can be easily introduced into the glyme molecules by changing a terminal alkyl group.[54] As a result, the number of conformers of the glyme-Li[TFSA] complex can be further increased. By substituting one of the terminal methyl groups of the glyme by a different alkyl group, the melting point and/or glass transition temperature can be decreased, and thereby, the liquid temperature range can be expanded. The viscosity exhibits a minimum value at the ethyl termination when one terminal is fixed as the methyl group and the other terminal alkyl chain length is varied. As the alkyl chain length is increased, the ionic concentration in the liquid is decreased, resulting in the relaxation of the columbic interaction between the ionic species. However, the longer alkyl chain length causes stronger van der Waals interactions. The viscosity minimum is attributed to the competition between the columbic interaction and the van der Waals interaction, just as seen alkylmethylimidazolium-based ILs.[18] Therefore, the physicochemical properties of solvate ILs can be tuned by changing the structure of ligands in a similar way to the approach used for common ILs. [17, 55-58]

3. Chelate effect.

Low molecular weight carbonate molecules are one of the most popular solvents used in non-aqueous electrolytes for Li-secondary batteries.[59] In these electrolytes, the carbonate molecules adopt the role of solvation that facilitates dissociation of Li salts. Li^+ ions in the solution are solvated by the carbonyl oxygen atoms of the carbonate molecules. The Gutmann's donor numbers of ethylene carbonate (EC) and propylene carbonate (PC) are approximately 15, and are comparable with those of CH_3CN and THF, which indicates high electron donating ability.[60] In general, the mixtures of alkali metal salts and CH_3CN or THF with/without some ligands often form characteristic solid complexes.[61-63] Similarly, it is thought that the carbonate molecules also serve as monodentate ligands, resulting in the formation of complexes.

In this section, we discuss the characteristics of various binary mixtures of Li[TFSA] and the PC system as a prototype for an extremely concentrated Li salt/carbonate solution in terms of coordination chemistry. As described in the previous section, $[O]/[Li^+] = 4$ appears to be the favorable coordination number for yielding robust Li-glyme complexes. Thus, the 1:4 mixture of Li[TFSA] and PC, abbreviated as $[Li(PC)_4][TFSA]$, is employed as a model electrolyte solution (**Figure 4**). Kameda et al.

reported that the first solvation shell of the Li^+ ion consists of 4.5 PC molecules on average, indicating the accuracy of this prediction.[40] In order to judge whether concentrated Li salt/PC solutions can be classified as solvate ILs, their physicochemical properties were carefully scrutinized. In addition to monodentate PC systems, bidentate monoglyme (G1) and tridentate diglyme (G2) systems were also investigated to elucidate the effect of the number of coordination sites within a single ligand molecule on the state of the corresponding mixture.

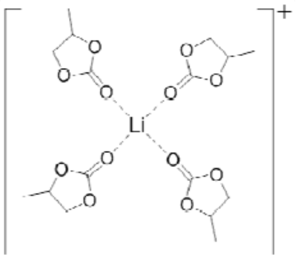


Figure 4. Solvate model of $[Li(PC)_4]^+$ cation.

The thermal stability of $[Li(PC)_4][TFSA]$ at 100 ºC is shown in **Figure 5**. For the sake of comparison with G3- and G4-complexes, isothermal TG curves of $[Li(G3)_1][TFSA]$ and $[Li(G4)_1][TFSA]$ are also presented in **Figure 5**. As described in the previous section, $[Li(glyme)_1][TFSA]$ exhibits negligible weight loss under these conditions. On the contrary, apparent weight loss due to the desolvation of PC molecules from Li^+ ions and evaporation of PC can be observed in $[Li(PC)_4][TFSA]$, although the coordination numbers of the Li^+ ion are the same for $[Li(PC)_4]^+$ and $[Li(G3)_1]^+$. This relatively low thermal stability of PC is also independent of the volatility differences between the pure solvents themselves. These results suggest that the stability of the solvate $[Li(PC)_4]^+$ with monodentate ligand PC is much lower than that of $[Li(G3 \text{ or } G4)_1]^+$ with the multidentate (chelate) ligand, and this leads to a shorter life-time of the solvates in Li salt/PC mixtures. Unlike the case of $[Li(G3 \text{ or } G4)_1][TFSA]$, in which the glymes and the Li^+ ions form stable solvate ions and diffuse together, the diffusion coefficients of the ligand PC molecules in the $[Li(PC)_4][TFSA]$ mixture, and even in the more concentrated $[Li(PC)_3][TFSA]$ mixture, are larger than those of the Li^+ ions (**Figure 6**). The ratios of the respective diffusion coefficients of the solvents and Li^+ ions, D_{sol}/D_{Li+}, for the $[Li(PC)_n][TFSA]$ systems are comparable with those for the solutions, $[Li(G3\ or\ G4)_4][TFSA]$. For the mixtures of $[Li(G3\ or\ G4)_4][TFSA]$ containing excess glyme, the value of D_{sol} is larger than that of D_{Li+}, and this is attributed to the contribution from the diffusion of the free (uncoordinated) glyme in the mixtures. In addition, the ligand exchange of $[Li(glyme)_1]^+$ takes place in the mixtures, leading to a short life-time of the complex cation in the excess-glyme-containing solutions.[23] Thus, the rapid ligand exchange of the Li^+ ion in the $[Li(PC)_n][TFSA]$ mixtures is responsible for the instability of the solvate $[Li(PC)_n]^+$ with monodentate ligand PC.

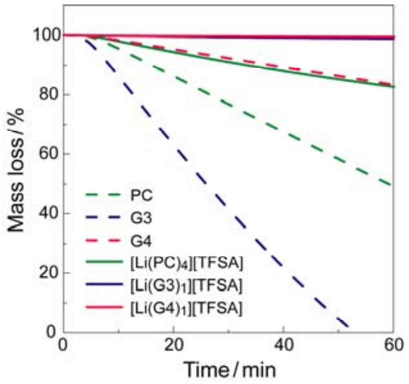


Figure 5. TG curves of $[Li(PC)_4][TFSA]$, $[Li(G3)_1][TFSA]$, and $[Li(G4)_1][TFSA]$ compared with those for the corresponding pure solvents at 100 °C sampled for 1 h.

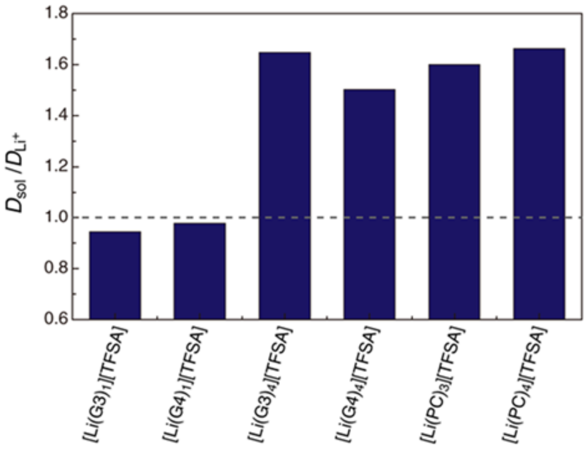


Figure 6. D_{sol}/D_{Li+} of various binary mixtures of Li[TFSA] and G3, G4, or PC.

In the cases of the binary mixtures of Li[TFSA] and bidentate G1 or tridentate G2, formations of crystalline solvates at certain molar ratios, such as [Li(G1)$_1$][TFSA], [Li(G1)$_2$][TFSA], [Li(G1)$_3$][TFSA], [Li(G2)$_{0.5}$][TFSA], and [Li(G2)$_2$][TFSA], were reported.[43, 64] However, as shown in **Figure 7**, the formations of the structurally stable complexes [Li(G1 or G2)$_n$][TFSA] in the solid state seem to have little effect on their thermal stabilities in the liquid state. In the crystalline solvates of [Li(G1 or G2)$_x$][TFSA], the coordination number of Li$^+$ is in the range of 4–6,[43] and excess glyme molecules exist in the electrolytes with [O]/[Li$^+$] > 6. The reduced volatility of glymes for [O]/[Li$^+$] > 6 is explained simply by the vapor pressure depression due to the mixing of solute and solvent. For [O]/[Li$^+$] < 6, it is anticipated that free (uncoordinated) glyme molecules scarcely exist in the [Li(G1 or G2)$_x$][TFSA] liquid. The ΔT_d values for [Li(G1)$_2$][TFSA] and [Li(G2)$_{1.33}$][TFSA] are apparently smaller than that of [Li(G3)$_1$][TFSA] (Figure 2) even though their [O]/[Li$^+$] numbers are adjusted to be 4. These results suggest that the coordination number, namely [O]/[Li$^+$], is not the critical factor determining the stability of the liquid complexes (or concentrated solutions), and that there are other key factors that can be used to classify them as solvate ILs.

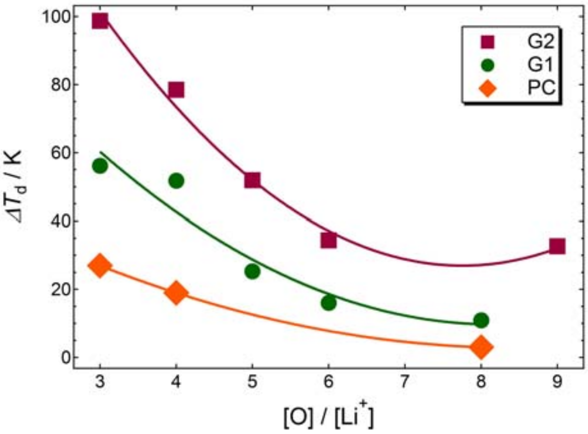


Figure 7. Correlation between thermal stability and [O]/[Li$^+$] of different solvent-Li[TFSA] mixtures. The lines in the figure are visual guides only.

The complex formation constant, K_{complex}, is one of the most important parameters describing the stability of complexes. Unfortunately, there are no reports addressing these constants for the binary mixtures of Li[TFSA] with PC or G1–G4. However, the K_{complex} values for the dilute systems involving lithium pictate and some ligand molecules in dioxane have been studied by Tsvetanov and co-workers.[65] The K_{complex} values between $\mathrm{Li^+}$ ions and the ligand molecules in dioxane were reported to be 1.8, 2.1, 8.5, 17.0, and 24.5 for PC, G1, G2, G3, and G4, respectively. The K_{complex} value becomes larger with increasing number of the coordinating sites in a single ligand molecule. This indicates that longer glymes can form more stable and long-lived complex cations. The cause of K_{complex} difference between various ligand molecules with different coordination-site numbers is well known as the "chelate effect". The entropy change caused by the formation of a complex with a multidentate ligand is smaller than that caused by the formation of a complex with the relevant monodentate ligand, resulting in a higher stabilization energy for the former. Actually, the difference in K_{complex} values between these ligand molecules closely correlates with the corresponding differences in the ΔT_{d} values among $\mathrm{[Li(PC)_4][TFSA]}$, $\mathrm{[Li(G1)_2][TFSA]}$, $\mathrm{[Li(G2)_{1.33}][TFSA]}$, and $\mathrm{[Li(G3)_1][TFSA]}$ (Figures 2 and 7). The ΔT_{d} values increase with an increasing number of coordination sites within a ligand. The values of the diffusion coefficients of the components in each mixture also support the hypothesis that the complex cation or solvate with the higher K_{complex} value also has higher stability and longer life-time. Therefore, it can be concluded that the formation of crystalline solid complexes is not a sufficient condition, but rather that the K_{complex} value is one of the most important parameters required to classify molten mixtures as solvate ILs.

The chelate effect is more pronounced for crown ethers having higher K_{complex} values than those of glymes, whereas the melting points of their complexes with $\mathrm{Li^+}$ ions are frequently higher than those of the corresponding glyme complexes with $\mathrm{Li^+}$ ions and increase to values above 100 °C.[26-29] However, a 1:1 mixture of 18-crown-6 ether and Li[TFSA] yields a low-melting complex, $\mathrm{[Li(18\text{-}crown\text{-}6)_1][TFSA]}$, that melts at approximately 40 °C.[28] Similar to $\mathrm{[Li(G3)_1][TFSA]}$ and $\mathrm{[Li(G4)_1][TFSA]}$, the diffusion coefficients of the $\mathrm{Li^+}$ ions and the ligand molecules measured using pulsed-field-gradient NMR spectroscopy were completely identical in liquid $\mathrm{[Li(18\text{-}crown\text{-}6)_1][TFSA]}$: $D_{\mathrm{Li+}} = 1.39 \times 10^{-8}\ \mathrm{cm^2\ s^{-1}}$

and $D_{\text{18-crown-6}}$ =1.39 × 10^{-8} cm^2 s^{-1} at 30 °C (supercooled), $D_{\text{Li+}}$ = 1.12 × 10^{-7} cm^2 s^{-1} and $D_{\text{18-crown-6}}$ = 1.12 × 10^{-7} cm^2 s^{-1} at 60 °C, respectively. In addition, the thermal stability of the 18-crown-6 molecules was also enhanced by complexation with Li$^+$ ions. Therefore, the chelate effect has a significant impact on the physicochemical nature of the complexes.

It should be noted that not simply K_{complex} but rather K_n (high-order complex formation constant, n = 1, 2, 3...) becomes important for determining the solvate stability in certain cases. For instance, glymes have a potential to form cross-linked binuclear or polymerized complexes in the crystalline state, such as [Li(G3)$_1$]ClO$_4$ and [Li(G4)$_1$]AsF$_6$, respectively,[32, 33] and also multi-legand complexes such as [Li(G1)$_2$][TFSA] and [Li(G1)$_3$][TFSA].[43, 64] In these systems, not only simple K_{complex} but rather K_n should be considered. In the K_n, the last one should be large enough to stabilize discrete cationic species. Unfortunately, there are no reports addressing the K_n for glymes. In such cases K_{complex} can be expressed as $K_{\text{complex}} = \Pi K_n$. The studied solvate stability correlates well with the reported K_{complex}, and thus, we used K_{complex} as one of the measures to discuss the chelate effect on the stability in this work. However, K_n can be a more suitable measure to ensure the formation of stable complexes than K_{complex} for these systems.

4. Anionic effect.

Here, the properties of glyme-Li salt (LiX) 1:1 mixtures with different anionic structures, [Li(glyem)$_1$]X, are discussed to examine the effects of counter anions of Li salts on the formation of the complex cation [Li(glyme)$_1$]$^+$ and its stability.[66] Because glyme molecules that act as donors are expected to preferentially interact with Li$^+$ ions, competitive interactions between the Li$^+$ ions and the counter anions and also those between the Li$^+$ ions and glymes must be considered. In this section, we emphasize that the contrasting strengths of the interactions between the Li$^+$ ions and glymes and those between the Li$^+$ ions and anions directly reflect the states of the mixtures. The relevant physicochemical properties and coordinating structure of $[Li(glyme)_1]X$ are well correlated with the Lewis basicity (a donor property) of the anions.

In addition to the aforementioned Li[TFSA], different lithium salts can yield a homogeneous, room-temperature liquid (or supercooled) mixture when mixed with an equimolar amount of G3 or G4. As mentioned earlier, the ratio D_{sol}/D_{Li+} is a useful measure of the long-lived $[Li(glyme)_1]^+$ since the diffusivity data were collected over tens of milliseconds using a pulsed-field-gradient NMR technique.[49, 67] In **Figure 8**, this D_{sol}/D_{Li+} ratio is plotted as a function of another important gauge, the molar conductivity ratio[68, 69] ($\Lambda_{imp}/\Lambda_{NMR}$ and $\Lambda_{imp}/\Lambda_{ideal}$, termed as ionicity), which is effective in quantifying how ionic they are or more simply, an interaction parameter between ions in the concentrated systems like the present cases. For weakly coordinating anions of X such as ClO_4^-, $[TFSA]^-$, and other perfluorinated sulfonylamide derivatives, D_{sol}/D_{Li+} is almost unity, i.e., glyme and Li^+ ion diffuse together, suggesting the presence of expected complex cations with a long life-time. In addition, the ionicity scales for $[Li(glyme)_1]X$ with these anions are higher than those for the others, and similar to reported data for aprotic ILs.[68] These results support the hypothesis for the formation of solvate ILs, which comprise complex cations $[Li(glyme)_1]^+$ and X^-. By contrast, D_{sol}/D_{Li+} is clearly higher than 1 for X = trifluoroacetate ($[TFA]^-$), NO_3^-, triflate ($[OTf]^-$), and it decreases in the order of the anions $[TFA]^-$ > NO_3^- > $[OTf]^-$, where this order is consistent with the increasing order of the ionicity. Here, D_{sol}/D_{Li+} is higher than 1, and this is due either to fast ligand exchange between unstable $[Li(glyme)_1]^+$ cations or to glymes that are free from the coordination of Li^+; on the other hand, the lower ionicity can be attributed to ion-paired LiX or strong inter-ionic interactions. These two indices do not conflict with each other, but mutually corroborate that $[Li(glyme)_1]X$ with $[TFA]^-$, NO_3^-, and $[OTf]^-$ contain more or less time-and-space-averaged non-ionic species (e.g., LiX) and free glymes rather than the intended complex cation and simple anions X^-. $[Li(G4)_1]BF_4$ showed intermediate values for D_{sol}/D_{Li}^+ and ionicity. Probably, the donating properties of G4 and BF_4^- are similar.

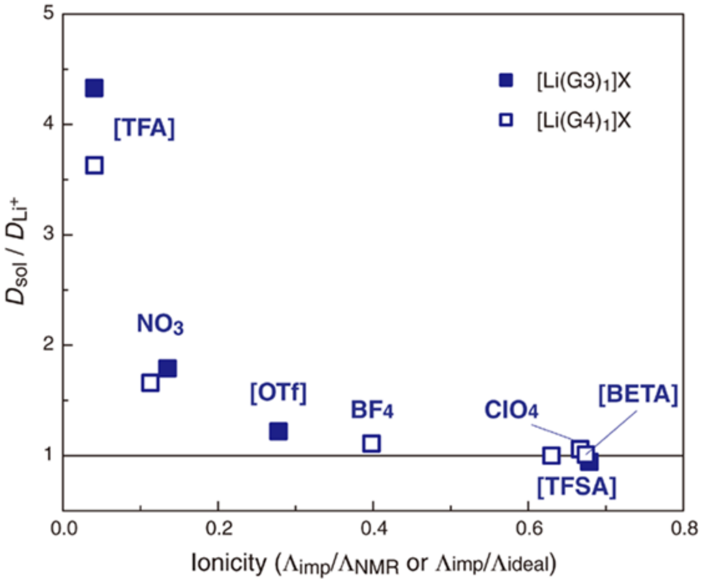


Figure 8. Correlation between D_{sol}/D_{Li^+} and ionicity. Data from ref 65 were reorganized.

Thus far, the complex cations have been mostly characterized using a set of bulk properties (thermal and physicochemical), however, their coordination structures also require clarification at molecular level. In this respect, Raman spectroscopy of the mixtures, in combination with X-ray crystallography of their single crystal structures (if available), is a powerful tool for studying the local coordinating structure. For glymes, it is well known that the Raman spectral region in range 800–900 cm^{-1} involves coupled motions of symmetric stretching vibrations of the COC group and rocking of the CH_2 group, and thus is very sensitive to conformational changes of glymes.[70-72] In particular, a remarkable band emerged at 870–890 cm^{-1} that corresponds to the complexation of the glymes with metal ions (the so-called, breathing mode), which is absent in pure glymes. **Figure 9** shows Raman spectra for $[Li(G3)_1]X$ liquids with $[TFA]^-$ and $[TFSA]^-$ anions. The data for crystalline $[Li(G3)_1][BETA]$ and for the solution of Li[BETA] in G3 containing excess glymes (molar ratio of Li[BETA]/G3 = 15/100) are also shown for comparison. The spectral shape of $[Li(G3)_1][TFSA]$ closely resembles that for $[Li(G3)_1][BETA]$ crystal, in which the crown-ether like conformation[43] of the $[Li(G3)_1]^+$ complex cation was proved as described in **Figure 3**. Therefore, similar crown-ether-like $[Li(G3)_1]^+$ cations are more likely to exist even in liquid $[Li(G3)_1][TFSA]$. In sharp contrast, $[Li(G3)_1][TFA]$ showed a Raman spectrum analogous to that for the dilute solution of Li[BETI] in G3, indicating “free” or only weakly interacting glymes in $[Li(G3)_1][TFA]$, despite the equimolar mixture. Thus, information obtained from the ratio D_{sol}/D_{Li+} concerning the complex cation can be further verified by Raman spectra.

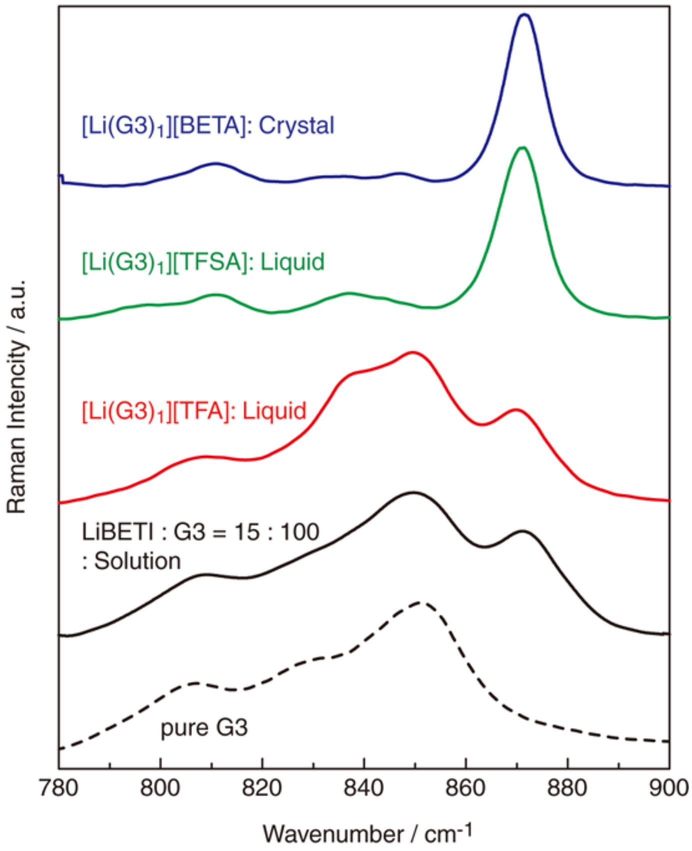


Figure 9. Raman spectra of certain mixtures of LiX and G3.

Mass spectrometry is often used for characterizing ion-aggregates in ILs,[17, 73, 74] and may also be useful in detecting the complex cation in $[Li(glyme)_1]X$.[75] In **Figure 10**, the highest peak at $M^+/Z = 185$ (assigned to $[Li(G3)_1]^+$) can be seen in positive mass spectra using FAB-MAS (fast atom bombardment mass spectroscopy) for both $[Li(G3)_1][TFSA]$ and $[Li(G3)_1][TFA]$. The mass ion of $M^+/Z = 59$ is attributed to $CH_3OCH_2CH_2^+$ that is produced during decomposition of G3 upon ionization.[76] The relatively higher intensity of this peak for $[Li(G3)_1][TFA]$ compared with that for $[Li(G3)_1][TFSA]$ may also suggest the existence of “free” or only weakly interacting glymes with a higher content in

[Li(G3)$_1$][TFA]. It is likely that the mass spectra can corroborate the presence of the complex cations found in the diffusion measurements (Figure 8) and Raman spectra (Figure 9), although we recognize that the results of such mass spectra do not always accurately represent the situation in bulk liquids.

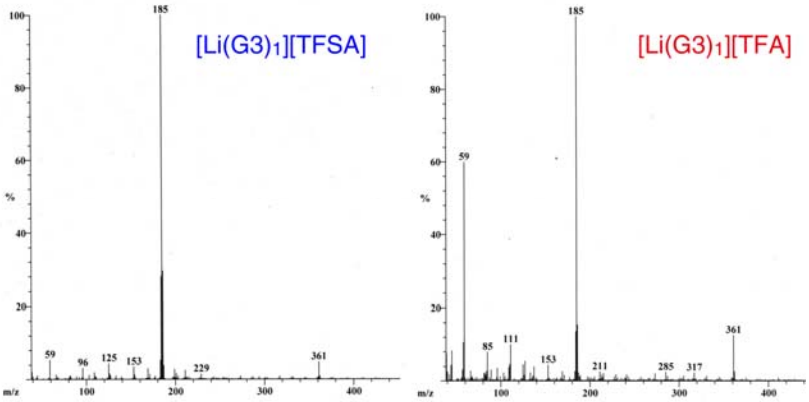


Figure 10. Positive FAB-MS spectra for [Li(G3)$_1$][TFSA] and [Li(G3)$_1$][TFA].

Based on the results discussed above, we can arrange the anions, in terms of the stability of [Li (glyme)$_1$]$^+$, in the order: [TFA]$^-$ < NO_3^- < [OTf]$^-$ < BF_4^- < ClO_4^- < [TFSA]$^-$ and its derivatives. This order is in accordance with the order of Lewis basicity (or the donor property) of the anions[77] and/or Li-X ion-pair dissociation energy ($E_{\mathrm{Li}^+\mathrm{X}^-}$) by *ab initio* calculation.[78] It is clear that the formation of long-lived robust [Li(glyme)$_1$]$^+$ complex cations, which can be a criterion for solvate ILs, is dominated by the competition between glymes and X anions to interact with Li^+ ions, and this complex formation is accomplished only by weak (soft) anions such as ClO_4^- and [TFSA]$^-$.

5. On the criteria of “solvate ionic liquids”.

A series of binary mixtures of Li salts and ligand molecules were compared systematically with respect to the concentration of Li salts, type of ligand molecules, and anionic structures present. Based on the aforementioned discussion, we would like to highlight the criteria used to judge whether target compounds can be classified as solvate ILs, as follows: The compound should:

1. Form a solvate compound between an ion and a ligand(s) in a certain stoichiometric ratio.

2. Consist entirely of complex ions (solvates) and their counter ions in the molten state.

3. Show no physicochemical properties based on both pure ligands and precursor salts under using conditions.

4. Have a melting point below 100 °C, which satisfies the criterion for typical ILs.

5. Have a negligible vapor pressure under typical application conditions.

Certain compounds of the systems discussed in this perspective can satisfy all of these criteria. The 1:1 mixtures, $[Li(G3\ or\ G4)_1]X$ (X = [TFSA], [BETI], and ClO_4), and $[Li(18\text{-crown-}6)_1][TFSA]$, can be categorized as solvate ILs on the basis of satisfactory evidence; they exhibit appropriate phase diagrams,[79] crystal structures,[32, 33, 43] Raman spectra,[64] diffusivity ratios (D_{sol}/D_{Li+}),[66] and physicochemical properties (e.g., ΔT_d and electrochemical oxidative stability).[66]

We recognize that there are many binary systems of Li salts and ligand molecules that only partially meet the above criteria. They apparently satisfy the condition of the formation of certain complexes (criteria 1), but their thermal, electrochemical, and diffusion properties are obviously different from those of the representative solvate ILs, such as $[Li(G3)_1][TFSA]$. For example, $[Li(G2)_2][TFSA]$ forms a crystalline solid at ambient temperature due to the formation of a complex cation $[Li(G2)_2]^+$.[43] However, G2 molecules coordinating to Li^+ ions easily evaporate at temperatures higher than the complex melting point. This is attributed to the instability and short life-time of the complex $[Li(G2)_2]^+$ cation in the liquid state: namely, a weak chelate effect (low $K_{complex}$). The same is true for shorter glyme-Li[TFSA] complexes such as $[Li(G1)_2][TFSA]$ and $[Li(G1)_3][TFSA]$, which showed only small increases in ΔT_d. Furthermore, low-melting solvate compounds are also formed in $[Li(G3)_1]NO_3$, $[Li(G3)_1][OTf]$, and $[Li(G4)_1]BF_4$.[32, 33, 79] However, these liquids with highly Lewis basic anions (higher $E_{Li^+X^-}$) more or less contain free glymes as proved for $D_{sol}/D_{Li+} > 1$, and the enhancement of their thermal and electrochemical properties was also less significant than those for $[Li(G3\ or\ G4)_1][TFSA]$.[66] Nevertheless, it is not suitable to classify these mixtures as common concentrated electrolyte solutions because their characters are intermediate between the definitive solvate ILs and concentrated solutions. Thus, a further classification of solvate ILs might be necessary to more accurately identify various types of concentrated electrolyte solution.

In the case of ILs (especially for protic ILs), they can be categorized into three groups on the basis of deviation from the Walden plots; good ILs, poor ILs, and super ILs.[80] In these categories, the physicochemical properties of poor ILs exhibit no resemblance to those of good (typical) ILs.[81] According to these categories, the solvate ILs can also be subdivided into at least two groups: "good" solvate ILs and "poor" ones. $[Li(G3)_1][TFSA]$ is a representative of good solvate ILs, but the intermediate systems, such as $[Li(G1)_m][TFSA]$ ($m \leq 3$), $[Li(G2)_l][TFSA]$ ($l \leq 2$), and $[Li(G3\text{ or }G4)_1]X$ ($X = NO_3$, [OTf], and BF_4), can be classified as poor solvate ILs. The differences between good and poor solvate ILs emerge clearly in their structural and physicochemical properties in the liquid state as described above.

Other mixtures including $[Li(PC)_n][TFSA]$ ($n \leq 4$) and $[Li(G3\text{ or }G4)_1][TFA]$ should be regarded as concentrated solutions because their solvate compounds have not yet been identified, and their behavior in the liquid state is significantly different to that of solvate ILs, as it is rather similar to typical solution behavior as can be seen in Figures 5–9. However, the border between poor solvate ILs and concentrated solutions remains ambiguous. For example, the crystalline solvate phase of a 1:4 mixture of acetonitrile (AN) and Li[TFSA], $[Li(AN)_4][TFSA]$, is known.[82] It may be categorized as a poor solvate IL under the subdivided criteria; however, at the same time it is considered as an analog of $[Li(PC)_4][TFSA]$ (concentrated solution) with reference to monodentate ligand-based mixtures.

$[Li(12\text{-crown-}4)_1][TFSA]$ and many other complexes of 12-crown-4 ether and Li salts do not melt at temperatures under 100 °C,[26-29] and so they do not satisfy the definition of an IL. For the same reason, the reported glyme-Li salt complexes, $[Li(G3)_1]AsF_6$ and $[Li(G3)_1][BPh_4]$,[32] and a number of crown ether-based complexes are not classified as "solvate ILs" but as "solid chelate complexes" instead at ambient temperatures or as "molten solvate complexes" above their melting temperatures even though they satisfy the other criteria in the liquid state.

The classification of solvate ILs composed of a series of LiX salts and ligand molecules is summarized in **Figure 11**. As shown in the figure, only limited combinations of Li salts and ligand molecules can be classified as good solvate ILs.

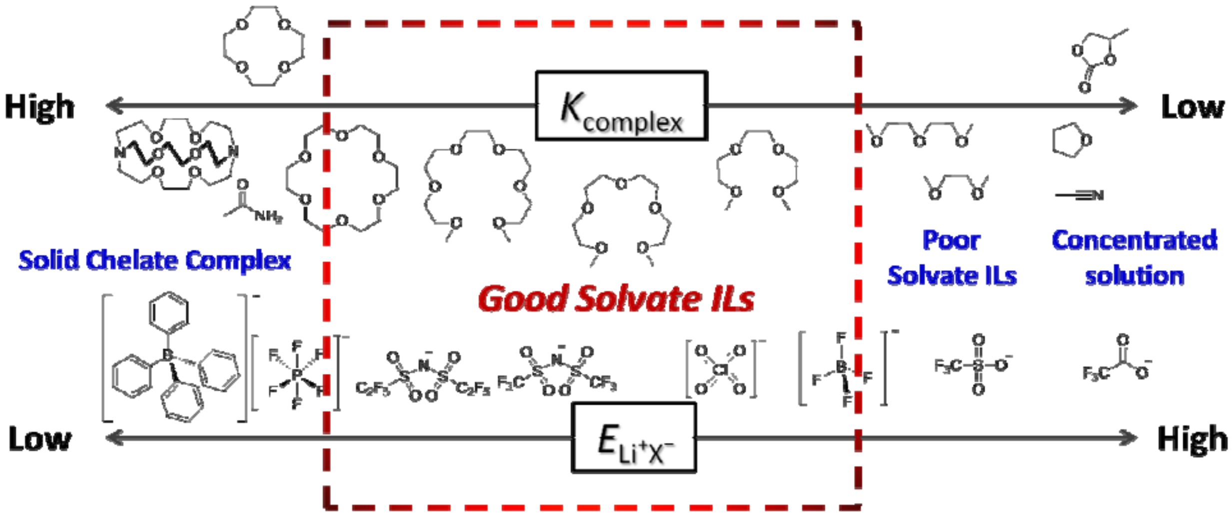


Figure 11. Schematic model of classification of solvate ionic liquids.

Concluding remarks

An overview of glyme-based "solvate ILs" has been presented in this article, and the criteria for defining whether or not a selection of mixtures belong to the class of solvate ILs have been discussed on the basis of their chemical nature and various physicochemical properties. Comprehensive studies on these complicated systems revealed that there are at least three crucial factors influencing their intrinsic nature: (1) the ratio of coordination sites to Li^+ ions ($[O]/[Li^+]$), (2) the complex formation constant $K_{complex}$ (that describes the chelate effect for multidentate ligands), and (3) the ion-pair interaction energy $E_{Li^+X^-}$ (Lewis basicity of anions). As the concentration ratio of Li[TFSA] to triglyme (G3) or tetraglyme (G4) increases, the thermal and electrochemical stability of the resulting binary mixtures gradually improve. In particular, the 1:1 equimolar mixtures possess outstandingly high stability.[23] Furthermore, the diffusion coefficients of the glyme and the Li^+ ions for the equimolar mixture exhibit identical values, implying the formation of long-lived robust complex cations. The physicochemical properties of the glyme-Li salt equimolar mixture can be simply tailored by chemical modification of the ligand glyme molecules. Comparison of G3- and G4-Li[TFSA] systems with binary mixtures consisting of other low molecular ligands and Li[TFSA] revealed that the number of coordination-sites within a single ligand molecule predominantly affects the stability of the complexes that it forms (chelate effect). The paired anion species also strongly contribute to the states of mixtures because the respective interactions between the Li^+ ions and glymes, and between the Li^+ ions and counter anions, compete in the mixtures; these interactions are closely related to the Lewis basicity of the anions. It is found that the formation of robust $[Li(glyme)]^+$ complex cations was accomplished only with soft anions with low Lewis basicity such as ClO_4^- and $[TFSA]^-$. Thus, only certain systems, such as $[Li(G3)_1][TFSA]$ and $[Li(G4)_1]ClO_4$, meet all of the criteria for solvate ILs. Nevertheless, there are a number of systems deviating only slightly from these criteria. To discriminate these candidates from conventional electrolyte solutions, a subdivision of solvate ILs into poor and good solvate ILs might be possible.

Glyme-based solvate ILs have versatility for use in various applications, in particular, as electrolytes for lithium secondary batteries. For example, $[Li(G3)_1][TFSA]$ and $[Li(G4)_1][TFSA]$, which are typical good solvate ILs, are available for use as electrolytes in batteries with 4V class cathode materials such as $LiCoO_2$ and $LiMn_2O_4$[22, 23, 83, 84] because of the high resistance to electrochemical oxidation of $[Li(glyme)_1]^+$ cations resulting from the donation of lone pairs of ether oxygen atoms to the Li^+ ions.[6,7] Moreover, the low coordinating ability of the $[Li(glyme)_1]^+$ cations suggests their utility as electrolytes for lithium-sulfur (Li-S) secondary batteries.[85, 86] In general, non-aqueous organic electrolyte solutions containing ethers and carbonates are not suitable for use in Li-S batteries because lithium polysulfides, the intermediate products of the redox reaction of sulfur, easily elute into the electrolyte solutions, leading to the loss of active materials and serious side reactions in the cell. By contrast, $[Li(glyme)_1][TFSA]$ complexes possesses much less solubility of lithium polysulfides, regardless of the use of ether-based electrolytes, resulting from the complete complexation of the glyme molecules with the Li^+ ions. Therefore, the charge/discharge of sulfur in $[Li(glyme)_1][TFSA]$ exhibits good reversibility and large capacity, suggesting that the glyme-based (good) solvate ILs are excellent electrolytes for use in Li-S batteries.

In this article, we have paid attention especially to the glyme-Li-based solvate ILs. Taking note of the similar chemical nature of congeners, a combination of other alkali metal salts (MX) and glymes should potentially form solvate ILs. The ionic states and physicochemical features of glyme-Na salt binary mixtures have already been investigated.[87] Based on the above criteria, appropriate stoichiometric mixtures can also be regarded as solvate ILs. In addition to complexed cation systems, a series of ILs composed of certain cations and fluorohydrogenate anions $[F\cdot(HF)_n]^-$ or oligomeric acetic acid anions $[(AcO)_xH_{x-1}]^-$ are good examples.[88-90] For instance, the chemical properties originating from HF, such as its corrosive nature, are not observed, indicating the formation of a robust $[F\cdot(HF)_{2.3}]^-$ complexed anion.[88] Eutectic mixtures of hydrogen bond donors (e.g., ethylene glycol and urea) and alkylammonium halides (e.g., choline chloride), termed as deep eutectic solvents (DESs), [91, 92] are also good candidates of solvate ILs. In DESs, complex anions are formed through hydrogen bond interactions between the hydrogen bond donors and halide anions, and they show characteristic properties that are similar to those of traditional ILs. Because solvate ILs generally possess such remarkable properties, these results enable us to broaden the usage of ILs in diverse applications. However, to realize this, systematic research, especially on $[M(glyme)_n][X]$, is necessary to achieve a deeper understanding of the intrinsic nature of such complicated systems.

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