Communication: Investigation of ion aggregation in ionic liquids and their solutions with lithium salt under high pressure

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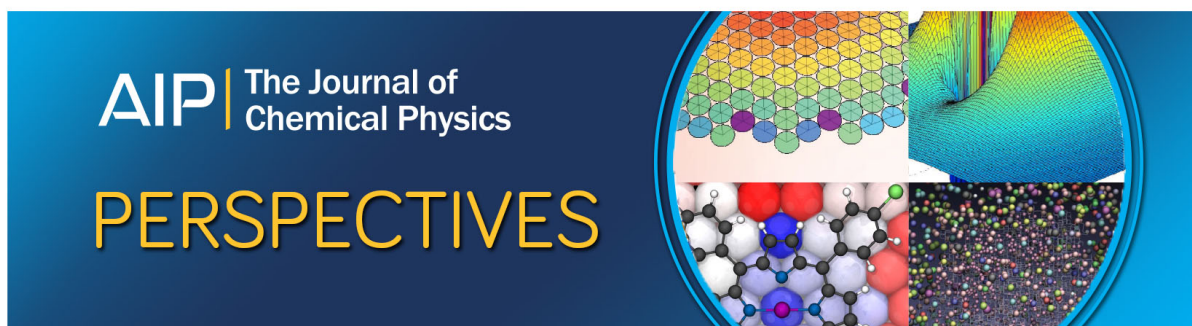
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X-ray scattering measurements were utilized to probe the effects of pressure on a series of ionic liquids, N-alkyl-N-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr$_{1A}$-TFSI) (A = 3, 6, and 9), along with mixtures of ionic liquid and 30 mol. % lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt. No evidence was found for crystallization of the pure ionic liquids or salt mixtures even at pressures up to 9.2 GPa. No phase separation or demixing was observed for the ionic liquid and salt mixtures. Shifts in the peak positions are indicative of compression of the ionic liquids and mixtures up to 2 GPa, after which samples reach a region of relative incompressibility, possibly indicative of a transition to a glassy state. With the application of pressure, the intensity of the prepeak was found to decrease significantly, indicating a reduction in cation alkyl chain aggregation. Additionally, incompressibility of the scattering peak associated with the distance between like-charges in the pure ionic liquids compared to that in mixtures with lithium salt suggests that the application of pressure could inhibit Li$^+$ coordination with TFSI$^-$ to form Li[TFSI$_2$]$^-$ complexes. This inhibition occurs through the suppression of TFSI$^-$ in the *trans* conformer, in favor of the smaller *cis* conformer, at high pressures. *Published by AIP Publishing.* https://doi.org/10.1063/1.5016049

Ionic liquids (ILs) are salts, which have low melting points, typically defined as below 100 °C. Due to several favorable properties, including low volatility, high thermal and chemical stabilities, large liquid temperature ranges, and tunability, ionic liquids have been utilized for applications in many industries, including textiles and energy storage. When mixed with lithium salts, ionic liquids have shown exceptional promise for use as electrolytes in secondary lithium-ion batteries.[1–10]

Previous studies, using both computational and experimental techniques, on ionic liquids containing cations with medium to long alkyl chains have shown a tendency for cations to form aggregates.[2,11,12] However, only limited data exist for these ionic liquids or their aggregates at high pressures. In this study, a set of N-alkyl-N-methyl-pyrrolidinium (Pyr$_{1A}$$^+$) based ionic liquids with a bis(trifluoromethanesulfonyl)imide (TFSI$^-$) anion was investigated. Of particular interest is the effect of adding lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt, which, while necessary for lithium battery applications, also introduces a degree of complexity in the ionic liquid structure due to the high charge density of the Li$^+$ ion. The alkyl chain length (A) on the pyrrolidinium cations used was varied to be three, six, or nine carbons in length. The ionic liquids were synthesized according to previously published procedures[2] and were studied in their pure form as well as in a solution with 30 mol. % LiTFSI salt. Solutions were made using dried LiTFSI by stirring and heating overnight. All samples were stored, handled, loaded, and sealed in diamond anvil cells within an argon glovebox.

A collimated molybdenum rotating anode x-ray source ($\lambda^* = 0.71$ Å) was utilized with a MAR345 image plate detector to make high pressure x-ray scattering measurements at the Laboratoire de Physique des Solides (Orsay, France). The experimental setup parameters were calibrated using CeO$_2$ powder resulting in a sample-detector distance of 412 mm. The exposure time was set to 1200 s for each diffractogram, providing the necessary statistics considering the signal-to-noise ratio.

The internal pressure of the diamond anvil cell was determined by fitting the spectral shift of the R$_1$ fluorescence line of a ruby chip placed within the sample, providing an accuracy of ±0.1 GPa.[13] Measurements were made ramping up from ambient to a maximum pressure between 5.5 and 9.2 GPa depending on the loading. All scattering patterns are presented with background signal subtracted out. Due to variation in the sample width at variable pressure, intensity calibration into absolute units was not possible. All scattering patterns are thus presented in arbitrary intensity units.
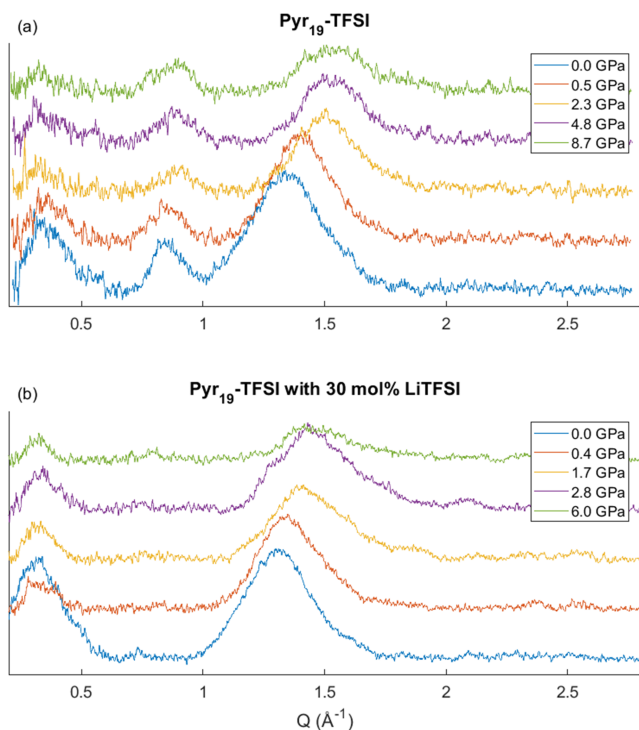
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FIG. 1. High pressure x-ray scattering results at selected pressures for Pyr$_{19}$-TFSI, both for (a) the pure ionic liquid and (b) the mixture with LiTFSI.

FIG. 2. High pressure x-ray scattering results at selected pressures for Pyr$_{13}$-TFSI, both for (a) the pure ionic liquid and (b) the mixture with LiTFSI.

It can be seen, in Fig. 1, that for pure Pyr$_{19}$-TFSI, three scattering peaks are observed, in conformity with literature.[12,14] A peak is located at $Q \approx 0.4$ Å^{-1}, which has been associated with medium to long alkyl chain lengths on the cation.[11,12,15,16] This peak is usually seen as indicative of cation alkyl chain segregation or more specifically, polar-nonpolar domain segregation and will be referred to as the prepeak or first scattering peak. Another peak is located at $Q \approx 0.8$ Å^{-1}, which has been associated with the distance between like-charges and shall be referred to as the second peak.[12,14,15,17–19] The largest peak, located at $Q \approx 1.4$ Å^{-1}, has been assigned to several inter- and intra-molecular contributions, predominantly from cation polar head-anion correlations.[14,20] This peak shall be referred to as the third scattering peak.

Figures 2 and 3 show that for ionic liquids with $A = 3, 6$, no prepeak is observed. This is in disagreement with previously reported ambient pressure x-ray scattering data, in which a prepeak was found for Pyr$_{16}$-TFSI.[12] The missing prepeak is likely due to its previously reported broad nature,[12] along with the low signal-to-noise ratio inherent with diamond anvil cell x-ray scattering experiments. This causes the signal from the prepeak to become mixed with the subtracted background.

In addition to high pressure measurements taken using a diamond anvil cell, ambient pressure x-ray scattering measurements for all samples were taken with samples in 5 mm diameter capillaries. These results, not shown, were entirely consistent with previously published results.[12,14]

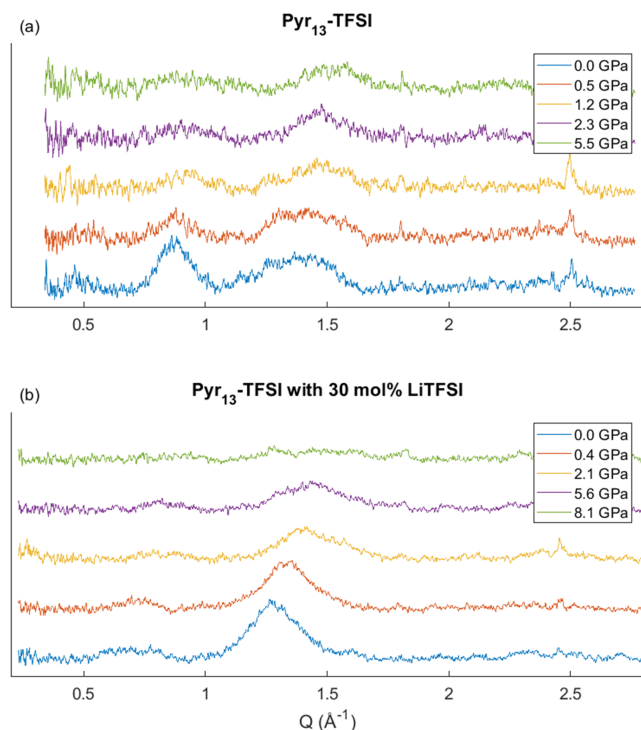Previous studies on imidazolium-based ionic liquids have shown ionic liquids with hexafluorophosphate (PF$_6^-$) anions to crystallize much more easily than those with tetrafluoroborate (BF$_4^-$) anions when subjected to high pressure.[21–25] This demonstrates a strong relationship between the ionic liquid anion and phase behavior as a function of pressure.

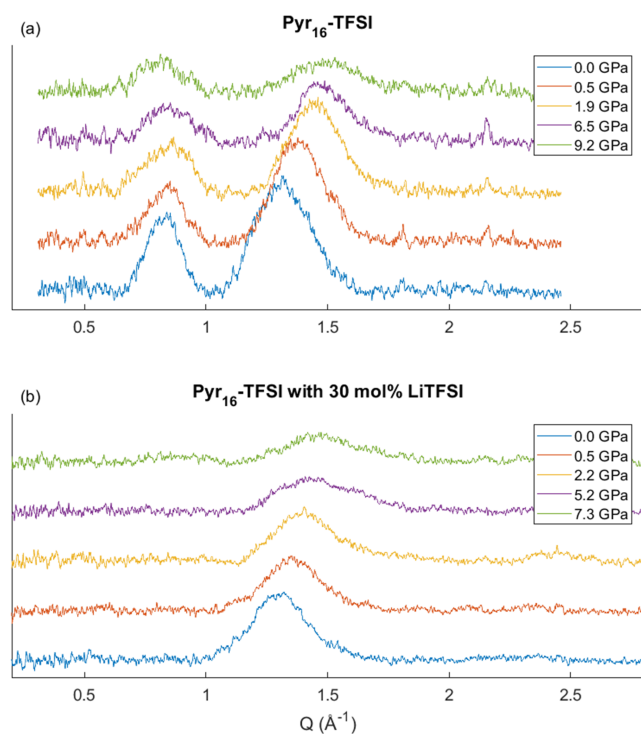Previous experimental and computational studies of 1-octyl-3-methylimidazolium tetrafluoroborate (OMIM-BF$_4$)

FIG. 3. High pressure x-ray scattering results at selected pressures for Pyr$_{16}$-TFSI, both for (a) the pure ionic liquid and (b) the mixture with LiTFSI.

have shown an x-ray scattering prepeak whose intensity decreases significantly with the application of pressure, even disappearing at pressures as low as 2 GPa, which has been associated with a superpressed state.[26,27] For Pyr$_{19}$-TFSI, a discernable prepeak is still observed at higher pressures, up to the experimental limit of 8.7 GPa. Due to the similarities between OMIM$^+$ and Pyr$_{19}^+$ cations, it is likely that the different scattering patterns are due to the effects of the anion. It is probable that the much larger size, greater charge delocalization, and higher conformational flexibility of the TFSI$^-$ compared to BF$_4^-$ or PF$_6^-$ prevent the crystallization or superpression of the ionic liquid at pressures below 9 GPa. This conclusion is supported by Raman studies which found no crystallization of *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI) at pressures up to 5.5 GPa.[28]

A strong correlation is observed between the addition of LiTFSI and the decrease in the intensity of the second scattering peak, associated with charge ordering. Previous studies have shown that IL mixtures with LiTFSI can form stable coordinations between Li cations and two TFSI anions, one in the *cis* and one in the *trans* conformer, effectively forming a single larger anion with a charge of −1.[29–31] This variance in the size of single TFSI anions vs. Li[TFSI$_2$]$^-$ complexes can lead to a noticeable decrease in the intensity of the second scattering peak. Also, due to the larger size of the Li[TFSI$_2$]$^-$ complex, the second and third scattering peaks can be seen to shift to smaller Q values.[12] This latter effect can be seen in Figs. 4 and 5. In ionic liquids with an observable prepeak, these effects cause a convolution between the prepeak and the second scattering peak, which has been previously
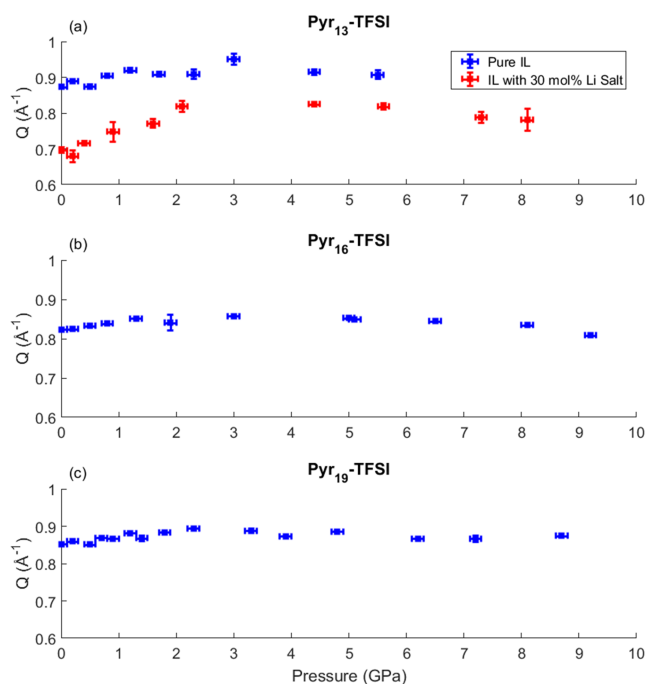

FIG. 5. Plots depicting the position of the third scattering peak for (a) Pyr$_{13}$-TFSI, (b) Pyr$_{16}$-TFSI, and (c) Pyr$_{19}$-TFSI, as well as their mixtures with lithium salt. Vertical error bars which are not seen lie within the printed data point.
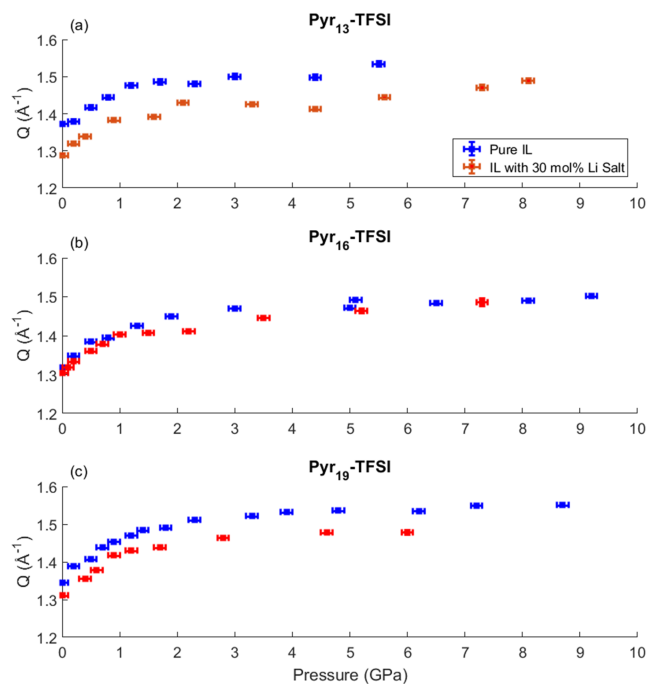
reported.[12] Due to this, along with the lower signal-to-noise ratio, second scattering peaks were indiscernible in ionic liquid and lithium salt mixtures with cation alkyl chain lengths of 6 or 9.

With increased pressure, a shift in the position for the third scattering peak to larger Q values is observed for all samples, as shown in Fig. 5. This is indicative of compression of the distances between cation rings and anions.

Interestingly, the second peak, associated with distances between like-charges, also shifts to larger Q values with the application of pressure for samples containing lithium salt, but no noticeable change is observed for the second peak in the pure ionic liquids. In the pure ionic liquids, the Coulombic interactions could prevent the compression of distances between similarly charged ions.

Previous high pressure studies on ionic liquids utilizing TFSI anions have shown how pressure can limit conformational changes of TFSI$^-$ between *cis* and *trans* conformers, favoring the smaller *cis* conformer with increasing pressure.[32–34] These findings suggest that the application of pressure can inhibit coordination between Li$^+$ and TFSI$^-$, preventing the formation of Li[TFSI$_2$]$^-$ complexes. The reduced size of the TFSI anion vs the Li[TFSI$_2$] anion allows for closer characteristic distances between like-charges in the ionic liquid and salt mixtures with the application of pressure.

The shift of scattering peak positions, when observed, is most significant below 2 GPa. Similar ionic liquids have shown evidence of a transition to a glassy state through Raman and IR spectroscopy at similar pressures.[32,33] This incompressibility beyond 2 GPa could be indicative of such a transition into a glassy state.

FIG. 4. Plots depicting the position of the second scattering peak for (a) Pyr$_{13}$-TFSI, (b) Pyr$_{16}$-TFSI, and (c) Pyr$_{19}$-TFSI, as well as their mixtures with lithium salt. Vertical error bars which are not seen lie within the printed data point.

Molecular dynamics simulations in which 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (OMIM-TFSI) exhibited polar-nonpolar domain segregation, with the octyl chain being characterized by a high fraction of the *trans* conformation, have been reported.[26] With increased pressure, a decrease in the simulated prepeak intensity was attributed to an increased fraction of the *gauche* conformation along the octyl chain.[26] Additional computational studies have shown similar results in 1-decyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (DMIM-TFSI), in which the application of pressure led to curling of the alkyl chain in an attempt to lay parallel to the charge network interface, thereby reducing the volume of the apolar pockets and changing the shape of the nonpolar domains.[35] This effect may also result in the smearing of spatial correlations, in turn, reducing the prepeak intensity. Results shown in Fig. 1 for Pyr$_{19}$-TFSI in both its pure form as well as with 30 mol. % LiTFSI seem to corroborate these findings, where an increase in the applied pressure reduces the intensity of the prepeak.

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