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Phase Behavior and Crystalline Phases of Ionic Liquid-Lithium Salt Mixtures with 1-Alkyl-3-methylimidazolium Salts[†]

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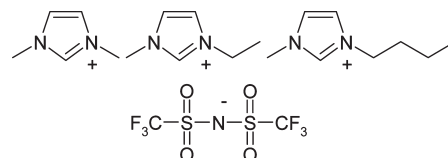
The thermal phase behavior of 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (IM_{10R}TFSI where *R* = 1, 2, or 4 for methyl, ethyl or butyl, respectively) ionic liquid binary mixtures with LiTFSI have been investigated as models for electrolytes for lithium batteries. Diverse phase behavior is found with significant variations noted from similar mixtures in which the imidazolium cations are replaced with *N*-alkyl-*N*-methylpyrrolidinium cations. The crystal structure for a (1−*x*) IM₁₀₁TFSI-(*x*) LiTFSI (*x* = 0.50) (or 1/1 IM₁₀₁TFSI/LiTFSI) phase is reported to further clarify the molecular level interactions occurring in these binary salt mixtures.

Introduction

Ionic liquids (ILs) may ultimately prove to be an indispensable component of advanced electrolytes for the lithium batteries intended for plug-in hybrid electric vehicle (PHEV) and electric vehicle (EV) traction. To reduce the cost, raise the energy density and improve the safety of large-format lithium battery packs for PHEVs and EVs, there is an increasing emphasis on the use of high-voltage, high-energy electrodes requiring electrolytes that are stable above 4.3 V (vs Li/Li⁺) and have high thermal stability. The general formulation for current state-of-the-art electrolytes, which consist of a mixture of ethylene carbonate (EC) and a linear carbonate such as diethyl carbonate (DEC) with LiPF₆,¹ used in small Li-ion batteries has varied only marginally over the past 20 years and is inadequate for high-voltage electrode materials. ILs are one of the few classes of materials available that may have a suitably high electrochemical and thermal stability for these new batteries. At present, however, there is only limited information available regarding the phase behavior of IL-LiX mixtures^{2–7} despite the tremendous insight into electrolyte properties such information provides.

This study focuses on mixtures of lithium bis-(trifluoromethanesulfonyl)imide (LiTFSI) with ILs consisting of 1-alkyl-3-methylimidazolium cations and the

TFSI[−] anion (IM_{10R}TFSI with *R* = 1, 2, or 4 for methyl, ethyl, or butyl, respectively)



These ILs were not selected with the intent of optimizing practical battery electrolytes as the imidazolium cations are well-known to have an unsuitably low electrochemical stability (both cathodic and anodic).^{8,9} These ILs and the analogous *N*-alkyl-*N*-methylpyrrolidinium (PY_{1R}TFSI) ILs, however, are the most widely studied ILs for which the greatest amount of information regarding their properties is available.^{2,3,10–21} It is,

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- (1) Xu, K. *Chem. Rev.* **2004**, *104*, 4303.
- (2) Henderson, W. A.; Passerini, S. *Chem. Mater.* **2004**, *16*, 2881.
- (3) Matsumoto, K.; Hagiwara, R.; Tamada, O. *Solid State Sci.* **2006**, *8*, 1103.
- (4) Burba, C. M.; Rocher, N. M.; Frech, R.; Powell, D. R. *J. Phys. Chem. B* **2008**, *112*, 2991.
- (5) Lerner, H.-W.; Bolte, M. *Acta Crystallogr., Sect. E* **2003**, *59*, m625.
- (6) MacFarlane, D. R.; Forsyth, M. *Adv. Mater.* **2001**, *13*, 957.
- (7) MacFarlane, D. R.; Huang, J.; Forsyth, M. *Nature* **1999**, *402*, 792.

- (8) Matsumoto, H.; Sakaebe, H.; Tatsumi, K. *J. Power Sources* **2005**, *146*, 45.
- (9) Matsumoto, H.; Sakaebe, H.; Tatsumi, K.; Kikuta, M.; Ishiko, E.; Kono, M. *J. Power Sources* **2006**, *160*, 1308.
- (10) Lassègues, J.-C.; Grondin, J.; Talaga, D. *Phys. Chem. Chem. Phys.* **2006**, *8*, 5629.
- (11) Dulaud, S.; Grondin, J.; Bruneel, J.-L.; Pianet, I.; Grélaud, A.; Campet, G.; Delville, M.-H.; Lassègues, J.-C. *J. Raman Spectrosc.* **2008**, *39*, 627.
- (12) Umebayashi, Y.; Mitsugi, T.; Fukuda, S.; Fujimori, T.; Fujii, K.; Kanzaki, R.; Takeuchi, M.; Ishiguro, S. *J. Phys. Chem. B* **2007**, *111*, 13028.
- (13) Lassègues, J.-C.; Grondin, J.; Aupetit, C.; Johansson, P. *J. Phys. Chem. A* **2009**, *113*, 305.
- (14) Borodin, O.; Smith, G. D.; Henderson, W. A. *J. Phys. Chem. B* **2006**, *110*, 16879.
- (15) Umebayashi, Y.; Yamaguchi, T.; Fukuda, S.; Mitsugi, T.; Takeuchi, M.; Fujii, K.; Ishiguro, S. *Anal. Sci.* **2008**, *24*, 1297.
- (16) Fujii, K.; Fujimori, T.; Takamuka, T.; Kanzaki, R.; Umebayashi, Y.; Ishiguro, S. *J. Phys. Chem. B* **2006**, *110*, 8179.
- (17) Lassègues, J.-C.; Grondin, J.; Holomb, R.; Johansson, P. *J. Raman Spectrosc.* **2007**, *38*, 551.
- (18) Fujii, K.; Soejima, Y.; Kyoshoin, Y.; Fukuda, S.; Kanzaki, R.; Umebayashi, Y.; Yamaguchi, T.; Ishiguro, S.; Takamuka, T. *J. Phys. Chem. B* **2008**, *112*, 4329.
- (19) Fukuda, S.; Takeuchi, M.; Fujii, K.; Kanzaki, R.; Takamuka, T.; Chiba, K.; Yamamoto, H.; Umebayashi, Y.; Ishiguro, S. *J. Mol. Struct.* **2008**, *143*, 2.

therefore, quite informative to compare the phase behavior of IM_{10R}TFSI–LiTFSI mixtures with that of PY_{1R}TFSI–LiTFSI mixtures.² Note that although aprotic solvent–LiTFSI electrolytes are known to corrode Al current collectors,^{22–26} there is evidence to suggest that such corrosion by the TFSI[−] anion in ILs is greatly reduced or inhibited.^{27–29}

Experimental Section

Materials. 1-Methylimidazole (99%), iodomethane (99%), iodoethane (99%), and 1-iodobutane (99%) were purchased from Aldrich and used as received. LiTFSI was purchased from 3M. The LiTFSI was dried under a vacuum at 120 °C for 12 h before use.

Sample Preparation. The 1-alkyl-3-methylimidazolium salts were prepared by combining 1-methylimidazole with a stoichiometric amount of alkyl iodide in ethyl acetate (Aldrich). The resulting white or yellow crystalline IM_{10R}I salts were repeatedly washed using ethyl acetate. The IM_{10R}I salts were then dissolved in deionized water, stoichiometric amounts of LiTFSI dissolved in deionized water were added, and the mixtures were stirred. The aqueous phase with dissolved LiI was removed and the remaining ILs were washed 8 times with deionized water to remove reagents and contaminants from the IM_{10R}TFSI salts. The final aqueous layers were removed and the salts were heated while stirring on a hot plate for several hours at 120–140 °C to remove most of the residual water. Activated carbon (Darco-G60, Aldrich) was added and the mixtures were stirred on a hot plate at 140 °C for 48 h. The mixtures were then cooled to room temperature; ethyl acetate was added to dilute the solutions, and the solutions were then filtered through an activated alumina (acidic, Brockmann I, Aldrich) column. The ethyl acetate was then removed by a rotary evaporator and the salts were dried under high vacuum at 120 °C overnight and then at 140 °C for another 8 h. After purification and drying, the ILs were clear, colorless liquids at room temperature. The materials were stored in hermetically sealed bottles in a N₂ glovebox (water concentration <0.5 ppm).

(1−*x*)IM_{10R}TFSI-(*x*) LiTFSI mixtures were prepared in the glovebox by combining appropriate amounts of the IM_{10R}TFSI and LiTFSI salts in vials and then heated on a hot plate while stirring to form homogeneous mixtures. The resulting IL–LiX mixtures were clear and colorless with a moisture content below 10 ppm (tested by Karl Fischer titration). The materials were stored in hermetically sealed glass vials in the glovebox.

Thermal Measurements. Thermal measurements were performed using a TA Instruments Q2000 differential scanning calorimeter (DSC) with liquid N₂ cooling. The instrument was

calibrated with cyclohexane (solid–solid phase transition at −87.06 °C, melt transition at 6.54 °C) and indium (melt transition at 156.60 °C). Hermetically sealed Al pans were prepared in the glovebox. Typically, sample pans were slowly cooled (5 °C min^{−1}) to −150 °C and then heated (5 °C min^{−1}) to 100 °C or higher (determined by the composition of the sample). In some cases, it was necessary to hold or cycle the samples at various subambient temperatures in the instrument prior to the measurements to ensure complete crystallization. Some of the sample pans were also stored in a freezer prior to analysis and then transferred into the instrument quickly (to aid in crystallization for slowly nucleating samples).

X-ray Structural Determination. Single crystals of the of the 1/1 (*x* = 0.50) IM₁₀₁TFSI/LiTFSI phase formed in the *x* = 0.20 sample vial after storage at room temperature. A crystal was mounted on a nylon loop with a small amount of Paratone N oil. All X-ray measurements were made on a Bruker-Nonius Kappa Axis X8 Apex2 diffractometer at a temperature of −163 °C. Data collection was carried out using Mo K α radiation. The unit cell dimensions were determined from a symmetry constrained fit of 9889 reflections with 4.56° < 2 θ < 76.28°. The data collection strategy was a number of ω and ϕ scans that collected data up to 76.58° (2 θ). The frame integration was performed using SAINT.³⁰ The resulting raw data was scaled and absorption corrected using a multiscan averaging of symmetry equivalent data using SADABS.³¹ The structure was solved by direct methods using the SIR92 program.³² All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The structural model was fit to the data using full matrix least-squares based on *F*². The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the XL program from SHELXTL.³³ Crystallographic figures were drawn using Mercury 2.2 software.

Results and Discussion

DSC heating traces for (1−*x*) IM₁₀₁TFSI-(*x*) LiTFSI mixtures are shown in Figure 1a. Adding LiTFSI initially slightly lowers the melting point (*T*_m) of the samples from that of the neat IM₁₀₁TFSI salt (*T*_m 24 °C). The data indicate that new mixed-salt crystalline phases exist for *x* = 0.50 and what appears to be a 0.75 composition (corresponding to 1/1 and 1/3 IM₁₀₁TFSI/LiTFSI phases, respectively). 1/1 crystalline phases have been previously reported for IM₁₀₂CF₃SO₃/LiCF₃SO₃, Et₃NHCF₃SO₃/LiCF₃SO₃, and IM₁₀₂AlCl₄/NaAlCl₄ mixtures.^{4,5,34} In all of these structures, each anion is coordinated to two Li⁺ cations. Each Li⁺ cation, in turn, is coordinated by four different anions (4-fold coordination) resulting in polymeric [Li⁺⋯(anion)₂]_n chains. For electrostatic neutrality, the organic cations (either IM₁₀₂⁺ or Et₃NH⁺ cations) surround these ionic

- (20) Umebayashi, Y.; Mitsugi, T.; Fujii, K.; Seki, S.; Chiba, K.; Yamamoto, H.; Canongia Lopes, J. N.; Pádua, A. A. H.; Takeuchi, M.; Kanzaki, R.; Ishiguro, S. *J. Phys. Chem. B* **2009**, *113*, 4338.
- (21) Canongia Lopes, J. N.; Shimizu, K.; Pádua, A. A. H.; Umebayashi, Y.; Fukuda, S.; Fujii, K.; Ishiguro, S. *J. Phys. Chem. B* **2008**, *112*, 1465.
- (22) Zhang, X.; Devine, T. M. *J. Electrochem. Soc.* **2006**, *153*, B375.
- (23) Behl, W. K.; Plichta, E. J. *J. Power Sources* **1998**, *72*, 132.
- (24) Morita, M.; Shibata, T.; Yoshimoto, N.; Ishikawa, M. *Electrochim. Acta* **2002**, *47*, 2787.
- (25) Kanamura, K.; Umegaki, T.; Shiraishi, S.; Ohashi, M.; Takehara, Z. *J. Electrochem. Soc.* **2002**, *149*, A185.
- (26) Zhang, S. S.; Jow, T. R. *J. Power Sources* **2002**, *109*, 458.
- (27) Garcia, B.; Armand, M. *J. Power Sources* **2004**, *132*, 206.
- (28) Peng, C.; Yang, L.; Zhang, Z.; Tachibana, K.; Yang, Y. *J. Power Sources* **2007**, *173*, 510.
- (29) Peng, C.; Yang, L.; Zhang, Z.; Tachibana, K.; Yang, Y.; Zhao, S. *Electrochim. Acta* **2008**, *53*, 4764.

- (30) SAINT version 2008.6; Bruker-Nonius: Madison, WI, 2008.
- (31) SADABS version 2008.4; Bruker-Nonius: Madison, WI, 2008.
- (32) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.
- (33) SHELXTL version 6.12; Bruker-AXS: Madison, WI.
- (34) Boon, J. A.; Carlin, R. T.; Elias, A. M.; Wilkes, J. S. *J. Chem. Crystallogr.* **1995**, *25*, 57.

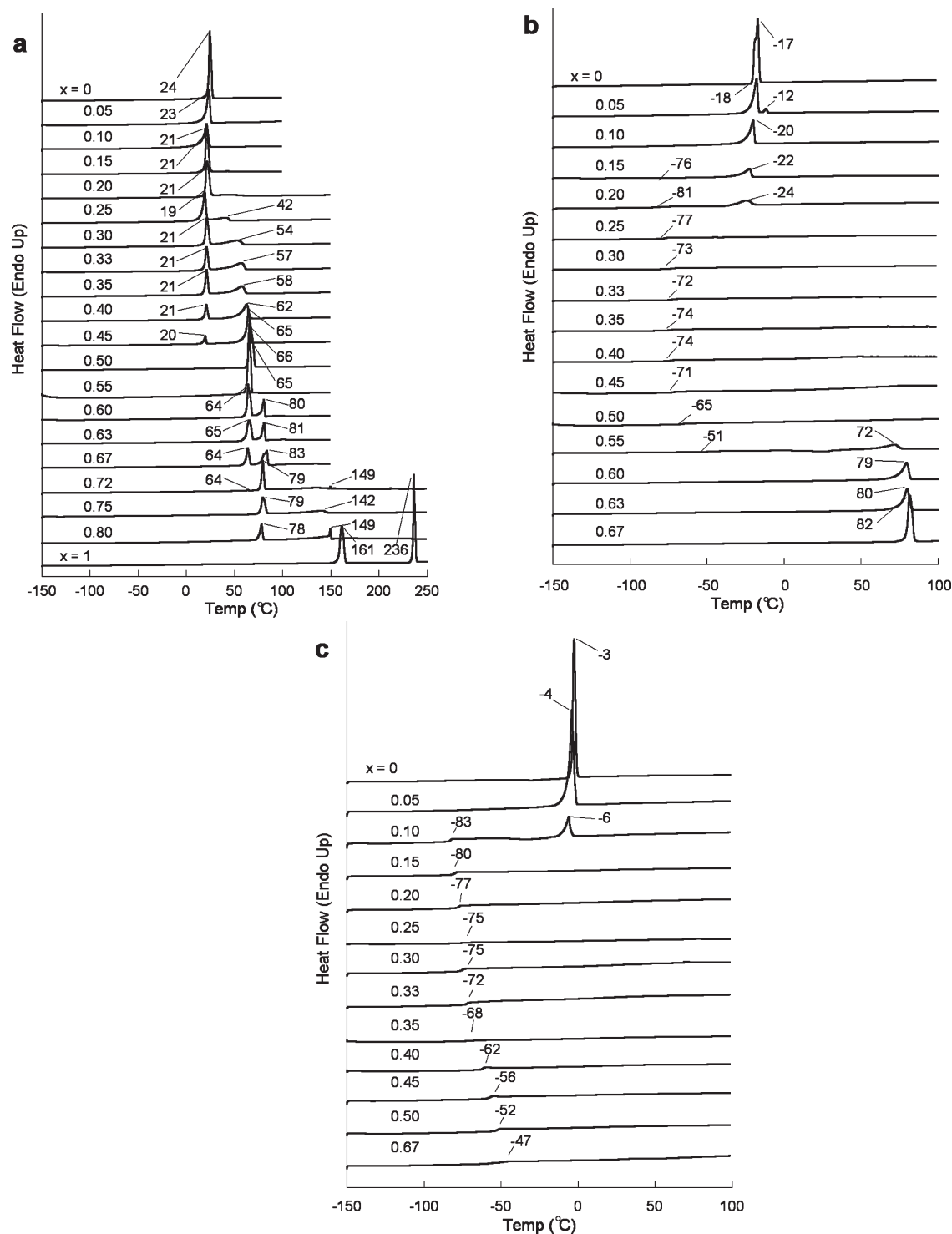


Figure 1. DSC heating traces ($5\text{ }^{\circ}\text{C min}^{-1}$) of $(1-x)\text{IM}_{10R}\text{TFSI}-(x)\text{LiTFSI}$ mixtures (a) $R = 1$, (b) $R = 2$, and (c) $R = 4$ (peak and T_g temperatures noted).

chains and have a single hydrogen bond to the anions. The crystal structure of the 1/1 ($x = 0.50$) $\text{IM}_{101}\text{TFSI}/\text{LiTFSI}$ phase (Table 1 and Figure 2) bears some resemblance to these structures. Polymeric $[\text{Li}^+\cdots(\text{TFSI}^-)_2]_n$ chains are present with each anion coordinated to two Li^+ cations. The difference is that the Li^+ cations now have 6-fold coordination (Figure 3). The IM_{101}^+ cations are located in rows between these ionic polymer chains. The hydrogen bond to the carbon at position C2 of the cation

is coordinated through a hydrogen bond to one anion oxygen, whereas the cation C4 and C5 hydrogens are both hydrogen bonded to another anion oxygen. One of these hydrogen also may have an additional hydrogen bond to another oxygen from a third anion (Figure 4). Note that oxygen atoms from addition anions are also closely positioned over the positively charged ring nitrogen atoms (not shown in Figure 4), adding further stability to this manner of ion packing. It is notable that all of the

Table 1. Crystal and Refinement Data

structure	[IM ₁₀₁ TFSI] ₁ [LiTFSI] ₁
chemical formula	C ₉ H ₉ F ₁₂ LiN ₄ O ₈ S ₄
fw	664.38
cryst syst	triclinic
space group	$P\bar{1}$
temperature (K)	110
<i>a</i> (Å)	5.3707(2)
<i>b</i> (Å)	11.7032(5)
<i>c</i> (Å)	17.9205(7)
α (deg)	88.6792(18)
β (deg)	84.198(2)
γ (deg)	82.7165(17)
<i>V</i> (Å ³)	1111.51(8)
<i>Z</i>	2
ρ_{calcd} (g cm ⁻³)	1.985
μ (mm ⁻¹)	0.575
crystsize (mm ³)	0.38 × 0.33 × 0.18
<i>F</i> (000)	660
$2\theta_{\text{max}}$ (deg)	76.58
<i>N</i> (<i>R</i> _{int})	51556 (0.0248)
<i>N</i> [<i>I</i> > 2 σ (<i>I</i>)]	12123
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0297, 0.0766
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.0411, 0.0829
GOF ^c	1.005
$\Delta e_{\text{min,max}}$ (e Å ⁻³)	-0.369, 0.647

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|, ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}, ^c \text{GOF} = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}.$$

anions have the *C*₁ conformation,^{35–39} which is also found for the anion conformations in crystalline IM₁₀₁-TFSI.³⁸ In the 1/1 phase with LiTFSI, this conformation is favored as it enables the 6-fold coordination of the anions to the Li⁺ cations (and IM₁₀₁⁺ hydrogen bonding), whereas in the neat IM₁₀₁TFSI structure, this conformation enables a favorable lattice of hydrogen bonds to form between the cations and anions.

The *T*_m of IM₁₀₂TFSI is either -17 or -10 °C – the IL is polymorphic with two different crystalline phases able to form depending upon the salt's thermal history. Neither of these phases undergoes a solid–solid phase transition prior to melting.⁴⁰ DSC heating traces for (1-*x*)IM₁₀₂TFSI-(*x*) LiTFSI mixtures (Figure 1b) indicate that as the LiTFSI mole fraction (*x*) increases, the crystallization process becomes more difficult, and no crystalline phase was observed for 0.25 ≤ *x* ≤ 0.50 mixtures. The glass transition (*T*_g) of the amorphous samples tends to increase with increasing fraction of LiTFSI, as expected. For samples with high concentration (*x* > 0.50), however, a new crystalline peak for a 1/2 (*x* = 0.67) IM₁₀₂TFSI/LiTFSI phase is observed. The crystal structure of this phase has been previously reported and a portion of this structure is shown in the Supporting Information.³ The ions of this 1/2 phase form two-dimensional planar sheets stacked together. The Li⁺ cations have 5-fold coordinated by anion oxygens (from either three or four different TFSI⁻ anions).

Different anions are coordinated differently, but each anion has either three or all four of the oxygens atoms coordinated to Li⁺ cations, thereby creating the planar sheets. The sheets (composed of Li⁺ cations and TFSI⁻ anions) result in the formation of cavities in which reside two uncoordinated IM₁₀₂⁺ cations (see the Supporting Information).

For the (1-*x*) IM₁₀₄TFSI-(*x*) LiTFSI mixtures, it was not possible to crystallize the samples when *x* ≥ 0.15 using either slower cooling/heating rates (1 °C min⁻¹) or by annealing the mixtures for extended periods of time at low temperature, despite extensive efforts to do so. Only a fraction of the neat IM₁₀₄TFSI phase could be crystallized for dilute samples with *x* < 0.15 (Figure 1c). Thus, no crystalline phase forms (up to a composition of *x* = 0.67) that contains the LiTFSI salt. The *T*_g of the *x* = 0.67 mixture is remarkably low for a sample composed of 2/3 lithium salt.

A comparison of the phase behavior of the IM_{10*R*}TFSI and PY_{1*R*}TFSI salt mixtures with LiTFSI shows both similarities and differences in behavior. For example, there is no evidence that the IM_{10*R*}TFSI salts form a 2/1 (*x* = 0.33) IL/LiTFSI phase, which is a predominant feature of the PY_{1*R*}TFSI mixtures.² The reason for this is unknown at present. There are no structural models (crystal structures) known for such a composition to aid in clarifying this. The IM₁₀₂TFSI salt does, however, form the 1/2 phase (*x* = 0.67), which is also a common feature of the PY_{1*R*}TFSI mixtures.² The known structure for this phase shows that cavities form in the Li⁺...TFSI⁻ anion planar lattice that hold two organic cations that remain essentially uncoordinated. It is easy to envision that the cations can be readily replaced with other cations of similar size to create the same phase with a different IL. Interestingly, the IM₁₀₄TFSI salt does not form this phase. One possible explanation is that the IM₁₀₄⁺ cations are too large to fit within the cavities, but this does not explain why the IM₁₀₁TFSI salt also does not form this phase unless it is because the IM₁₀₁⁺ cations are too small and leave too much void space in the structure. An alternative, and more likely, explanation, however, is that the coordination in the high LiTFSI composition phase (assumed to be *x* = 0.75) is more energetically favorable than that of the 1/2 phase. The crystal structures are low energy structures formed by optimizing all of the interactions (packing of ions, electrostatics, hydrogen bonding, etc.), not just the Li⁺...TFSI⁻ coordination.

In addition, the 1/1 phase forms readily for the IM₁₀₁-TFSI salt, but the IM₁₀₂TFSI and IM₁₀₄TFSI salts remain amorphous instead of forming this phase. There is some evidence that the PY_{1*R*}TFSI-LiTFSI mixtures also form a 1/1 phase, although this appears to be a metastable phase for some of the ILs.² Once again, this variance in behavior may be an ion size/shape effect that prevents the ions from packing together in the optimal manner to form the “preferred” structures dictated by optimized Li⁺...TFSI⁻ coordination and other energetic considerations. The amorphous phase may then

- (35) Foropoulos, J., Jr.; DesMarteau, D. D. *Inorg. Chem.* **1984**, *23*, 3720.
 (36) Arnaud, R.; Benrabah, D.; Sanchez, J.-Y. *J. Phys. Chem.* **1996**, *100*, 10882.
 (37) Johansson, P.; Gejji, S. P.; Tegenfeldt, J.; Lindgren, J. *Electrochim. Acta* **1998**, *43*, 1375.
 (38) Holbrey, J. D.; Reichert, W. M.; Rogers, R. D. *Dalton Trans.* **2004**, 2267.
 (39) Rey, I.; Johansson, P.; Lindgren, J.; Lassègues, J. C.; Servant, L. *J. Phys. Chem. A* **1998**, *102*, 3249.
 (40) Unpublished data.

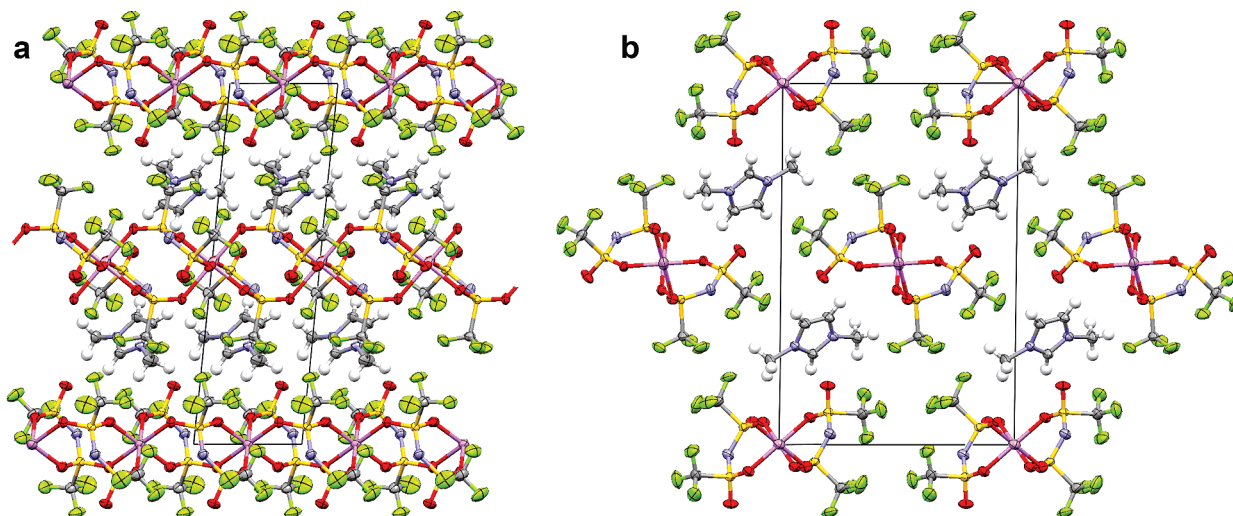


Figure 2. Ion packing in the 1/1 ($x = 0.50$) IM₁₀₁TFSI/LiTFSI crystalline phase viewed along the (a) b - and (b) a -axis (Li, purple; O, red; S, gold; C, gray; F, green).

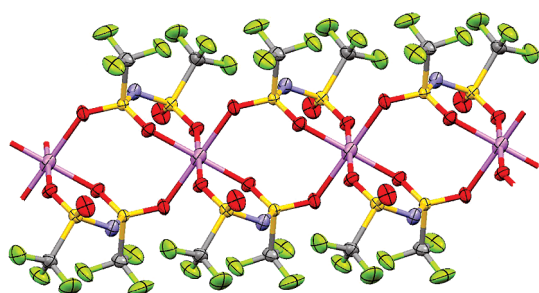


Figure 3. Ion coordination in the polymeric $[\text{Li}^+ \cdots (\text{TFSI}^-)_2]_n$ chains in the 1/1 ($x = 0.50$) IM₁₀₁TFSI/LiTFSI crystalline phase (Li, purple; O, red; S, gold; C, gray; F, green).

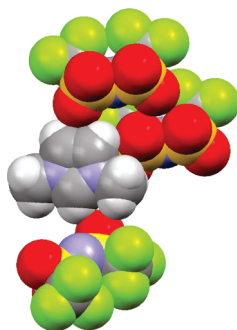


Figure 4. Space-filling model of anion hydrogen bonding to the IM₁₀₁⁺ cations in the 1/1 ($x = 0.50$) IM₁₀₁TFSI/LiTFSI crystalline phase (Li, purple; O, red; S, gold; C, gray; F, green).

be viewed as a “frustrated” phase in which many of the ions in the frozen glass or supercooled liquid have the same or similar coordination as found in the crystalline phases of similar composition, but the entire ensemble of the crystal structures cannot come together because of the poor fit of the organic cations within such a structure.

It has been suggested that the addition of LiTFSI to either IM₁₀₂TFSI or IM₁₀₄TFSI results in Li⁺ cations with an anion solvation number of approximately two.^{10–12} A spectroscopic analysis with DFT calculations of possible $[\text{Li}(\text{TFSI})_2]^-$ complexes was conducted in which the conformation of the anion was varied.¹³ These complexes

were also compared with a $[\text{Li}(\text{TFSI})_4]^{3-}$ complex. The conclusion was the Li⁺ cations exist in these ILs as $[\text{Li}(\text{TFSI})_2]^-$ complexes in which the anions predominantly have an equal mix of C_1 and C_2 conformations. This type of complex, however, requires that the TFSI[−] anions have two of their oxygen atoms coordinated to the same Li⁺ cation. If one closely scrutinizes the coordination in the 1/2 IM₁₀₂TFSI/LiTFSI phase, such coordination is found for anions with both C_1 and C_2 symmetry (see the Supporting Information), although the anions are also coordinated to other Li⁺ cations (as required for such a concentrated composition). The 1/1 ($x = 0.50$) IM₁₀₁-TFSI/LiTFSI phase also has anions with two oxygen atoms coordinating the same Li⁺ cation. A molecular dynamics (MD) simulation of $(1-x)$ PY_{1R}TFSI- (x) LiTFSI ($x = 0.25$, $R = 1$ and 3) at 227 °C, however, reported that the probability that a single TFSI[−] anion contributes a second oxygen atom to the coordination shell of the same Li⁺ cation was < 5%.¹⁴ The MD simulation work¹⁴ also emphasized the formation of $\text{Li}^+ \cdots \text{O}=\text{S}=\text{O} \cdots \text{Li}^+$ coordination that is present for all of the anions in the known crystalline 1/1 and 1/2 phases (Figure 3 and the Supporting Information). This form of coordination facilitates the creation of polymeric aggregates. Such a liquid structure might reasonably occur with short aggregated ionic chains with anions having both C_1 and C_2 conformations in which all of the anions have two oxygens coordinated to two Li⁺ cations.

Given that the liquid phase is being considered, a variety of forms of coordination may actually coexist. At this time, therefore, it is not possible to fully confirm the liquid phase Li⁺ cation coordination, but the interactions between the cations and anions is what dictates the ionic conductivity (mechanisms for Li⁺ cation transport) and other physical properties for these electrolytes and therefore is of considerable interest. It must be emphasized that the electrolyte components of an ideal battery electrolyte should be unable to crystallize within the battery operating temperature range as the capture of

the Li^+ cations in a solid IL-LiX phase generally drastically reduces the conductivity of the electroactive Li^+ cations and thus the ability of the battery to operate.⁴¹ With this in mind, the phase information in panels b and c in Figure 1 is intriguing, as concentrated electrolyte mixtures may be prepared in which crystallization is completely inhibited. If an explanation for why this occurs is forthcoming, then such information may aid in the optimization of future choices of ILs for battery electrolytes.

Conclusion

The thermal phase behavior of $\text{IM}_{10R}\text{TFSI-LiTFSI}$ mixtures with imidazolium ILs are reported here and compared with information known about the analogous mixtures with pyrrolidinium ILs. Intriguing variations in crystalline phases formed are noted, as is the presence of

crystallinity gaps in which it was not possible to crystallize some or all of the mixtures. The reported crystal structure of the 1/1 ($x = 0.50$) $\text{IM}_{101}\text{TFSI/LiTFSI}$ phase provides crucial insight into ion coordination and packing, especially when compared to the known crystal structure of the 1/2 ($x = 0.67$) $\text{IM}_{102}\text{TFSI/LiTFSI}$ phase. This information should aid in computational modeling of these electrolytes, as well as deconvoluting wide variations in the transport properties of the liquid phase of such materials.

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Supporting Information Available: Experimental details and schematic illustrations of crystal structures (PDF) and X-ray crystallographic data (CIF) for $[\text{IM}_{101}\text{TFSI}]_1[\text{LiTFSI}]_1$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(41) Sakaebe, H.; Matsumoto, H. *Electrochem. Commun.* **2003**, 5, 594.