

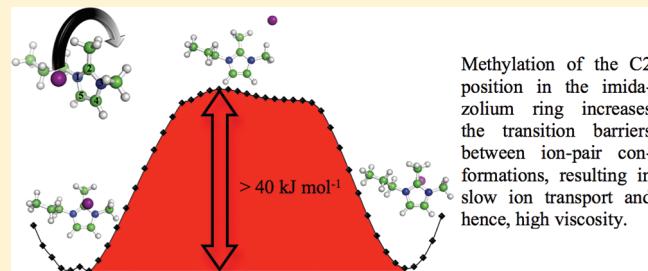
Understanding the Effect of the C2 Proton in Promoting Low Viscosities and High Conductivities in Imidazolium-Based Ionic Liquids: Part I. Weakly Coordinating Anions

Ekaterina I. Izgorodina,^{*†} Radha Maganti,[†] Vanessa Armel,[†] Pamela M. Dean,[†] Jennifer M. Pringle,[†] Kenneth R. Seddon,[‡] and Douglas R. MacFarlane[†]

[†]School of Chemistry, Monash University, Wellington Rd, Clayton, VIC 3800, Australia

[‡]The Quill Research Centre, The Queen's University of Belfast, Stranmillis Road, Belfast, BT9 5AG, United Kingdom

ABSTRACT: 1,3-Disubstituted imidazolium ionic liquids have been the subject of numerous theoretical and experimental studies due to their low viscosity—often the very lowest for any given cation/anion family. One of the mysteries in the imidazolium family of salts is the sharp increase in viscosity that is observed on methylation at the C2 position in the ring. In the nonmethylated case, the C2 proton is observed to be distinctly acidic and, where this is undesirable, substitution of the C2 position removes the problem, but produces an unexpected increase in viscosity. Methylation at other positions on the ring does not produce such a significant effect. In this study, two possible structural or energetic sources of the increased viscosity were investigated: (1) ion association, as probed by the Walden rule, and (2) differences in the potential energy surface profiles that favor ionic transport in the non C2-methylated imidazolium ionic liquids. The second hypothesis was investigated using high-level ab initio theory. The higher viscosity of C2-methylated imidazolium ionic liquids is shown to be a result of high potential energy barriers (significantly above the available thermal energy) between the energetically preferred conformations on the potential energy surface, thus restricting movement of ions in the liquid state to only small oscillations and inhibiting the overall ion transport.



Methylation of the C2 position in the imidazolium ring increases the transition barriers between ion-pair conformations, resulting in slow ion transport and hence, high viscosity.

INTRODUCTION

Ionic liquids have been intensively studied as replacements for traditional solvents in various chemical processes, and as electrolytes in alternative energy generation/storage devices such as lithium batteries, fuel cells, and solar cells.^{1–10} Imidazolium-based ionic liquids have attracted particular attention due to their low viscosity—one of the main prerequisites for a solvent to be useful, or for an electrolyte to achieve adequate performance in electrochemical devices.^{11–15} However, variation in substituents on the imidazolium ring is found to have a drastic impact on transport properties, especially viscosity. A substitution of the hydrogen in the C2 position of the imidazolium ring by a methyl group (see Figure 1) leads to a very significant increase in viscosity^{16–19} and melting point.²⁰ The increase is quite unexpected on the basis of the small structural change involved. For example, Bonhôte et al.¹⁶ showed that the ionic liquid 1-ethyl-2,3-dimethylimidazolium bis{[(trifluoromethyl)sulfonyl]amide}, [C₂m₂im][NTf₂], with the C2 position methylated was more viscous than its nonmethylated (i.e., protonated) analogue, [C₂mim][NTf₂], by about a factor of 3. This observation seems to be rather puzzling as the methylation in the C2 position reduces potential hydrogen bonding and, hence, could even have been expected to lead to a decrease in viscosity. Even more puzzling is the fact that methylation of the imidazolium ring in the C4 or C5 positions produces little change in the viscosity.¹⁶ This all suggests that the hydrogen in the C2 position has an

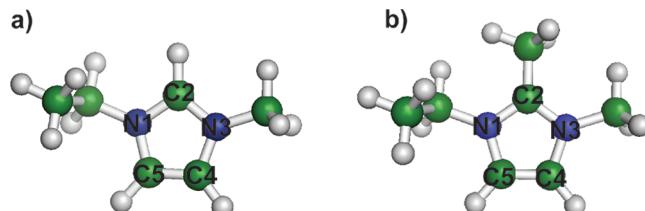


Figure 1. Structure of (a) the protonated and (b) C2-methylated imidazolium cations.

important, but not well understood, role in achieving highly fluid imidazolium ionic liquids—an effect that is of broader interest in designing and synthesizing low viscosity ionic liquids.

A number of hypotheses have been brought forward in an attempt to explain this unusual behavior. Hunt conducted a computational study of the energetics of ion pairs of 1-butyl-3-methylimidazolium, [C₄mim]⁺, and 1-butyl-2,3-dimethylimidazolium, [C₄m₂im]⁺, with the chloride ion.²¹ The interaction energies of the ion-pair conformations corresponding to various positions of the chloride anion around the imidazolium ring differed insignificantly (i.e., by only a few kJ mol⁻¹) between the

Received: September 6, 2011

Revised: October 23, 2011

Published: October 24, 2011

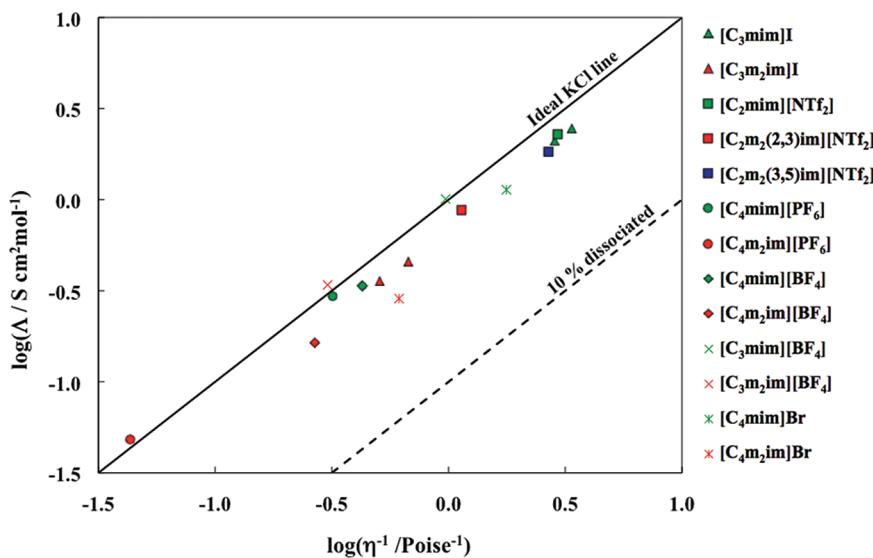


Figure 2. Walden plot of the protonated and methylated imidazolium-based ionic liquids.

C2-protonated, $[C_4mim]^+$, and C2-methylated, $[C_4m_2im]^+$, ionic liquids. The main difference observed was that no stable, in-plane conformations were found for $[C_4m_2im]Cl$, of the type that are found in $[C_4mim]Cl$, in which the chloride anion interacts with the C2–H bond in the ring plane, thus reducing the conformational space. The striking change in viscosity was therefore hypothesized to be due in part to a loss of entropy. In addition, a second hypothesis was proposed²¹ relating to the rotational barrier of the butyl chain in the lowest-energy conformation of the $\{[C_4m_2im]Cl\}$ ion pair, which was calculated to be about 35 kJ mol⁻¹, more than 3 times higher than in the $\{[C_4mim]Cl\}$ ion pair. Thus, the methyl group in the C2 position enforces a restricted rotation of the butyl chain, promoting alkyl chain association between cations and, as a consequence, further increasing the overall viscosity. Classic molecular dynamics simulations with polarizable force fields for the $[C_4mim][NTf_2]$ and $[C_4m_2im][NTf_2]$ ionic liquids showed that methylation of the C2 hydrogen prevented the NTf₂ anion from interacting with the C2 atom of the imidazolium ring.^{22,23} It was hypothesized that the absence of the relaxation pathway above the C2 atom might be responsible for the slower ion transport of the methylated ionic liquids.

Counterintuitively, Fumino et al.²⁴ linked the directional C2–H hydrogen bonding with anions to the high fluidity of imidazolium-based ionic liquids. It was hypothesized that the C2–H hydrogen bond disrupted the ionic network by altering the charge symmetry of the ions, thus introducing additional “defects” in the system and making the corresponding ionic liquid more fluid. Although this hypothesis could explain a slight variation in transport properties due to disruption of Coulombic interactions, it does not seem able to fully explain a change in viscosity by as much as seven times.

Recently Li et al.²⁵ introduced a theoretical quantity called the charge lever momentum (CLM) that contains detailed information about the charge and mass distribution in the ion accounting for the degree of Coulombic interactions with neighboring ions and the rate of the rotational and translational dynamic response. Using this parameter, they correlated the momentum with the viscosity in some room temperature ionic liquids, with the larger

CLM leading to lower viscosities. Surprisingly, the C2-methylated imidazolium cations, $[C_2m_2im]^+$ and $[C_3m_2im]^+$, were found to possess relatively low CLMs, correlating with their higher viscosities in bistriflame, $[NTf_2]^-$, ionic liquids, thus suggesting that hydrogen bonding is not the key factor governing viscosity in 2-methylated imidazolium ionic liquids. However, no clear explanation was given as to why the methylation of the C2 position of the imidazolium ring should cause much lower CLMs in these cations compared to protonated ones.

The goal of this paper is to further investigate the structural and energetic factors that lead to increased viscosity in 2-methylated imidazolium ionic liquids coupled with weakly coordinating anions, and thereby understand more clearly what is potentially unique in providing low viscosities in the $[C_nmim]^+$ family of ionic liquids. There are three main factors that have been previously identified that could potentially contribute to the difference in transport properties of these ionic liquids: (a) the presence of strong C2–H hydrogen bonding in the nonmethylated ionic liquids; (b) loss of entropy due to a decrease in conformation space in the C2 methylated ionic liquids, and (c) restricted ion mobility in the C2-methylated ionic liquids for structural and/or energetic reasons. There is a further important factor that has not been addressed so far involving ion association mechanisms in the liquid state (be it ion pairing, or higher-order aggregate formation) that might also result in lower viscosities in the nonmethylated imidazolium ionic liquids, as observed in some previous work.²⁶ Hence, the following hypotheses were tested in this study:

- (1) That changes in ion association as a result of C2 methylation have a strong effect on the transport properties. To investigate this, a Walden plot²⁷ (Figure 2) was used to reveal any changes in the degree of ion association in a number of pairs of imidazolium-based ionic liquids;
- (2) That differences in the potential energy surface profiles favor the weakly coordinating anion transport around the imidazolium ring in the presence of the proton in the C2 position. To probe this hypothesis, Boltzmann distributions of ion pair binding energies at room temperature

were calculated, to compare the conformational space of the C2-protonated versus C2-methylated cations (i.e., the number of energetically preferable ion pair conformations). The potential energy surfaces were generated by moving the iodide anion as an archetype of weakly coordinating anions along various trajectories to connect the minima and thus predict the energy barriers that need to be overcome to transport iodide in $[C_3\text{mim}]I$ and $[C_3\text{m}_2\text{im}]I$.

From this study, it emerges that hypothesis 2 is the most likely to provide a general explanation of the increased viscosity phenomenon in C2-methylated imidazolium ionic liquids with weakly coordinating anions.

■ EXPERIMENTAL PROCEDURES

Ionic liquids, $[C_4\text{mim}]Br$ and $[C_4\text{m}_2\text{im}]Br$, were purchased from Iolitec with 99% purity and were used as received. Water contents were determined to be 570 ppm and 980 ppm, respectively (as measured by Karl Fischer titration). Both of these ionic liquids are colorless solids at room temperature. $[C_3\text{m}_2\text{im}]I$ was synthesized for the first time in this work, following literature methods.¹⁶ Chemicals: 1-methylimidazole (99%, purified by redistillation), 1,2-dimethylimidazole (98%), and 1-iodopropane (99%) were supplied by Sigma-Aldrich. $[C_3\text{mim}]I$ was synthesized according to the literature method.¹⁶ For both cases, 1-iodopropane was freshly distilled prior to use.

Synthesis of 1-Propyl-3-methylimidazolium iodide ($[C_3\text{mim}]I$). In a three-necked, round-bottomed flask (1000 cm³) equipped with a condenser, dropping funnel (250 cm³) and magnetic stirrer, 1-methylimidazole (50 cm³; 0.630 mol) was diluted in isopropanol (100 cm³) under a dinitrogen atmosphere. Then 1-iodopropane (124 cm³; 1.26 mol) was added dropwise for over 1 h. A viscous yellowish liquid was formed at the bottom of the flask. The product was then isolated by using a separating funnel and was washed several times with hexane and finally dried in vacuo for several days at 70 °C. (Crude yield: 80%) ¹H NMR δ/ppm (d^6 -DMSO, 300 MHz): 0.80–0.87 (t, 3H), 1.7–1.9 (m, 2H), 3.86–3.88, 4.10–4.18 (t, 2H), (s, 3H), 7.7–7.8 (m, 2H) 9.10 (s, 1H). ES⁺ *m/z* 125.1 ($C_7\text{H}_{13}\text{N}_2^+$); ES⁻ *m/z* 126.9 (I⁻).

Synthesis of 1-Propyl-2,3-dimethylimidazolium iodide ($[C_3\text{m}_2\text{im}]I$). 1-Iodopropane (40 cm³, 0.410 mol) was added dropwise to 1,2-dimethylimidazolium (28 cm³, 0.310 mol) in ethyl ethanoate (100 cm³), and the solution was stirred overnight at room temperature under a dinitrogen atmosphere. The yellow precipitate was isolated by filtration under a dinitrogen atmosphere and recrystallized from isopropanol and ethyl ethanoate. The product was obtained in the form of yellow crystals (70 g, 0.276 mol, 88%). ¹H NMR δ/ppm (d^6 -DMSO, 300 MHz) 0.86–0.88 (t, 3H), 1.71–1.90 (m, 2H), 2.59 (s, 3H), 3.76 (s, 3H), 4.04–4.09 (t, 2H), 7.63–7.66 (m, 2H). ES⁺ *m/z* 139.1 ($C_8\text{H}_{15}\text{N}_2^+$); ES⁻ *m/z*, 126.9 (I⁻). Found C, 36.4; H, 5.5; N, 10.55; I, 47.4%. $C_8\text{H}_{15}\text{N}_2\text{I}$ requires C, 36.1; H, 5.7; N, 10.5; I, 47.7%.

Thermogravimetric analysis (TGA) performed at a scanning rate of 10 °C min⁻¹ showed equivalent decomposition temperatures for $[C_3\text{mim}]I$ and $[C_3\text{m}_2\text{im}]I$ at ca. 250 °C. To achieve the driest possible state, the samples were placed in a glovebox vacuum oven at temperatures between 80 and 90 °C until the water content could not be further reduced. The water content, measured using a Metrohm 831 KF coulometer, was 565 and 400 ppm in $[C_3\text{mim}]I$ and $[C_3\text{m}_2\text{im}]I$, respectively.

Conductivity Measurements. Alternating current (AC) conductivities of $[C_3\text{mim}]I$, $[C_3\text{m}_2\text{im}]I$, $[C_4\text{mim}]Br$ and $[C_4\text{m}_2\text{im}]Br$ were measured using a dip cell with two platinum wires sheathed in glass. A frequency sweep of 10 MHz and 0.01 Hz was applied for the iodide salts at 85 and 90 °C, at 100 °C for $[C_4\text{mim}]Br$, and 110 °C for $[C_4\text{m}_2\text{im}]Br$ with an accuracy of ±1 °C. The cell constant was measured using 0.01 M aqueous KCl at 25 °C. The instrumental error for AC conductivity is below 1%.

Viscosity (η) and Density (ρ) Measurements. Dynamic viscosity measurements of $[C_3\text{mim}]I$, $[C_3\text{m}_2\text{im}]I$, and $[C_4\text{mim}]Br$ were carried out using a falling ball technique on an Anton Paar AMVn viscometer at 85 and 90 °C for the iodide salts and at 100 °C for $[C_4\text{mim}]Br$. The instrumental error for dynamic viscosity is below 1%. Density measurements of these three ionic liquids were performed on a DMA 5000 densitometer at corresponding temperatures for comparable results, with an error of 10⁻⁶ g cm⁻³. Oscillatory rheometry was used to measure the viscosity of $[C_4\text{m}_2\text{im}]Br$ at 110 °C on an Anton Paar Physica Rheometer MCR 501. The viscosity measurements were performed with a 25 mm steel plate and 0.5 mm spacing enclosed in a jacket for a constant environment. The oscillating frequency was applied at 5% strain from 100 to 0.1 rad s⁻¹ with 5 points per decade.

Theoretical Procedures. Full conformation searches of the cations 1-propyl-3-methylimidazolium, $[C_3\text{mim}]^+$, and 1-propyl-2,3-dimethylimidazolium, $[C_3\text{m}_2\text{im}]^+$, were performed at the B3LYP/6-31+G(d) level of theory. The geometry optimizations of all possible conformations for ion pairs of $[C_3\text{mim}]I$ and $[C_3\text{m}_2\text{im}]I$ were performed at the MP2/aug-cc-pVDZ level of theory. For consistency sake, the B3LYP lowest energy conformations of the $[C_3\text{mim}]^+$ and $[C_3\text{m}_2\text{im}]^+$ cations were reoptimized at the same level of theory. Improved electronic energies of the ion pairs and individual ions were obtained at the MP2/aug-cc-pVTZ level of theory. Binding energies were counterpoise corrected using the Boys and Bernardi approach,²⁸ and also include zero-point vibrational energies (ZPVEs). Similar to the approach by Zahn et al.,²⁰ the potential energy surfaces were obtained by performing relaxed scans with a step of 5° at the MP2/aug-cc-pVDZ level of theory.

■ RESULTS AND DISCUSSION

Hypothesis (1): Ion Association. Table 1 presents transport property data of a series of ionic liquids that were either measured in this work or taken from literature sources. The selection in Table 1 contains pairs of ionic liquids incorporating the same anion coupled with either a C2-protonated or C2-methylated imidazolium cation. Inspection of the transport data reveals that the protonated imidazolium ionic liquids are more conductive, ranging by a factor of 1.8 for the $[C_4\text{mim}][\text{PF}_6]$ pair to as much as 6.5 for the $[C_3\text{mim}]I$ pair. As an important comparator, a bistriflamide ionic liquid, $[C_2\text{m}_2(3,5)\text{im}][\text{NTf}_2]$, is included, in which the cation is methylated in the C5 position rather than C2; in this case the conductivity is very close to that of the $[C_2\text{mim}][\text{NTf}_2]$ ionic liquid. Thus, the effect of C2-methylation is related to the removal of the C2 proton rather than the presence of an extra methyl group on the ring per se.

The trends in viscosity mirror the conductivities, with the C2-methylated ionic liquids displaying much higher viscosities, i.e., by a factor of 6.5 for $[C_3\text{m}_2\text{im}]I$ and 7.4 for $[C_4\text{m}_2\text{im}][\text{PF}_6]$.

Table 1. A Comparison of Transport Properties (Conductivity, σ , and Viscosity, η) and Densities, ρ , of C2-Methylated versus C2-Protonated Imidazolium-Based Ionic Liquids

ionic liquid	ρ ($\pm 1\%$)/ g cm $^{-3}$	σ ($\pm 5\%$)/ mS cm $^{-1}$	η ($\pm 5\%$)/ cP	ΔW (± 0.1)	T/ °C a	references
[C ₃ mim]I	1.49	12.6	35	0.14	85	this work
	1.49	14.6	30	0.14	90	
[C ₃ m ₂ im]I	1.45	1.95	195	0.16	85	this work
	1.44	2.48	148	0.18	90	
[C ₄ mim]Br ^b	1.419 ⁴²	7.34	57	0.19	100	this work
[C ₄ m ₂ im]Br ^b	1.425 ⁴³	1.75	163	0.33	100	this work
[C ₂ mim][NTf ₂]	1.52	8.8	34	0.11	22(ρ) 20(σ) 25(η)	16
[C ₂ m ₂ im][NTf ₂]	1.495	3.2	88	0.12	21(ρ) 20(σ) 20(η)	16
					22(ρ) 20(σ) 20(η)	
					22(ρ) 20(σ) 20(η)	
[C ₃ mim][BF ₄]	1.24	5.9	103	0.02	25	17
[C ₃ m ₂ im][BF ₄]	1.13	1.7	330	0.05	25	18a
[C ₄ mim][BF ₄]	1.17	1.73	233	0.11	20	18b
[C ₄ m ₂ im][BF ₄]	1.03	0.7	372	0.22	25	18a
[C ₄ mim][PF ₆]	1.36	1.4	312	0.04	20	18b
[C ₄ m ₂ im][PF ₆]	1.24	0.77	2312	0.05	23(ρ) 25(σ) 23(η)	19,44,45

^aTemperature at which density (ρ), conductivity (σ) and viscosity (η) measurements were conducted. When the temperatures are different, an individual temperature for each measurement is specified. ^bDensities are calculated from the corresponding crystal structures.

The Walden plot has been shown to be a useful tool in probing ion association in aprotic ionic liquids,^{26,29,30} with the deviation (ΔW) from the ideal line indicating the degree of ion association. ΔW values >1.0 indicate that less than 10% of the ionic liquid is dissociated in the liquid state, and that the majority of ions are “locked” in zero-charged, nonconductive pairs or clusters. Such neutral species can have the effect of decreasing the viscosity of the whole medium.²⁶ We have shown that ΔW correlates well with deviations from the Nernst–Einstein equation that links molar conductivity with diffusivity.³⁰ These deviations are also well understood to have their origin in ion association effects.^{31,32} A Walden plot incorporating the transport property data from Table 1 is presented in Figure 1. Analysis of the Walden plot indicates that the ionic liquids included do not show significant deviations from the ideal line, with the largest deviation being 0.33 for [C₄m₂im]Br. Ionic liquids with the same anion show similar deviations. For example, all three bis(triflamide) ionic liquids show similar deviations in a very narrow range between 0.11 and 0.17. Overall, the ΔW s within each pair are not significantly different for any of the six pairs of ionic liquids, indicating that there is no significant difference in ion association between the C2-protonated and C2-methylated imidazolium ionic liquids. Hence, the first hypothesis attributing the viscosity effect of C2 methylation to ion association in the ionic liquids is not supported by this evidence, as no significant deviation from the ideal line was found for any of the ionic liquids examined here.

Hypothesis 2: Differences in the Potential Energy Surface Profiles. *Binding Energies.* To explain the substantial difference in transport properties between the C2-protonated and C2-methylated imidazolium ionic liquids, binding energies of all possible ion-pair conformations in 1-propyl-3-methylimidazolium iodide, [C₃mim]I, and 1-propyl-2,3-dimethylimidazolium iodide, [C₃m₂im]I were studied. The iodide anion was selected as the perfect archetype of a weakly coordinating anion. The optimized geometries are shown in Figures 3 and 4, and the corresponding binding energies are presented in Table 2. The ion-pair conformations were constructed by taking the lowest energy geometries of the corresponding imidazolium cations. During the optimizations, the alkyl chain on both cations appeared to be strongly influenced by the position of the anion and is thus present in slightly different conformations in the optimized ion pair geometries (see Figures 3 and 4). In both ionic liquids, the two lowest energy conformations correspond to the iodide anion located either above or below the plane of the imidazolium cation. Energetically, there is only a slight difference, of less than 4 kJ mol $^{-1}$, between the protonated and methylated conformations, denoted here as IH_A/IH_B and IM_A/IM_B, respectively, where A indicates conformations above the imidazolium plane and B indicates those below the plane. The next lowest energy conformations in [C₃mim]I, denoted here as IH_C and IH_D, are the in-plane interactions between the iodide and the C2–H bond of the imidazolium ring (Figure 3). The binding energies of the in-plane IH_C and IH_D conformations are only marginally higher than those of IH_A/IH_B, the difference

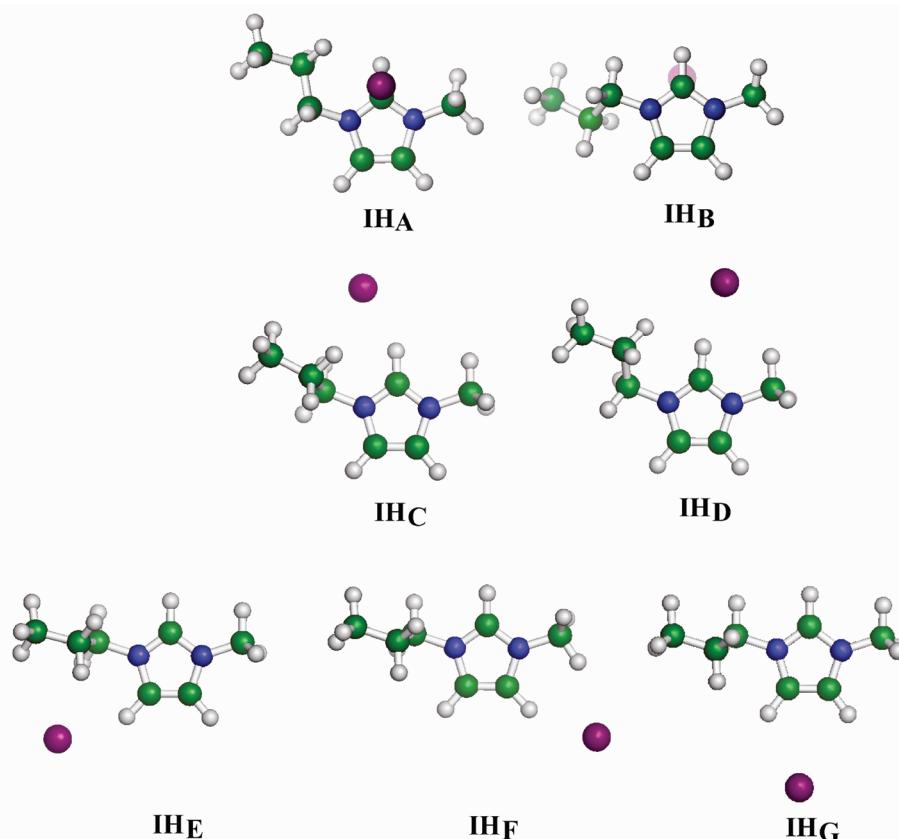


Figure 3. MP2/aug-cc-pVDZ optimized structures of the ion-pair conformations of the $[C_3\text{mim}]I$ ionic liquid.

falling in the range between 7 and 12 kJ mol^{-1} . The corresponding conformations in $[C_3\text{m}_2\text{im}]I$, IM_C , and IM_D , could not be located on the potential energy surface as true minima, as the optimizations always revert to the lowest energy conformations. These findings highlight the major difference in the conformational space between the protonated and methylated imidazolium ionic liquids, with the C2–H moiety significantly increasing the number of low energy conformations. The preference for interactions from above and below the plane between the imidazolium ring and anions with diffuse charge such as $[\text{PF}_6]^-$ and $[\text{NTf}_2]^-$ is also clearly observed in the liquid state of protonated imidazolium ionic liquids as measured by neutron diffraction data.^{33–36}

The rest of the conformations (IH_E/IM_E , IH_F/IM_F , and IH_G/IM_G) correspond to the in-plane interactions between the iodide anion and the C4–H and C5–H bonds. The binding energies of the IH_E , IH_F and IH_G conformations are much higher, within a range of 31 to 44 kJ mol^{-1} compared to IH_A , suggesting that these conformations are not significant in this context. Analogous trends are established for $[C_3\text{m}_2\text{im}]I$, with the binding energies of IM_E , IM_F and IM_G being higher than that of IM_A within a range of 34 to 60 kJ mol^{-1} . These results indicate that the conformations arising from the interactions with the C4–H and C5–H bonds are energetically much less preferable. The experimental results on transport properties of $[C_2\text{mim}] [\text{NTf}_2]$ and its analogue with the methylated C5 position, $[C_2\text{m}_{2(3,5)}\text{im}] [\text{NTf}_2]$, further support this finding, as no significant difference in conductivity and viscosity of these two ionic liquids was observed (see Table 1). Thus, it appears overall that

the main impact of C2 methylation is to hinder the in-plane interactions with the C2 position.

Boltzmann distributions (BDs) of the ion pair binding energies for $[C_3\text{mim}]I$ and $[C_3\text{m}_2\text{im}]I$, calculated at room temperature, are summarized in Table 2. Analysis of the contributions of the binding energies reveals that the probability of finding the iodide interacting from above/below the plane of the imidazolium cation is very high, approaching 97% for the protonated ionic liquid and 100% for the methylated ionic liquid. In $[C_3\text{mim}]I$, the remaining 3% is distributed between the two in-plane conformations, IH_C and IH_D . In both ionic liquids, the rest of the conformations resulting from the interactions with the backbone of the imidazolium cation, the C4 and C5 atoms, contribute substantially less than 0.001%.

In summary, no significant energetic difference is observed between the lowest energy ion-pair conformations of the protonated and methylated ionic liquids with a weakly coordinating anion such as iodide. The major difference stems from the fact that the methyl group in the methylated salt blocks the in-plane interactions of the anion with the C2 position of the ring, decreasing the number of accessible conformations; yet this observation does not significantly affect the Boltzmann distribution of conformations, with the IH_A/IM_A and IH_B/IM_B conformations predominating in both cases. This finding indicates that methylated imidazolium ionic liquids do not possess a smaller configurational space compared to the protonated ones. The hypothesis proposed by Hunt²¹ on a loss of entropy for C2-methylated imidazolium ionic liquids due to the decreased conformational space does not, therefore, seem to provide a full explanation of the transport properties.

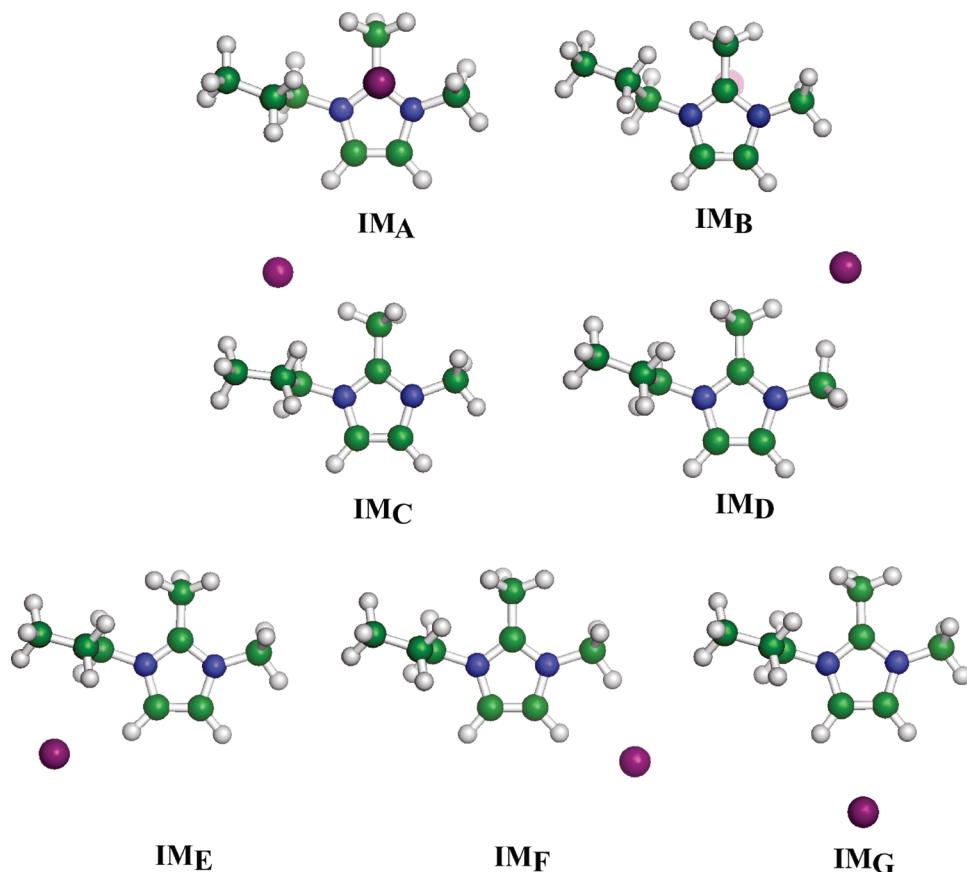


Figure 4. MP2/aug-cc-pVDZ optimized structures of the ion-pair conformations of the $[C_3m_2im]I$ ionic liquid.

Table 2. Comparison of Counterpoise-Corrected Binding Energies (BE/kJ mol⁻¹) of the Protonated $[C_3mim]I$ Structures (IH) and Methylated $[C_3m_2im]I$ Structures (IM), and Boltzmann distribution (BD, in %) of the Ion-Pair Binding Energies at Room Temperature

$[C_3mim]I$							
configuration	IH _A	IH _B	IH _C	IH _D	IH _E	IH _F	IH _G
BE	-357.2	-356.9	-349.6	-345.7	-326.4	-315.3	-303.0
BD	52	45	2	1	0	0	0

$[C_3m_2im]I$							
configuration	IM _A	IM _B	IM _C	IM _D	IM _E	IM _F	IM _G
BE	-353.9	-353.1	-315.1 ^a	-304.8 ^a	-320.2	-310.1	-294.1
BD	58	42	0	0	0	0	0

^a No true minima were located for these in-plane conformations. Instead, the binding energies of the conformations, for which the anion was fixed in the plane of the cation, are given.

Potential Energy Surfaces. Possibly of more significance are two other aspects of these pair wise conformations not discussed so far:

- (1) How are the ions able to move along the potential energy surface between these ion-pair conformations, including the less preferred ones such as IH_C and IH_D?
- (2) How high are the potential barriers that separate them?

Only when the barriers are within the available thermal energy of the molecular system at a given temperature can the ion transport be considered facile. The energy landscape paradigm first introduced by Goldstein³⁷ addresses these issues, and has been successfully applied to explain fluidity in condensed molecular systems in terms of the potential energy barriers that separate local minima on the potential energy surface.^{27,38–41} If these barriers are higher than the available thermal energy at a given temperature, then the liquid does not flow easily and, hence, the overall viscosity is large. The opposite is then true for highly fluid liquids; these have low potential barriers that can be easily overcome even under ambient conditions.

According to the Boltzmann distribution discussed above, four ion-pair conformations, IH_A, IH_B, IH_C, and IH_D, predominantly contribute to the overall energetics of the $[C_3mim]I$ ionic liquid. In order to probe the detail of the potential energy surface that might provide an energetically preferable pathway between these conformations, a relaxed computational scan was performed on the IH_A conformation by changing the C5–N1–C2–I dihedral angle in steps of 5°. This dihedral angle corresponds to moving the iodide anion over the imidazolium ring through the in-plane conformation, IH_D, to the conformation below the ring, IH_B. As seen from Figure 5, the resulting potential energy surface consists of three local minima, corresponding to the IH_A, IH_D, and IH_B conformations that are separated by two local maxima with relatively low transition barriers. To reach the in-plane conformation, IH_D, the iodide anion needs to overcome a transition barrier of ca. 15 kJ mol⁻¹. If the iodide is already located in the in-plane conformation minimum, IH_D, on the potential energy

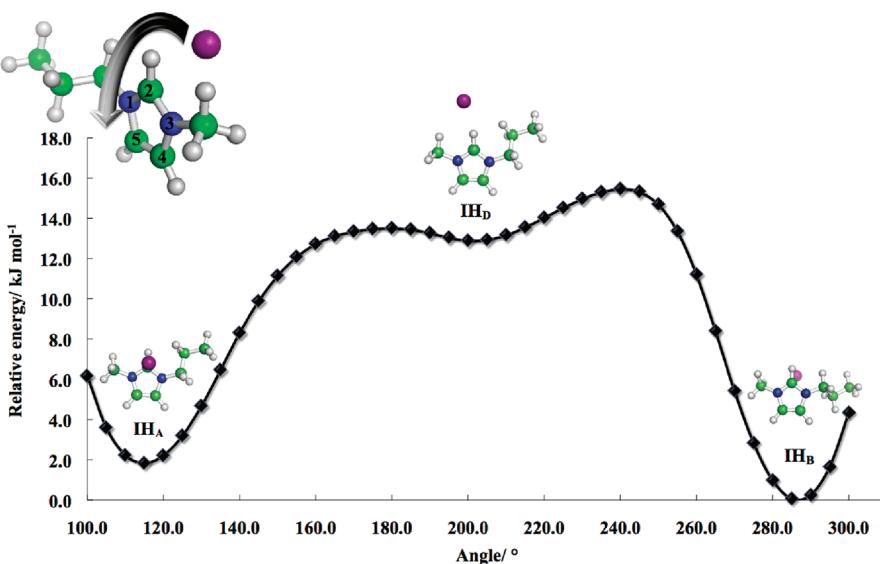


Figure 5. Potential energy surface (in the form of relative energies in kJ mol^{-1}) obtained by varying the C5–N1–C2–I dihedral angle via the IH_A , IH_D , and IH_B conformations.

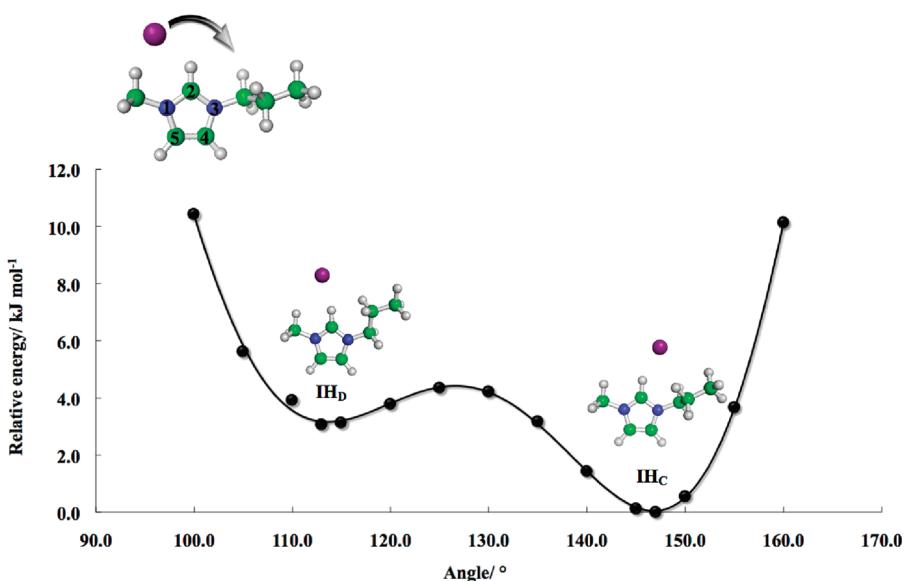


Figure 6. Potential energy surface (in the form of relative energies in kJ mol^{-1}) obtained by varying the N1–C2–I angle and freezing the C5–N1–C2–I dihedral angle to 180° via the IH_D and IH_C conformations.

surface (as shown in Figure 5), it takes only 2 kJ mol^{-1} to overcome the barrier to reach the second lowest-energy minimum, IH_B , and only 1 kJ mol^{-1} to reach the lowest-energy minimum, IH_A , on the potential energy surface. Thus, in this case, the iodide anion is relatively mobile, as it can move at relatively low cost along the potential energy surface (maximum of 15 kJ mol^{-1} barrier compared with the thermal energy at room temperature of ca. 7.4 kJ mol^{-1}). The iodide has additional freedom if it is located in the second minimum, IH_D , as the anion can now move in the plane of the imidazolium cation. The corresponding in-plane potential energy surface was obtained by varying the N1–C2–I angle in steps of 5° and freezing the C5–N1–C2–I dihedral angle at 180° , thus allowing the anion to stay in the plane of the imidazolium ring,

As seen in Figure 6, the energetic pathway from the in-plane conformation IH_D to that of IH_C has only one transition barrier of as little as 1 kJ mol^{-1} . Thus, the iodide anion in the protonated imidazolium ionic liquid is rather mobile, as the potential energy surface has a number of local minima, which are separated by energetically low transition barriers, thus leading to high ion mobility.

A totally different scenario is observed for the methylated ionic liquid (see Figure 7). The potential energy surface connecting IM_A (above the plane) to IM_B (below the plane) via IM_D (the in-plane conformation that in fact is a local maximum on the potential energy surface) reveals a very high transition barrier of 43 kJ mol^{-1} . This is far above the thermal energy available even at elevated temperatures, thus inhibiting

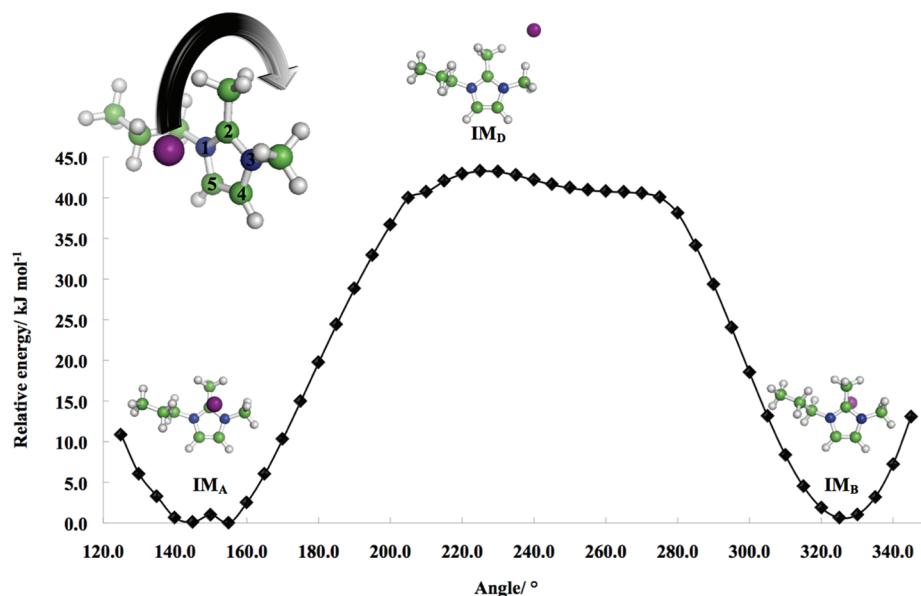


Figure 7. Potential energy surface (in the form of relative energies in kJ mol^{-1}) obtained by varying the C5–N1–C2–I dihedral angle via the IM_A, IM_D, and IM_B conformations.

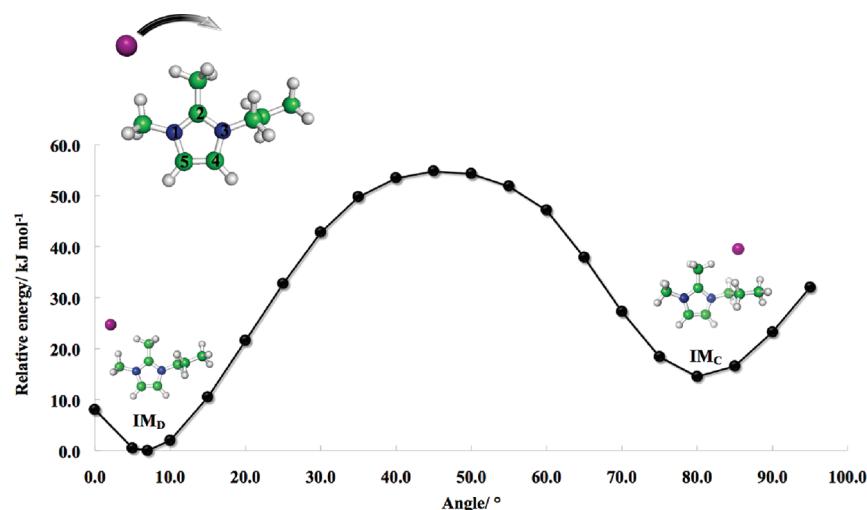


Figure 8. Potential energy surface (in the form of relative energies in kJ mol^{-1}) obtained by varying the N1–C2–I angle and freezing the C5–N1–C2–I dihedral angle to 180° via the IM_D and IM_C conformations.

the ion mobility, and therefore the iodide anion is constrained to small oscillations above and below the imidazolium ring not far from the cation. The potential energy surface does not have a smooth behavior around the IM_A minimum and at the C5–N1–C2–I dihedral angle of 210° . The slight spikes on the PES appear due to the fact that when the iodide moves around the imidazolium ring, it causes the alkyl chain to slightly rotate out of its lowest energy conformation. When the iodide anion reaches the IM_D conformation it will have difficulty moving in the plane of the C2–CH₃ bond, with the methyl group introducing a substantial steric hindrance that is reflected in a transition barrier of $>50 \text{ kJ mol}^{-1}$ to in-plane movement, as shown in Figure 8. Due to very high potential barriers, this ionic liquid should have low ion mobility and, hence, low fluidity.

In summary, the low conductivities and high viscosities of methylated ionic liquids appear to arise from the fact that the C2 position is blocked with respect to in-plane interactions in the C2-methylated case, and, therefore, only two local energy minima corresponding to the iodide interacting from above and below the imidazolium plane are available on the potential energy surface, with the rest separated by high transition barriers of at least 43 kJ mol^{-1} . Looking at this from the opposite perspective, the high conductivities and low viscosities of the protonated imidazolium ionic liquids are a result of the fact that ion-pair conformations of similar energies are separated by low transition barriers in the range of 1 to 15 kJ mol^{-1} on the PES, thus allowing the anion to easily move along the energy landscape. In other words, the presence of the C2–H moiety creates a low energy pathway for motion of the anion past the cation.

■ CONCLUSIONS

The effects that lead to an increase in viscosity and decrease in conductivity of the C2-methylated imidazolium-based ionic liquids compared to the protonated analogues were studied by testing two hypotheses: (1) ion association, and (2) differences in the potential energy surface profiles. In fact, none of the ionic liquids studied here showed significant ion association in the liquid state, with only small deviations (ΔW) from the ideal line on the Walden plot. More importantly, pairs of ionic liquids, i.e., protonated and methylated imidazolium cations coupled with the same anion, showed very similar ion association behavior. Therefore, ion association was eliminated as the reason for the large differences in viscosity. Investigation of the second hypothesis, through study of an iodide salt pair, uncovered some very significant differences between these ionic liquids. Although the energetic difference in ion pair conformations in the protonated and methylated cases is insignificant, the iodide ion is restricted to only two energetically preferable conformations in the methylated ionic liquids—from above and below the imidazolium ring—as the methyl group blocks the interaction with the C2 position. The Boltzmann distribution calculations did not show a significant difference in conformational space, with both protonated and methylated imidazolium ionic liquids mainly populating the above and below the plane conformations. Only 3% of the conformational space belongs to the in-plane conformations such as IH_C and IH_D in the protonated imidazolium ionic liquid, and the amount is negligible in the methylated species. The potential energy surfaces revealed that the iodide anion was restricted in its movement around the methylated imidazolium cation, and the potential barriers that separate the lowest-energy conformations exceed 40 kJ mol^{-1} , whereas the protonated imidazolium cation allows the anion to freely move around, while staying strongly bound with the cation. Therefore, on the potential energy surfaces, the methylated ionic liquids have only two minima separated by high potential barriers, whereas the protonated ionic liquids possess a number of local minima of similar energy separated by low transition barriers. Consequently, the C2-methylated imidazolium ionic liquids are expected to have much higher viscosity and lower conductivity than those of the protonated ones; this, although unproven here, is probably a generic truth for all such pairs of imidazolium ionic liquids with weakly coordinating anions. It appears that alkylation in the C4 or C5 position in the imidazolium ring does not affect the potential energy surface to the same degree. More theoretical studies are underway to confirm this generalization for other anions such as $[\text{NTf}_2^-]$ and $[\text{N}(\text{CN})_2^-]$. On the other hand, stronger coordinating anions such as chloride tend to form much shorter contacts with the imidazolium-type cation that leads to the formation of nonconducting dimers. In these dimers the chloride anion appears to preferentially interact with the backbone of the imidazolium ring.³² A theoretical study to understand this phenomenon is currently underway.

Broadly, then, it seems that the C2 protonated imidazolium cations are rather unique in the larger imidazolium family in possessing this favorable potential energy surface. Nonetheless, the same methodology could be used to probe other cation families, including those not yet synthesized, in pursuit of that ever-elusive goal of designing low viscosity and high conductivity ionic liquids.

■ ACKNOWLEDGMENT

We thank Arjulizan Rusli and Prof. Wayne Cook (Monash University) for help with rheometry measurements of $[\text{C}_4\text{m}_2\text{im}]$ -Br. We gratefully acknowledge generous allocations of computing time from the National Facility of the National Computational Infrastructure (Canberra, Australia) and the Monash Sun Grid Cluster at the e-research centre of Monash University, Australia. We thank the Australian Research Council for funding a Discovery grant to EII and DRM, an Australian Postdoctoral Fellowship for EII, a QEII Fellowship for JMP and a Federation Fellowship for DRM.

■ REFERENCES

- (1) MacFarlane, D. R.; Forsyth, M.; Howlett, P. C.; Pringle, J. M.; Sun, J.; Annat, G.; Neil, W.; Izgorodina, E. I. *Acc. Chem. Res.* **2007**, *40*, 1165–1173.
- (2) Howlett, P. C.; MacFarlane, D. R.; Hollenkamp, A. F. *Electrochem. Solid-State Lett.* **2004**, *7*, A97–A101.
- (3) Shin, J.-H.; Henderson, W. A.; Scaccia, S.; Prosini, P. P.; Passerini, S. *J. Power Sources* **2006**, *156*, 560–566.
- (4) Dai, Q.; Menzies, D. B.; MacFarlane, D. R.; Batten, S. R.; Forsyth, S.; Spiccia, L.; Cheng, Y.-B.; Forsyth, M. *C. R. Chem.* **2006**, *9*, 617–621.
- (5) Kuang, D.; Wang, P.; Ito, S.; Zakeeruddin, S. M.; Graetzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 7732–7733.
- (6) Belieres, J.-P.; Gevasio, D.; Angell, C. A. *Chem. Commun.* **2006**, 4799–4801.
- (7) Pringle, J. M. Ionic Liquids in Dye-Sensitized Solar Cells. In *Ionic Liquids Further UnCOILED*; Rogers, R. D., Plechko, N. V., Seddon, K. R., Eds.; Wiley, Ltd.: Chichester, U.K., 2011 (in press).
- (8) Armel, V.; Pringle, J. M.; Forsyth, M.; MacFarlane, D. R.; Officer, D. L.; Wagner, P. *Chem. Commun.* **2010**, *46*, 3146–3148.
- (9) Freemantle, M. *An Introduction to Ionic Liquids*; The Royal Society of Chemistry: Cambridge, U.K., 2010; p 281.
- (10) Abraham, T. J.; MacFarlane, D. R.; Pringle, J. M. *Chem. Commun.* **2011**, *47*, 6260–6262.
- (11) Kawano, R.; Matsui, H.; Matsuyama, C.; Sato, A.; Susan, M. A. B. H.; Tanabe, N.; Watanabe, M. *J. Photochem. Photobiol. A* **2004**, *164*, 87–92.
- (12) Seki, S.; Kobayashi, Y.; Miyashiro, H.; Ohno, Y.; Usami, A.; Mita, Y.; Kihira, N.; Watanabe, M.; Terada, N. *J. Phys. Chem. B* **2006**, *110*, 10228–10230.
- (13) Gorlov, M.; Kloot, L. *Dalton Trans.* **2008**, 2655–2666.
- (14) Goodenough, J. B.; Kim, Y. *Chem. Mater.* **2009**, *22*, 587–603.
- (15) Bayley, P. M.; Best, A. S.; MacFarlane, D. R.; Forsyth, M. *ChemPhysChem* **2011**, *12*, 823–827.
- (16) Bonhôte, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 1168–1178.
- (17) Nishida, T.; Tashiro, Y.; Yamamoto, M. *J. Fluor. Chem.* **2003**, *120*, 135–141.
- (18) (a) Min, G.-H.; Yim, T.; Lee, H. Y.; Kim, H.-J.; Mun, J.; Kim, S.; Oh, S. M.; Kim, Y. G. *Bull. Korean Chem. Soc.* **2007**, *28*, 1562–1566. (b) Carda-Broch, S.; Berthod, A.; Armstrong, D. W. *Anal. Bioanal. Chem.* **2003**, *375*, 191–199.
- (19) Strehmel, V.; Laschewsky, A.; Wetzel, H.; Gornitz, E. *Macromolecules* **2006**, *39*, 923–930.
- (20) Zahn, S.; Bruns, G.; Thar, J.; Kirchner, B. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6921–6924.
- (21) Hunt, P. A. *J. Phys. Chem. B* **2007**, *111*, 4844–4853.
- (22) Borodin, O. *J. Phys. Chem. B* **2009**, *113*, 12353–12357.
- (23) Borodin, O. *J. Phys. Chem. B* **2009**, *113*, 11463–11478.
- (24) Fumino, K.; Wulf, A.; Ludwig, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 8731–8734.
- (25) Li, H.; Ibrahim, M.; Agberemi, I.; Kobrak, M. N. *J. Chem. Phys.* **2008**, *129*, 124507(124512 pp).
- (26) Fraser, K. J.; Izgorodina, E. I.; Forsyth, M.; Scott, J. L.; MacFarlane, D. R. *Chem. Commun.* **2007**, 3817–3819.

- (27) Xu, W.; Cooper, E. I.; Angell, C. A. *J. Phys. Chem. B* **2003**, *107*, 6170–6178.
- (28) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553–566.
- (29) Yoshizawa, M.; Xu, W.; Angell, C. A. *J. Am. Chem. Soc.* **2003**, *125*, 15411–15419.
- (30) MacFarlane, D. R.; Forsyth, M.; Izgorodina, E. I.; Abbott, A. P.; Annat, G.; Fraser, K. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4962–4967.
- (31) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2005**, *109*, 6103–6110.
- (32) Tokuda, H.; Ishii, K.; Susan, M. A. B. H.; Tsuzuki, S.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2006**, *110*, 2833–2839.
- (33) Deetlefs, M.; Hardacre, C.; Nieuwenhuyzen, M.; Pádua, A. A.; Sheppard, O.; Soper, A. K. *J. Phys. Chem. B* **2006**, *110*, 12055–12061.
- (34) Hardacre, C.; Holbrey, J. D.; Mullan, C. L.; Youngs, T. G. A.; Bowron, D. T. *J. Chem. Phys.* **2010**, *133*, 074510–074517.
- (35) Hardacre, C.; Holbrey, J. D.; Nieuwenhuyzen, M.; Youngs, T. G. A. *Acc. Chem. Res.* **2007**, *40*, 1146–1155.
- (36) Hardacre, C.; McMath, S. E. J.; Nieuwenhuyzen, M.; Bowron, D. T.; Soper, A. K. *J. Phys. C* **2003**, *15*, S159–S166.
- (37) Goldstein, M. *J. Chem. Phys.* **1969**, *51*, 3728–3739.
- (38) Dimitrov, V. I. *J. Non-Cryst. Solids* **2006**, *352*, 216–231.
- (39) Jiang, M.; Dai, L. *Phys. Rev. B* **2007**, *76*, 054204.
- (40) Debenedetti, P. G.; Stillinger, F. H. *Nature* **2001**, *410*, 259–267.
- (41) Angell, C. A. *Science* **1995**, *267*, 1924–1935.
- (42) Ozawa, R.; Hayashi, S.; Saha, S.; Kobayashi, A.; Hamaguchi, H. *Chem. Lett.* **2003**, *32*, 948.
- (43) Kutuniva, J.; Oilunkaniemi, R.; Laitinen, R. S.; Asikkala, J.; Kärkkäinen, J.; Lajunen, M. K. Z. *Naturforsch.* **2007**, *62b*, 868–870.
- (44) Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. *J. Chem. Eng. Data* **2004**, *49*, 954–964.
- (45) Kölle, P.; Dronskowski, R. *Eur. J. Inorg. Chem.* **2004**, *2004*, 2989–2989.