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Phase Behavior of Ionic Liquid−LiX Mixtures: Pyrrolidinium Cations and TFSI$^-$ Anions

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Phase diagrams are reported for mixtures between bis(trifluoromethanesulfonyl)imide (TFSI$^-$) salts containing Li$^+$ and *N*-alkyl-*N*-methylpyrrolidinium (PYR$_{1R}$$^+$) cations. The latter salts readily form both room temperature ionic liquids and plastic crystalline phases. Mixed salt crystalline phases are found which are likely to influence the performance of such mixed salt systems when utilized as electrolytes for electrochemical devices as well as give insight into ionic liquid−solute interactions.

Introduction

Room-temperature ionic liquids (RTILs)—salts which are molten at ambient temperature—have been attracting wide attention for use as "green" solvents for catalysis, chemical synthesis, and separations.[1−3] Such RTIL salts may also find application as heat carriers in solar−thermal energy generators due to favorable properties such as negligible volatility, high chemical and thermal stability, and, in some cases, hydrophobicity. Other properties such as high ionic conductivity and electrochemical stability have led to their scrutinization for electrolyte applications such as the electrodeposition of electropositive metals, light-emitting electrochemical cells, photoelectrochemical cells, electrochemical capacitors, fuel cells, and batteries.[4−10]

Rechargeable lithium batteries are currently under development for use in portable electronic, telecommunication, and electric vehicle propulsion applications. The substitution of solvents with RTILs in traditional solvent−salt electrolyte mixtures is under investigation worldwide. A topic related to RTILs is that of room-temperature plastic crystalline salts which have melting points above ambient temperature, but order−disorder solid-phase transitions at subambient temperatures.[11] The plastic crystalline salts may thus have a high degree of disorder of the ions resulting in significant ionic conduction in the solid-state materials. Because the ions in both RTILs and plastic crystalline salts are not electroactive in lithium batteries, the salts must be doped with a suitable LiX salt.[8,9,12]

The physical properties of RTILs and plastic crystalline salts consisting of *N*-alkyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imides (PYR$_{1R}$TFSI) (subscripts are for alkyl groups with 1 (methyl) − 4 (butyl)) have been extensively studied.[13−15] The crystal structure of PYR$_{11}$TFSI is known.[16] It has been reported that doping the plastic crystalline salt PYR$_{12}$TFSI with small amounts of LiTFSI leads to large increases in the solid-state ionic conductivity of this material.[17−19] This work suggested that a solid solution forms between the PYR$_{12}$TFSI and LiTFSI salts. Electrolytes for commercial devices, however, are likely to require much larger concentrations of Li$^+$ cations for high power applications. Very little is known about the mixed phase behavior of salts with organic ammonium and alkali cations and common anions. The formation of a crystalline solid in a liquid $(1 - x)$N$_{1113}$TFSI−(x)LiTFSI ($x = 0.12$) (N$_{1113}$ = trimethylpropylammonium) electrolyte mixture was found to be very detrimental to the performance of Li/electrolyte/LiCoO$_2$ batteries.[9] Here we report on the mixed phase behavior of LiTFSI with several salts consisting of *N*-alkyl-*N*-methylpyrrolidinium cations and TFSI$^-$ anions.

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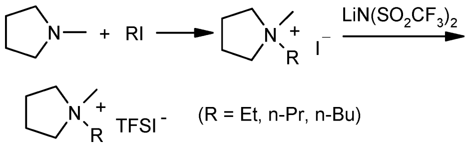
Experimental Section

Materials. 1-Methylpyrrolidine (97%), iodoethane (99%), 1-iodopropane (99%) and 1-iodobutane (99%) were purchased from Aldrich and used as received. LiTFSI was kindly provided by 3M. LiTFSI was dried under vacuum at 150 °C for 12 h.

Sample Preparation. The *N*-alkyl-*N*-methylpyrrolidinium TFSI salts were prepared by combining 1-methylpyrrolidine with a stoichiometric amount of alkyliodide in an ethyl acetate solution. The resulting white or yellow crystalline PYR$_{1R}$I salts were recrystallized in acetone/ethyl acetate and repeatedly washed using ethyl acetate until pure white salts were obtained. The PYR$_{1R}$I salts were then dissolved in deionized water resulting in clear, colorless solutions. 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 white solids or viscous liquids were washed 5× with hot deionized water to purify the PYR$_{1R}$TFSI salts (Scheme 1). The aqueous layer was removed and the salts were heated while stirring on a hot plate for several h at 120−140 °C to remove residual water. Acetone and activated carbon (Darco-G60, Aldrich) were added and the mixtures were stirred on a hot plate overnight just below the boiling point of the acetone. The mixtures were then filtered through an activated alumina (acidic, Brockmann I, Aldrich) column. The acetone was boiled off and the salts were dried under high vacuum at 80 °C for 24 h and then 120 °C for 2−4 h. After purification and drying, the salts were either a white solid (PYR$_{12}$TFSI) or clear, colorless liquids (PYR$_{13}$TFSI and PYR$_{14}$TFSI) at room temperature. The materials were stored in a dry room (<0.2% RH, 20 °C).

Scheme 1



Mixed salts were prepared in the dry room by combining appropriate amounts of the PYR$_{1R}$TFSI and LiTFSI salts in a vial. Anhydrous CH$_3$CN was then added and the solutions were heated and stirred to form clear solutions. Most of the CH$_3$CN was removed by heating on a hot plate. The remaining CH$_3$CN was removed by heating under vacuum at 80 °C for 24 h and then 120 °C for 2−4 h.

Thermal Measurements. Thermal measurements for the phase diagrams were performed using a TA model 2910 differential scanning calorimeter (DSC). Hermetically sealed Al pans were prepared in the dry room. The pans containing the samples with $x = 0{-}0.35$ were stored in a refrigerator, whereas those with $x = 0.55{-}0.75$ were heated to 180 °C and then annealed at 100, 80, 50, 40, and 20 °C (6−12 h at each temperature) to permit the mixtures to fully crystallize. The latter procedure was found to give more reproduceable thermal behavior than storing the pans at room temperature after melting the samples. Typically the samples were cooled at 10 °C/min from room temperature to −140 °C and then heated at 10 °C/min to 300 °C. In some cases, the samples were thermally annealed in the DSC instrument by repeatedly cycling and/or holding the samples at subambient temperatures for varying periods of time to permit complete crystallization.

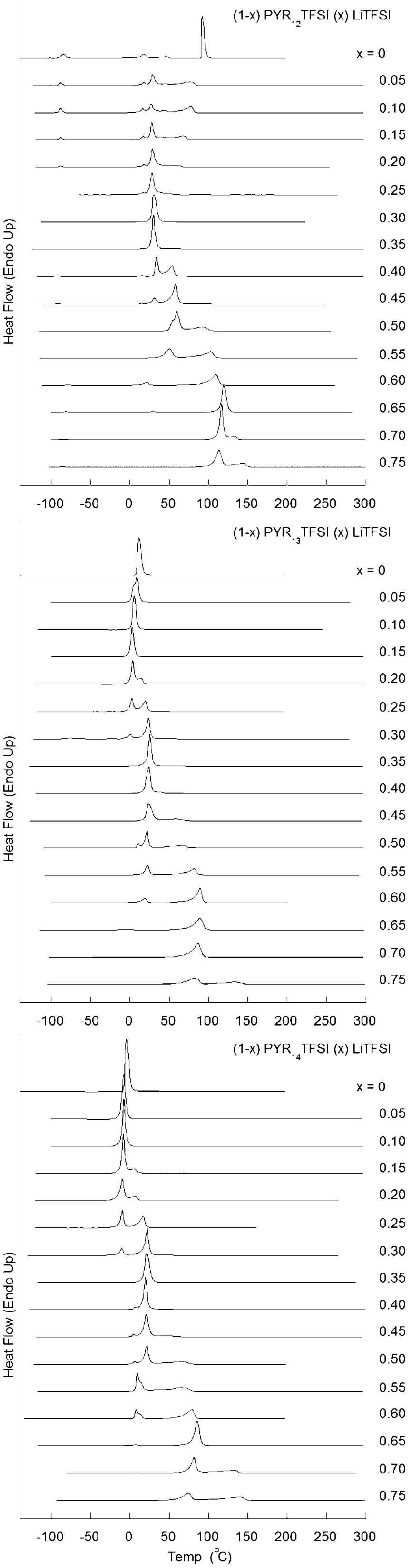


Figure 1. DSC heating traces (10 °C/min) for $(1-x)$PYR$_{1R}$TFSI−(x)LiTFSI (R = 2−4) mixtures.

Results and Discussion

Pure PYR$_{1R}$TFSI Phase Behavior. DSC heating traces for the pure PYR$_{1R}$TFSI salts (R = 2−4, $x = 0$) are shown in Figure 1. The heating trace for PYR$_{12}$TFSI is similar to that previously reported.[13,15] The traces for PYR$_{13}$TFSI and PYR$_{14}$TFSI, however, differ from those in these references. It was noted that PYR$_{14}$TFSI has a solid−solid phase transition at −24 °C and melts at −18 °C.[15] In contrast, we have observed only a single melting peak at −3 °C when the salt was fully crystalline. If, however, the salt is supercooled and cold-crystallized relatively rapidly during the heating scan, a thermal behavior similar to that previously reported is found (Figure 2). This suggests that with rapid crystallization

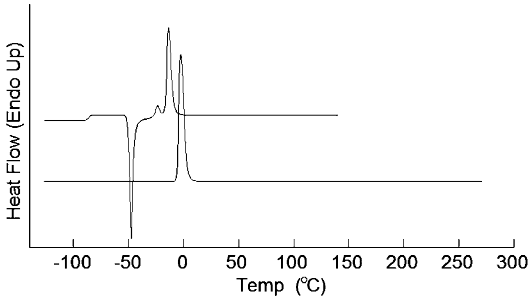


Figure 2. DSC heating traces (10 °C/min) for $PYR_{14}TFSI$ after quenching (top) or slow cooling/annealing (bottom) from room temperature.

a metastable $PYR_{14}TFSI$ crystalline phase forms. PYR_{13}-TFSI was also reported to have a solid−solid phase transition[14] which we have not observed when the sample is crystallized at low temperatures. A similar metastable phase may account for the differences in the previously reported and observed phase behavior of this salt.

$PYR_{1R}TFSI/LiTFSI$ Mixtures. DSC heating traces for the $(1 - x)PYR_{1R}TFSI-(x)LiTFSI$ ($R = 2-4$) mixtures are shown in Figure 1. The corresponding phase diagrams are shown in Figure 3. The thermal behavior of these mixtures is quite complex, especially for the mixtures with $PYR_{12}TFSI$.

Several notable points are immediately evident in comparing the phase behavior of the $(1 - x)PYR_{1R}TFSI-(x)LiTFSI$ ($R = 2-4$) mixtures (Figure 3). All of the pyrrolidinium salts examined form stoichiometric 2/1 and 1/2 (PYR_{1R}^+/Li^+) crystalline phases with LiTFSI. Further, the melting points of these phases are remarkably similar given that the pure pyrrolidinium salts melt over a widely variable temperature range.

The crystal structures for all of the mixed PYR_{1R}-TFSI−LiTFSI phases will contain strong $Li^+...TFSI^-$ interactions, most likely between the Li^+ cations and anion oxygens as this is what is observed in crystalline LiTFSI,[20] $(H_2O)_1$:LiTFSI,[21] (monoglyme)$_1$:LiTFSI,[22] (diglyme)$_{1/2}$:LiTFSI,[23] and poly(ethylene oxide)$_3$:LiTFSI.[24,25] These relatively strong ionic coordination bonds will control the resulting crystal structure. All or only part of the $TFSI^-$ anions may be coordinated to the Li^+ cations. The anions have only weak electrostatic interactions with the PYR_{1R}^+ cations due to the steric shielding of the positive charge.[16] Note that the $Li^+/TFSI^-$ ionic ratios are 1/3 and 2/3 for the PYR_{1R}^+/Li^+ 2/1 and 1/2 phases, respectively. A crystal structure has previously been reported for a 1-methyl-3-ethylimidazolium$^+$/Na^+ phase with $AlCl_4^-$ anions and a 1/1 stoichiometry.[26] The Na^+ cations form ionic chains in which each is coordinated by four $AlCl_4^-$ anions. The imidazolium cations are uncoordinated and fill the regions between the $[(Na^+)(AlCl_4^-)_2]_n$ columns.

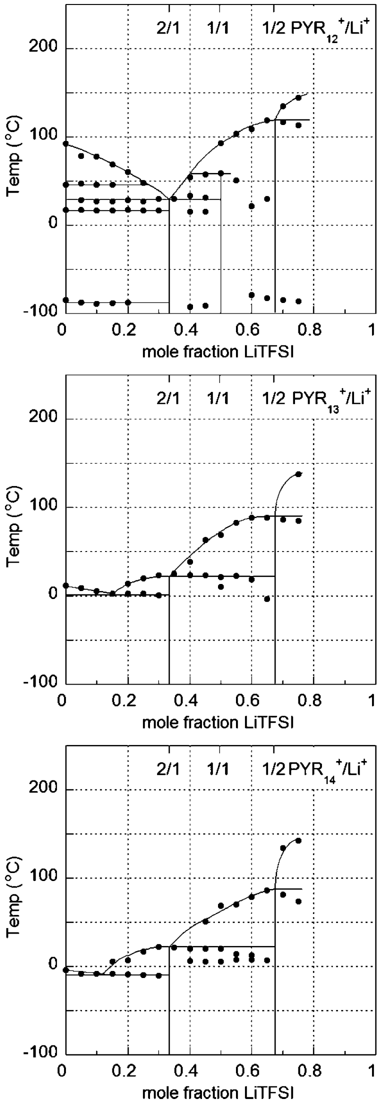


Figure 3. $(1 - x)PYR_{1R}TFSI-(x)LiTFSI$ ($R = 2-4$) phase diagrams.

1/1 $PYR_{1R}TFSI/LiTFSI$ Metastable Phases? A 1/1 crystalline phase also appears to form in the PYR_{12}-TFSI−LiTFSI mixtures. This has a distinct melting endotherm for compositions with $x = 0.40-0.60$. For the $x = 0.50$ samples, however, three endothermic peaks are found. Efforts to melt the mixture and thermally anneal it under various conditions to form a homogeneous 1/1 phase failed. Rather, multiple endothermic peaks were always found. This suggests that perhaps the 1/1 phase is metastable.

During the course of the thermal analysis of the $(1-x)PYR_{14}TFSI-(x)LiTFSI$ mixtures, different results were often obtained for the same samples upon repeated thermal cycling and annealing. This was particularly true for samples with $x = 0.40-0.60$ compositions. The origin of this again appears to be the formation of a metastable 1/1 phase. If an $x = 0.50$ sample is equilibrated for several hours to days at room temperature, some of the 1/2 phase crystallizes. When the sample is then cooled, the remaining melt crystallizes into what appears to be the 2/1 phase and some of a 1/1 phase. If, instead, the sample is heated to form a homogeneous

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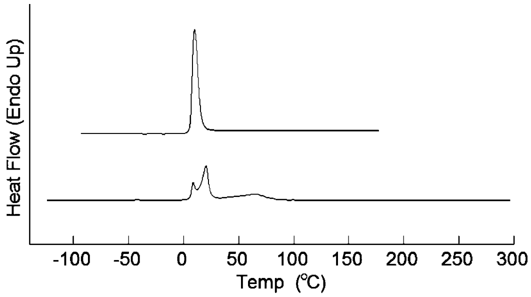

Figure 4. DSC heating traces (10 °C/min) for a $(1 - x)$PYR$_{14}$TFSI$-(x)$LiTFSI ($x = 0.50$) mixture after cooling from the melt at 90 °C (top) or 20 °C (equilibrated for several days) (bottom) and crystallizing.

melt (90 °C) and then cooled, the melt forms an amorphous glass (Figure 4). If the sample is then heated and cooled repeatedly at submelting temperatures (crystallizing/annealing thermally cycled), the sample crystallizes into a single phase. This metastable 1/1 phase accounts for the variable thermal behavior of the samples in this concentration range. For the samples with $x = 0.05-0.35$ and $0.65-0.75$, no such difficulties were encountered.

Comparison with Previous Reports. The PYR$_{12}$TFSI salt is interesting in that it appears to have three solid-phase transitions (−92, 14, and 45 °C) before melting at 90 °C.[14] The salt is thus a plastic crystal at room temperature and has a corresponding waxy appearance. Each phase transition results in an increase in the crystal disorder. The ionic conductivity of the pure PYR$_{12}$TFSI salt increases linearly with temperature up to −15 °C (the onset of the 14 °C transition).[14] The activation energy for the ionic conductivity then decreases and is linear up to 45 °C, at which point it increases sharply, and is again linear up to 75−80 °C. The conductivity continuously rises with temperature, but the thermal activation process for the conductivity varies with the disorder of the ions in the different phases.

Thermal characterization of $(1 - x)$PYR$_{12}$TFSI$-(x)$LiTFSI ($x = 0-0.50$) mixtures has been previously reported.[17−19] Up to $x = 0.05$ concentrations, no additional DSC peaks were observed. Only the final melting peak was found to broaden. A new endothermic peak was observed at about 35 °C for mixtures with $x = 0.09-0.50$. This peak reached a maximum for the $x = 0.33$ composition although small peaks at −92 and 14 °C were still observed. The authors suggested that the transition at 35 °C is due to a eutectic with a composition of $x = 0.33$ and that a solid solution forms between the LiTFSI and PYR$_{12}$TFSI salts for $x < 0.09$ compositions. For the $x = 0.50$ sample, new endothermic peaks were found at 52 and about 90 °C. These latter peaks were not reproduceable on thermally cycling the sample. It was suggested that the peak at 52 °C may represent a peritectic melting of a 1/1 phase.

The authors noted above prepared the $(1-x)$PYR$_{12}$TFSI$-(x)$LiTFSI ($x = 0-0.50$) mixtures by combining the PYR$_{12}$TFSI and LiTFSI salts and stirring at 100 °C for 1 h. This procedure may not homogeneously mix the samples with the highest LiTFSI mole fractions (LiTFSI has a T_m of 234 °C)[27] since endothermic peaks for the pure PYR$_{12}$TFSI salt were observed with the $x = 0.33$ sample. Note that the DSC measurements by these authors were obtained by quenching the samples from room temperature and then heating at a rate of 20 °C/min. Often, the samples formed glasses on quenching due to slow crystallization kinetics. On heating, the samples partially or fully cold-crystallized. In contrast, the samples reported in Figure 1 were fully crystallized before the measurements and the heating rate was 10 °C/min. The results reported in Figure 1 are thus more representative of the equilibrium thermal behavior of the $(1 - x)$PYR$_{12}$TFSI$-(x)$LiTFSI mixtures.

The endothermic peak at 35 °C is not due to a eutectic, but rather to a 2/1 crystalline phase (as is evident by the formation of a similar phase with the PYR$_{13}$TFSI and PYR$_{14}$TFSI salts). In Figure 1, a distinct endothermic peak for the 2/1 phase is present even in the $(1 - x)$PYR$_{12}$TFSI$-(x)$LiTFSI ($x = 0.05$) mixture suggesting that a solid solution does not form at low LiTFSI compositions. Note that small quantities of the $(1 - x)$PYR$_{1R}$TFSI$-(x)$LiTFSI ($x = 0.30-0.35$) mixtures often remain liquids indefinitely on standing at 20 °C. The 2/1 phases form only when the mixtures are supercooled further, and the crystallization kinetics for this phase are sluggish even at −5 °C. Crystallization may occur at 20 °C, however, for larger sample sizes suggesting that crystallization is limited by nucleation of the crystalline phase. Some of the ionic conductivity results reported for the $(1 - x)$PYR$_{12}$TFSI$-(x)$LiTFSI ($x = 0.05-0.50$) mixtures[17−19] may thus be due not to a solid solution of LiTFSI in crystalline PYR$_{12}$TFSI, but rather to the presence of a liquid (or glassy) phase with the 2/1 ($x = 0.33$) composition mixed with the PYR$_{12}$TFSI crystalline phase. These measurements were obtained by initially cooling the conductivity cells with liquid nitrogen and then heating at a 0.2 °C/min rate.[19] It is unclear if the samples were equilibrated by this procedure. The ^{7}Li NMR line widths for an $x = 0.09$ sample began to decrease rapidly at about −30 °C indicating the onset of diffuse Li$^+$ cation motions from a static state.[17,18] This may be due to the presence of an amorphous $(1 - x)$PYR$_{12}$TFSI$-(x)$LiTFSI ($x = 0.33$) phase (with a T_g near −30 °C) which was quenched into a glass on cooling. There was no distinct ^{7}Li NMR line width narrowing transition which occurred for this sample from 0 to 50 °C as might be expected if a crystalline 2/1 phase melted.[17] It is possible this narrowing is somehow associated with the solid-phase transition for the PYR$_{12}$TFSI salt (to a plastic crystal). For an $x = 0.33$ sample, however, a narrow ^{7}Li NMR peak was observed at −19 °C and the broad peak disappeared at 9 °C[18] even though the 2/1 crystalline phase melts at 29 °C (onset near 15 °C) and has no evident solid-phase transitions (Figure 1). It is not clear why this is so. In the conductivity measurements, however, the conductivity of the $x = 0.05-0.50$ samples does tend to rise sharply until approximately 30 °C, at which point a transition is observed after which the conductivity increases more slowly with increasing temperature. This is typical behavior for a solid-melt transition which indicates that for these measurements the samples were fully crystalline. These observations suggest that the Li$^+$ cations may gain some mobility with increasing temperature in the 2/1 crystalline phase

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prior to melting (despite the absense of solid-phase transitions). Further work in which the crystalline state of the (1 − x)PYR$_{1R}$TFSI−(x)LiTFSI materials is known should clarify the origin of these observations.

The formation of mixed (1 − x)PYR$_{1R}$TFSI−(x)LiTFSI crystalline phases has important implications for electrolyte applications using RTIL−LiX mixtures. The possible rigid coordination of the Li$^+$ cations in these crystalline phases may dramatically reduce the Li$^+$ cation conductivity. One might initially assume that the phase diagrams readily identify the compositions which are useful (i.e., which exist as a melt at the desired device operating temperature to ensure high ionic conductivity). But concentration gradients within the electrolyte during battery charging/discharging may lead to crystallization of the high melting LiTFSI salt rich phase which might, in turn, drastically change the properties of the electrolytes over time.

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