DISCUSSIONS

Ionic liquids at interfaces: general discussion

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Ruth Lynden-Bell, [ID] Doug MacFarlane, [ID] Florian Maier,
Markus Mezger, [ID] Agílio Pádua, Octavian D. Pavel, [ID] Susan Perkin,
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Betul Uralcan, William Wallace, Masayoshi Watanabe
and James Wishart [ID]

Seiji Tsuzuki opened the session with some general comments: I would like to comment on the interactions of ionic and non-polar species with conductor surfaces. The interactions of these species with conductor surfaces are somewhat different from interactions between molecules. I would like to explain the interactions with conductor surfaces by comparing the interactions between molecules. I would like to explain the origin of the attraction of induction and dispersion interactions between molecules. If a molecule has a permanent dipole or a charge, the electric field of the molecule polarizes the interacting molecule. The induced dipole is produced by the polarization. The attraction between the permanent dipole (or the charge) and the induced dipole is the induction interaction as shown in Fig. 1. Non-polar molecules sometimes have temporary dipoles owing to the motion of electrons. The electric field of the temporary dipole polarizes the interacting molecule. The attraction between the temporary dipole and the induced dipole is the dispersion interaction (Fig. 1). The induction energy of interacting molecules is approximately the sum of the polarization energy of atoms. Therefore, we can evaluate the induction energy sufficiently accurately from the magnitude of the electric field and atomic polarizability using the distributed polarization model developed by Anthony Stone.[1]

The primary source of the attraction between ionic species and conductor surfaces is the induction interaction, while the primary source of the attraction between non-polar species and conductor surfaces is dispersion interactions

Induction (polarization)   Dispersion

➡ Permanent dipole   ⇨ Temporary dipole
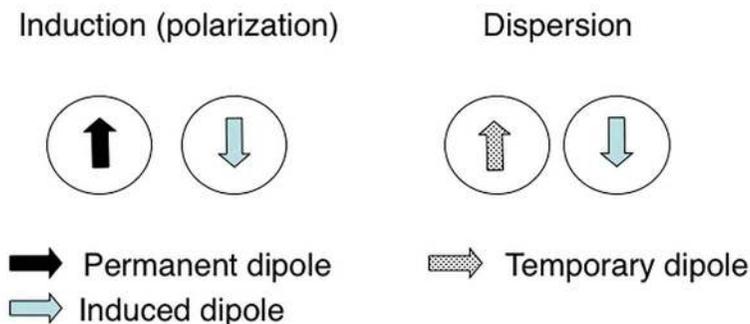⇨ Induced dipole

Fig. 1   Induction and dispersion interactions between molecules.

(Fig. 2). The mechanism of these interactions is somewhat different from the interactions between molecules.

When an ion comes close to a conductor surface, opposite sign charges gather in the surface near the ionic species to keep the electric potential of the conductor surface identical, as shown in Fig. 3. The charge is called a mirror charge. The coulombic interaction between ionic species and the mirror charge is the primary source of the attraction between ionic species and conductor surfaces. The charge-transfer from atom to atom occurs in the conductor. Owing to this reason, it will be difficult to evaluate the interaction between ionic species and mirror charges accurately using the distributed polarization model.

When a non-polar molecule near the conductor surface has a temporary dipole owing to the motion of electrons, an induced dipole is generated in the conductor (Fig. 3). The coulombic interaction between these two dipoles is the origin of the attraction between non-polar molecules and conductor surfaces. The electric field produced by ionic species is stronger than that produced by the temporary dipole of non-polar species. This shows that the attraction between ionic species and conductor surfaces is much stronger than that between non-polar species and
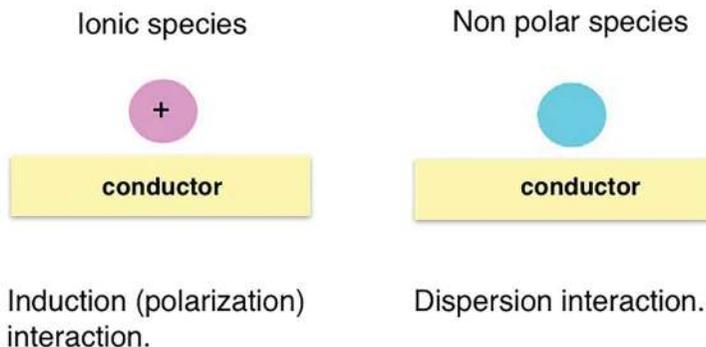
Major source of attraction

Ionic species   Non polar species

+

conductor   conductor

Induction (polarization)   Dispersion interaction.
interaction.

Fig. 2   Major source of attraction between ionic species and conductor surfaces and that between non-polar species and conductor surfaces.

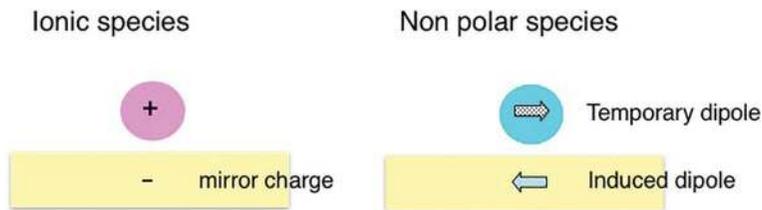Ionic species   Non polar species

Fig. 3 Origin of the induction interaction between ionic species and conductor surfaces and that of the dispersion interaction between non-polar species and conductor surfaces.

conductor surfaces. The interaction of ionic species with conductor surfaces (the interaction with mirror charges) is substantial, and therefore the interaction with mirror charges will play an important role in determining the distribution and orientation of ionic species near conductor surfaces. However, the interactions with mirror charges are not considered in most classical MD simulations of conductor surfaces. This shows that we have to take great care for the effects of the mirror charge interactions, if we use classical MD simulations for studying the distribution and orientation of ionic species near conductor surfaces.

1 A. J. Stone, *Mol. Phys.*, 1985, **56**, 1065–1082.

Agílio Pádua added: As I mentioned in my answer to your question in the session titled "Phase behaviour and thermodynamics" (DOI: c7fd90091k), the problem with the image-charge method is that it applies only to perfect, infinite flat surfaces. For simulation of realistic materials, with defects, curvature or roughness, it is necessary to use a representation of polarisation that can be put on an atomistic (site-site) framework.

Natalia Borisenko responded: We agree that induction interactions may play a role. The detailed aspects of theoretical MD calculations are beyond the scope of our paper (DOI: c7fd00165g).

Barbara Kirchner opened a general discussion of the paper by Susan Perkin: In the introduction of your talk you showed that nice example of mixing molecular liquids with ionic liquids. This mixture dissolves much more lithium salt than the pure ionic liquid. Do you know anything about the mobility of the lithium ions in these mixtures? Are they still mobile if you have a very saturated system?

Secondly, with regard to your simulations, can you give an estimate of how long the simulation box minimum has to be to be unaffected by the surfaces?

Susan Perkin replied: You refer to the example of the solubility of LiCl in water, which is approximately 14 M at room temperature, *i.e.* much higher than the molar concentration of pure ionic liquids without solvent (which are typically in the range of 3–6 M). The viscosity of LiCl aqueous solutions is very low, even close to the solubility limit, approximately one order of magnitude higher than pure water at the same temperature and pressure[1] and therefore substantially less viscous than pure ionic liquids. Nonetheless, conductivity of LiCl in water does go through a maximum and then decrease at the highest concentrations,[2] indicating

together that the mobility of ions decreases at the highest volume fractions. Regarding the box size: we checked that the box size is not altering the results, *i.e.* no interference between the two interfacial regions, by measuring the Poisson potential at different points and ensuring that it is flat in the centre.

1 I. M. Abdulagatov, A. B. Zeinalova and N. D. Azizov, *J. Mol. Liq.*, 2006, **126**, 75–88.
2 L. Varela, *Fluid Phase Equilib.*, 2010, **298**, 280–286.

Agílio Pádua opened a general discussion of the paper by Benjamin Cross: In your paper (DOI: c7fd00149e) you specify that the dynamic surface force measurements are performed at a frequency of 220 Hz. In a previous talk in this meeting by Dr Markus Mezger (DOI: c7fd00171a) we learned that a characteristic time of the order of 2 ms corresponds to cation and anion reorganisation at an electrode interface. Is there a link? How do your results depend on measurement frequency? Could this explain the thick boundary layer you observe in your measurements?

Benjamin Cross answered: The results of Dr Mezger show two characteristic times of reorganization of the ions at the electrode/ionic liquid interface. The short time you are talking about corresponds to a transverse reorganization of the ions which is an exchange of positive and negative ions close to the electrode. The motor of this exchange is the change of sign of the electric field at the vicinity of the electrode. In our case, the stresses are longitudinal and the transverse electric fields remain constant. It seems to me that we do not solicit the same processes, either electrically or geometrically.

Regarding the frequency dependency, I do not have enough elements to give a trend. However, over the frequency range on which we worked (5 Hz to 300 Hz), we measure a deviation on the hydrodynamic origin of the distances for the steady state and the oscillatory flows.

Agílio Pádua commented: Do you also observe a long-range tail in the interactions between charged surfaces across ionic liquids, as has been reported in the literature from several groups using surface-force apparatus?

Benjamin Cross responded: Indeed, we have elements on that. We have recently studied the influence of hydrodynamic interactions on force measurements, in particular on exponential interactions. We are finalizing our results before publishing them.

José Nuno Canongia Lopes returned to discussion of the paper by Susan Perkin: You said in your presentation that the surface charge density in the mica substrate during the experiments is estimated to be about $-20~\mu C$ sq cm^{-1} (about half the charge density of muscovite mica). This probably arises from the depletion of potassium ions at the surface. Do you use half of the potassium ions in the simulations? How do you model the mica surface?

Susan Perkin replied: Indeed this value of surface charge corresponds to roughly half the maximal charge on mica if all aluminosilicate sites were ionized, and potassium ions from the mica must be dispersed in the liquid. In the

experiments this corresponds to an entirely negligible concentration of potassium ions: in the region of 10^{14} ions are released from the mica which are then solvated in the ionic liquid and give rise to a potassium concentration of $\sim 10^{-6}$ M. It is therefore reasonable, we believe, to neglect these ions from the simulation which only contains a few hundred molecules in total. Perhaps you also refer to the lateral non-uniformity of charge on the mica surface once some potassium ions are removed. This we did not include in the simulations, and it may be interesting to consider in future the effect on the non-uniformity of surface charge.

José Nuno Canongia Lopes said: Considering that your assumption about the surface charge density is correct and part of the potassium ions are washed away, I think the remaining ones will be at very localized positions. Simulations with an average charge distribution will necessarily lose such information at a molecular level.

Susan Perkin responded: Thank you, this is a useful comment and in future it would be interesting to look into the effect of the lateral non-uniformity of surface charge. Indeed this was neglected in the current simulations but is probably present in experiments. The lateral distance between charges introduces an extra length scale into the system which must be considered when deciding what determines the wavelength and decay of surface forces (and relates to my response to Dr Mezger later in this section).

Mark Rutland asked: The surface charge is estimated from matching the long range electrostatic force measured between mica surfaces with that measured between template stripped gold surfaces. As you state, the surface charge cannot be obtained from fitting the long range force to Poisson–Boltzmann theory as in aqueous systems. The long range force appears for some compositions and not others. While you do not explicitly address this force in this paper, can you comment on the reasons for its appearance in some cases and not in others?

Susan Perkin answered: I think you refer to Fig. 1B and C in the paper (DOI: c7fd00168a) where it appears that a longer decaying component is measured in the case of 0.01 M (B), which is perhaps not so apparent in the 2.5 M case (C). It then appears again in Fig. 2 (a pure ionic liquid). We have studied the concentration dependence of the decay length and magnitude of this long range force in the past.[1,2] The magnitude and decay, i.e. B and λ_s in our eqn (1), both vary with concentration. The magnitude is also strongly solvent dependent, perhaps we can think of it as alteration of the effective surface charge outside of the structured region which induces the pressure variation as the surfaces are brought together.

1 A. M. Smith, A. A. Lee and S. Perkin, *J. Phys. Chem. Lett.*, 2016, **7**, 2157–2163.
2 A. A. Lee, C. Perez-Martinez, A. M. Smith and S. Perkin, *Phys. Rev. Lett.*, 2017, **119**, 026002.

Mark Rutland continued: Following from the previous question, since the magnitude of the long range force depends on the surface charge, or at least on the arrangement of the ions on the surface in some way, it should be possible to

change the surface potential and observe changes in this long range force. Could this have implications for our understanding of this force in ionic liquid systems?

Susan Perkin answered: Yes, I absolutely agree, and we plan to do these experiments. I do not like the asymmetric setup of mica–gold for this (as used in the surface charge experiment reported here), though, so for the most clear interpretation we will need a symmetric polarizable experiment to test the surface potential dependence in the way that you propose.

Betul Uralcan addressed Susan Perkin: This is very exciting work. I was curious if you have considered applying a constant potential to the electrodes as opposed to constant charge?

Susan Perkin responded: Thank you. Indeed we are also studying similar electrode–electrolyte interfaces using constant potential boundary conditions instead of constant charge as is used in this work and we will report the results of that in the future. However in this project we aimed for the most direct comparison between simulation and our experiments using mica sheets. Charge regulation takes place when mica surfaces approach across aqueous electrolytes and so the reality lies somewhere between the two extremes, but the fixed charge condition seemed closest to reality in this case.

Betul Uralcan asked Samuel Coles in relation to the paper by Susan Perkin: Could you elaborate on the electrode model that you used? Is the constant electrode charge uniformly distributed on the electrode surface, or does it have a Gaussian distribution?

Samuel Coles replied: First I will address the choice of electrode model, which was also previously discussed by Seiji Tsuzuki. It is indeed well known that the choice of electrode model has an effect on ionic liquid nanostructure at conductive materials.[1,2] In this case the aim of the work discussed is actually to model a general dielectric. To maintain backward compatibility with previous work the dielectric used has the form of graphene. However the intention of this work is not to model graphene. Specifically referring to the point made by Betul Uralcan, we do intend to expand this work to look at conductive surfaces at some point in the future. Further to this, Betul's excellent previous work looking at the charge correlation length of these liquids at electrodes with a potential difference of zero definitely has relevance to this work.[3] However, it must be viewed in conjunction with the previous work of Vatamanu et al.,[4] and Merlet et al.,[5] which show the presence of an oscillatory structure for solutions of ionic liquid in acetonitrile at fixed potential electrodes at higher potentials. It is in fact possible that the work of Vatamanu et al. shows the same oscillatory to monotonic transition,[4] which is the focus of this paper.

1 C. Merlet, C. Péan, B. Rotenberg, P. A. Madden, P. Simon and M. Salanne, *J. Phys. Chem. Lett.*, 2013, **4**, 264–268.
2 K. Breitsprecher, K. Szuttor and C. Holm, *J. Phys. Chem. C*, 2015, **119**, 22445–22451.
3 B. Uralcan, I. A. Aksay, P. G. Debenedetti and D. T. Limmer, *J. Phys. Chem. Lett.*, 2016, **7**, 2333–2338.

4 J. Vatamanu, M. Vatamanu, O. Borodin and D. Bedrov, *J. Phys.: Condens. Matter*, 2016, **28**, 464002.
5 C. Merlet, M. Salanne, B. Rotenberg and P. A. Madden, *Electrochim. Acta*, 2013, **101**, 262–271.

Kazuhisa Tamura opened a general discussion of the paper by Natalia Borisenko: In this paper, the pretreatment of the Au(111) electrode is not described. This information is highly important for electrochemists. Can you explain it?

Natalia Borisenko responded: Au(111) substrates were purchased from Agilent Technologies. The supplier suggests to use the substrates as received. In our previous measurements we have performed various treatments of Au(111) substrates (*e.g.* flame annealing, thermal annealing under vacuum, *etc.*). However, we have not observed any difference in our results after such pretreatments. Therefore, in this study the Au(111) substrates were used without any pretreatment.

Kazuhisa Tamura commented: The STM images shown in Fig. 1b in your paper (DOI: c7fd00165g) are similar to images published in Fig. 4 in a *Journal of Physical Chemistry B* paper (Fig. 4).[1] In that paper, the IL was [BMP]TFSA. As far as I can see, the observed structure is not the Au(111) surface, but the adsorbed IL molecules.[2] In this potential region, the Au surface is stable. I would like to know the details of the behavior of the absorbed IL molecules in this potential region and why these two IL molecules show the same behavior?

1 N. Borisenko, S. Zein El Abedin and F. Endres, *J. Phys. Chem. B*, 2006, **110**, 6250–6256.
2 K. Tamura, S. Miyaguchi, K. Sakaue, Y. Nishihata and J. Mizuki, *Electrochem. Commun.*, 2011, **13**, 411–413.

Natalia Borisenko answered: The behavior of these ILs is similar only in some potential regimes, but it is not the same for the whole potential regime.[1–3] Furthermore, the addition of TaF_5 significantly alters the IL/solid interface and this influence is different for $[Py_{1,4}]$TFSA and for $[Py_{1,4}]$FAP.[4] These two ionic liquids ($[Py_{1,4}]$TFSA—another abbreviation is [BMP]TFSA—and $[Py_{1,4}]$FAP) contain the same cation $[Py_{1,4}]^+$. At −0.2 V (open circuit potential, ocp) a rough gold surface with a "wormlike" structure is obtained for pure $[Py_{1,4}]$TFSA and for $[Py_{1,4}]$FAP containing TaF_5. The depth of these defects at the surface is 250 pm. *In situ* AFM results showed that at the ocp a strong adsorption of the $[Py_{1,4}]^+$ occurs,[5] which facilitates the gold reconstruction leading to a wormlike pattern. Furthermore, by reducing the electrode potential the $[Py_{1,4}]^+$ adopts an orientation more parallel to the surface that induces the "herringbone" reconstruction of the gold surface both in the case of $[Py_{1,4}]$TFSA,[1] and in the case of $[Py_{1,4}]$FAP.[3] Therefore, such a similarity can be due to the presence of the $[Py_{1,4}]^+$ cation and its specific orientation on the gold surface.

1 N. Borisenko, S. Zein El Abedin and F. Endres, *J. Phys. Chem. B*, 2006, **110**, 6250–6256.
2 F. Endres, S. Zein El Abedin and N. Borisenko, *Z. Phys. Chem.*, 2006, **220**, 1377–1394.
3 R. Atkin, N. Borisenko, M. Drüschler, S. Zein El Abedin, F. Endres, R. Hayes, B. Huber and B. Roling, *Phys. Chem. Chem. Phys.*, 2011, **13**, 6849–6857.
4 T. Carstens, A. Ispas, N. Borisenko, R. Atkin, A. Bund and F. Endres, *Electrochim. Acta*, 2016, **197**, 374–387.

5 R. Atkin, S. Zein El Abedin, R. Hayes, L. H. S. Gasparotto, N. Borisenko and F. Endres, *J. Phys. Chem. C*, 2009, **113**, 13266–13272.

José Nuno Canongia Lopes stated: This is a general comment for all speakers: when people place ILs near charged surfaces they tend to forget that in most cases the charges are not distributed equally across the molecular ions. Alkyl side chains are often present and can be quite long. Bistriflamide has two tri-fluoromethyl extremities with relatively low overall charge densities. When I see a cartoon full of charged spheres sitting at a charged surface something is missing. The nature of ILs is missing.

Susan Perkin answered: I agree that this is a very important consideration in respect of many aspects of the IL–solid interface. However I would like to respond with the reasoning behind the cartoons with spherical ions in our current paper. In this manuscript we are discussing the charge ordering in the direction perpendicular to the solid–liquid interface, and its connection to long-range surface forces observed in similar ionic liquids and electrolytes. We have shown in several recent papers that the experimentally-determined features of this structure and electrostatic interactions are common (in their scaling with ion size, concentration, dielectric constant *etc.*) for all electrolytes and ionic liquids studied, irrespective of the structural features of the ions.[1–3] Most definitively, the same scaling is seen for NaCl in water. This is important because it implies that the nanostructure in ionic liquids arising from alkyl chain aggregation *etc.* is not responsible for the observations we report in these articles. Because of this, we choose to use very simple cartoons of the ions and interface, in order that no inferences are made or drawn about the position or involvement of molecular structure or polarity from those schematic diagrams. In other work, where we report features which are clearly determined or dependent on the molecular structure and liquid nanostructure, we choose to use more nuanced cartoons.[4–5]

1 A. M. Smith, A. A. Lee and S. Perkin, *J. Phys. Chem. Lett.*, 2016, **7**, 2157–2163.
2 A. A. Lee, C. Perez-Martinez, A. M. Smith and S. Perkin, *Faraday Discuss.*, 2017, **119**, 239–259.
3 A. A. Lee, C. Perez-Martinez, A. M. Smith and S. Perkin, *Phys. Rev. Lett.*, 2017, **119**, 026002.
4 A. M. Smith, M. A. Parkes and S. Perkin, *J. Phys. Chem. Lett.*, 2014, **5**, 4032–4037.
5 A. M. Smith, K. R. J. Lovelock, N. N. Gosvami, P. Licence, A. Dolan, T. Welton and S. Perkin, *J. Phys. Chem. Lett.*, 2013, **4**, 378–382.

José Nuno Canongia Lopes continued discussion of the paper by Natalia Borisenko: This is potentially a very interesting way to control the deposition of metal at a surface that is modified by the presence of an IL. The experiments were performed with ILs containing C_4 side chains. What would be the morphological implications if you considered longer chains?

Natalia Borisenko replied: This is an interesting question. We have to expect a type of a templating effect induced by longer alkyl chains.

Markus Mezger returned to discussion of the paper by Susan Perkin: Fig. 4 in your manuscript shows that the crossover between the regimes where the decay is monotonous *vs.* oscillatory does not only depend on the IL concentration x but also on the surface charge σ.

Can you observe this transition with respect to surface charge/potential in your SFA experiments using the described template striped gold surfaces? Over which range can the surface charge be varied in this setup?

In the simulations shown in Fig. 3 in your manuscript, panel $x_{IL} = 50\%$, one observes a monotonous decay for σ of approximately $-30 \ \mu\text{C cm}^{-2}$. However, an inverted oscillatory decay, *i.e.* with opposite phase, is regained for even lower charges around 35 $\mu\text{C cm}^{-2}$. Could it be that for high IL concentrations, monotonous decays are only found for singular values of the surface charge, *e.g.* for values equivalent to an integer number of a cation or anion monolayers, whereas the generic oscillatory behaviour is obtained otherwise.

Susan Perkin responded: In theory we would indeed expect to see the crossover between oscillatory to monotonic decay in the surface force balance (SFB) experiment if we used a gold surface and varied its surface charge. However in practice we find it is not possible to detect any oscillatory forces with gold surfaces due to the nanoscale roughness of the template-stripped amorphous gold (despite it being only a few Angstrom rms roughness over the surface) so we are unlikely to be able to probe the transition with the gold surfaces. Now turning to your question about singular values of surface charge which appear to separate regions of oscillatory decay with opposite phase. This seems to me a really interesting point and we have not looked into its generality in the simulations, even though you are quite correct that it is apparent in the data. I think we could relate those singularities to the kappa = 1 scenario as in Kirchner *et al.*,[1] however the presence of solvent in our case allows an extra dimension to the phase diagram and clearly the surface charge at which this single screening monolayer forms varies with volume fraction of the solvent.

1 K. Kirchner, T. Kirchner, V. Ivaništšev and M. V. Fedorov, *Electrochim. Acta*, 2013, **110**, 762–771.

Andrew Abbott returned to discussion of the paper by Natalia Borisenko: In Fig. 1 in your manuscript the response C_1 in the CVs looks typical of under-potential deposition (UPD). Have you investigated whether this is UPD? Fig. 1(b) has a different current density to the other CVs. Do you also see UPD for the other metals that you studied?

Natalia Borisenko answered: This might be a possible explanation, which, however, will need more STM experiments to exclude any speculation.

Andrew Abbott continued: If you stop the potential scan before C_2 and reverse the direction of the scan is C_2 reversible, and if not, does this give you more information about what C_1 is?

Natalia Borisenko replied: We agree with the comment, however, we have not carried out CVs at various switching potentials and at various scan rates to find more about the processes C_1 and C_2.

Millicent Firestone inquired: Under the experimental conditions that generate multilayer structures do you observe any lateral organization? Have you carried

out any GISAXS (grazing incidence small angle X-ray scattering) studies to probe more fully the supported structure?

Natalia Borisenko replied: No, the GISAXS studies have not been performed for the studied systems. Unfortunately, these measurements cannot be performed at the chair. We would be very thankful for collaboration.

Markus Mezger added: For grazing incidence scattering experiments focusing on the lateral structure of anions and cations adjacent to electrodes, the refractive index $n = 1 - \delta$ of the solid substrate should be larger than the one of the liquid. Otherwise, the incident beam will penetrate into the bulk liquid, generating a bulk scattering signal that typically is much more intense than the interface signal originating from the lateral ion arrangement. Indeed, for solid/liquid metal interfaces, the in-plane structure of liquids adjacent to interfaces has been successfully studied by X-ray scattering.[1,2]

For neutrons, in ILs this contrast condition might be achieved by isotope exchange. However, their low flux compared to X-rays might make many experiments very challenging if not impossible.

To my knowledge, for hard X-rays there is no suitable (atomically smooth, flat, conductive, inert.) electrode material that could fulfil the condition described above, at least for the commonly used pure ILs. However, one possible exception I could think of might be electrolytes containing high concentrations of heavy metal ions. What is the highest metal salt concentration that could be used in your experiments to increase the electron density of the liquid?

1 H. Reichert, O. Klein, H. Dosch, M. Denk, V. Honkimäki, T. Lippmann and G. Reiter, *Nature*, 2000, **408**, 839–841.
2 W. J. Huisman, J. F. Peters, J. W. Derks and H. G. Ficke, *Rev. Sci. Instrum.*, 1997, **68**, 4169.

Jeffrey Everts continued discussion of the paper by Susan Perkin: In the charge-ordered regime of your simulations you find that the wavelength of the oscillations in the force between two mica sheets is the same as the size of an ion pair. To what extent can you say that Bjerrum pairs are formed due to structural correlations?

Susan Perkin responded: The wavelength is a ++ or −− correlation length in the z-direction, *i.e.* it can be considered as the length of a pair of ions, but I do not think it is useful to consider these as Bjerrum pairs. Firstly, this wavelength (probably) only corresponds to the structure in the z-direction (out of plane direction). Secondly, it is only an average structure, measured as an equilibrium force law and connected to the potential of mean force between the plates, so we are making no statement about timescales of rearrangement.

Jeffrey Everts said: Did you see any indication of Bjerrum pair formation in the charge monotonic regime or in the bulk of all simulations? In other words, do you expect that Bjerrum pair formation plays an important role in understanding the properties of concentrated electrolytes (such as the "anomalous" screening length dependence on salt concentration)?

Susan Perkin responded: This is an interesting question. Bjerrum pairs of course form in solvents of low dielectric constant and when the total salt concentration is moderate or high (so that the mean inter-ion distance is below the Bjerrum length). This is also sure to impact the measured screening length in those systems, even causing an inflation of the screening length as was shown in theory by Zwanikken and van Roij.[1] However it is clear from that work that it is not sufficient to describe the much larger "anomalous" increasing in screening length in concentrated electrolytes as was reported from experiments recently that you refer to.[2] The intricacy of the question is most apparent if we consider the extreme of salt concentration, *i.e.* the pure ionic liquid. In this case the measured screening length is long, typically 6–9 nm. Analysis of the expected ion-pair formation in pure ionic liquids showed that the majority of ions are free, with only about one third "tied up" in pairs at any time.[3] This precludes a Bjerrum-particle explanation for the long screening length. However, the definition of an ion pair in a pure ionic liquid is not obvious: all ions are surrounded by other ions which could at some instant be defined as their partner, and to be considered as a pair the ions should reside together for some time significantly longer than their diffusion timescale. Nonetheless, the concept of balancing ion–ion Coulomb attraction with their thermal energy is important and the Bjerrum length itself must play a crucial role in determining the length scales for inter-actions in concentrated electrolytes (in which case the Debye length is irrelevant). Recently we showed that the screening length in concentrated electrolytes actually scales linearly with the Bjerrum length for all 1 : 1 salts and solvents studied.[4] But to answer your most immediate question about pairs in the simulation: we did not look for them; perhaps we will do that, and thank you for the suggestion. However we do not really expect to see any signatures of the long range screening in such a small simulation.

1 J. Zwanikken and R. van Roij, *J. Phys.: Condens. Matter*, 2009, **21**, 424102.
2 A. M. Smith, A. A. Lee and S. Perkin, *J. Phys. Chem. Lett.*, 2016, **7**, 2157–2163.
3 A. A. Lee, D. Vella, S. Perkin and A. Goriely, *J. Phys. Chem. Lett.*, 2015, **6**, 159–163.
4 A. A. Lee, C. Perez-Martinez, A. M. Smith and S. Perkin, *Faraday Discuss.*, 2017, **119**, 239–259.

Mark Rutland returned to discussion of the paper by Benjamin Cross: You observe a thicker surface film on conducting surfaces than on the dielectric. At a recent Faraday Discussion (Chemical Physics of Electroactive Materials), Lydéric Bocquet and Jean Comtet presented work on capillary freezing of IL confined between conductors due to the Gibbs–Thomson effect.[1] Could your observation be related to this? If not can you speculate as to why you do not see such behaviour?

1 V. Kaiser, J. Comtet, A. Niguès, A. Siria, B. Coasne and L. Bocquet, *Faraday Discuss.*, 2017, **199**, 129–158.

Benjamin Cross responded: The effects reported by the group of Lydéric Bocquet in *Nature Materials*[1] and in a recent *Faraday Discussions* manuscript[2] show that, under confinement, ionic liquids could solidify due to surface effects (Gibbs–Thomson). This effect underlies a decrease in the interfacial energy of a solid phase of ionic liquids close to a surface of high conductivity. Our experiments do not allow to conclude a capillary freeing since the thickness of the

interfacial layers does not depend on the confinement. Nevertheless, there is a common tendency in our two experiments: in our case, the thickness of the interfacial layers increases with the conductivity of the confinement surfaces and in the case of the Bocquet group, the distance from which the capillary freezing occurs also increases with the conductivity of the surfaces. This common trend shows an interesting direction to explore. I think that beyond these common tendencies there are differences to be understood. The two experiments are done with different probe sizes (millimeters in our case and micrometers in the case of the Bocquet group). The size of the probe gives the length scale probed in the experiment. The length scale of the system could also play a role, particularly in the kinetics of capillary freezing as shown in the capillary condensation of a confined vapor.[3]

1 J. Comtet, A. Niguès, V. Kaiser, B. Coasne, L. Bocquet and A. Siria, *Nat. Mater.*, 2017, **16**, 634–639.
2 V. Kaiser, J. Comtet, A. Niguès, A. Siria, B. Coasne and L. Bocquet, *Faraday Discuss.*, 2017, **199**, 129–158.
3 M. M. Kohonen, N. Maeda, and H. K. Christenson, *Phys. Rev. Lett.*, 1999, **82**, 4667.

Mark Rutland said: (Supplementary to the previous question) Would you not agree that the geometry of your system and the rates used would *a priori* appear to be more favourable for such a transition?

Benjamin Cross answered: The confinement geometry of our system and the one used by the Bocquet group are the same: a sphere and a plane to create a confinement geometry. The main experimental differences are the rate of the oscillatory motion and the size of the probe. Our two groups use the linear response of the system to probe the hydrodynamic interactions at different frequencies (hundreds of Hz for us and a few tens of kHz for the Bocquet group). Since the system is in a linear regime, the average probing motion is zero over a period and we do not expect any influences of the oscillatory motion in general, and its rate in particular, on the static properties discussed here. On the other hand, the probe size and the length scale probed could be a relevant parameter to the kinetics of capillary freezing.

Natalia Borisenko answered: It depends on the solubility limit of the salts in the employed ILs that we have not investigated. The highest concentrations of the salts used in our studies in the ILs are 0.3 M for $GaCl_3$ in both $[Py_{1,4}]TFSA$ and $[Py_{1,4}]TfO$, 0.5 M for TaF_5 in $[Py_{1,4}]TFSA$ and 0.1 M for TaF_5 in $[Py_{1,4}]FAP$, and 0.25 M for $SiCl_4$ in $[Py_{1,4}]FAP$.

Markus Mezger continued: Experiments at solid/liquid interfaces usually tend to be challenging and time consuming. To map out the extensive matrix built from the large variety of possible concentrations, precursors, anions, and cations, bulk measurements might be helpful. For many cases, there are correlations between the structures observed in the bulk liquid and near solid/liquid interfaces (see S. Perkin *et al.* (DOI: c7fd00168a), ref. 1, and references therein). Are you aware of bulk simulations, scattering experiments, or other bulk measurements relevant to the studied systems? If any exist, do they provide hints to understand the large structural variety near electrodes observed in your work?

1 M. Mezger, R. Roth, H. Schröder, P. Reichert, D. Pontoni and H. Reichert, *J. Chem. Phys.*, 2015, **142**, 164707.

Natalia Borisenko responded: The bulk liquid structure can indeed be correlated with the interfacial structure and can provide some useful information to relate the bulk structure (variation of the bulk structure upon varying the ionic combinations of ILs, precursors and their concentration, *etc.*) with the interfacial structure. Unfortunately, such studies were not available for our systems.

Susan Perkin added: The relation between bulk correlations and surface forces has been considered in detail by Evans and colleagues in the 1990s,[1] and your own work illustrates the matter nicely. In essence, the asymptotic decay of the surface force should have parameters (wavelength and decay) arising from the bulk structure. However the near-surface structure and structural forces we probe here are not the asymptotic behavior (there is a longer range force), so the link is not as direct as we'd like, and we do not propose that our observed wavelength switch corresponds to the Q→N transition predicted by Evans. We have discussed this briefly in a recent article reporting the structural forces in these mixtures.[2] The question then turns to whether the asymptotic force, which in many cases is the longer range electrostatic force,[3] can be compared to bulk measurements or simulations. This should be possible but is difficult due to the requirements for large box size (for simulations) and small angle (scattering experiments) amongst other challenges and this has not yet been achieved with systems of comparable chemistry as far as I am aware.

1 R. J. F. Leote de Carvalho and R. Evans, *Mol. Phys.*, 1994, **83**, 619–654.
2 A. M. Smith, A. A. Lee and S. Perkin, *Phys. Rev. Lett.*, 2017, **118**, 096002.
3 A. A. Lee, C. Perez-Martinez, A. M. Smith and S. Perkin, *Phys. Rev. Lett.*, 2017, **119**, 026002.

Sichao Li continued discussion of the paper by Susan Perkin:

Q1: There are some small peaks in the CV curve (at around −1.0 V and +0.6 V respectively) of Fig. 2 in your manuscript. Are they involving some electrochemical reactions of ionic liquids or electrochemical deposition on the electrode? Have you considered the stable electrochemical window (EW) for your systems, pure ILs and ILs with propylene carbonate (PC)?

Q2: You have used several different electrodes: platinum quasi-reference electrodes, gold electrodes, and graphene electrodes for simulation. Is the fixed charge density the same for the different electrodes you used?

Q3: Did you try to select some positive values of the surface charge density in Fig. 3 in your manuscript to analyse whether it is the same arrangement of ions and PC?

Q4: What is the reason for the arrangement for "strong solvent layering which appears substantially dominant over the ion layering" for small IL concentration?

Susan Perkin answered: Our aim was to use the same fixed surface charge in the experiments and simulations. This is why we made an estimate of the surface charge on mica in the experiment (the use of gold was simply to provide a tunable surface charge in order to probe the charge of the mica), and arrived at −20 μC cm^{-2}. This was used as the fixed charge on the surfaces in the simulation. The simulation surfaces are not really intended to be a model for graphene, they are

simply a hexagonal lattice of atoms (with lattice parameters similar to that of graphene) holding fixed charge for the purposes of the simulation. Fig. 3 also shows positive surface charge, as seen on the left axes. The colour scale indicates the cation and anion excess. We also took cross sections and inspected the ion and solvent positions, which are essentially similar in trend for anodic and cathodic surface charges. The details are slightly different because of the asymmetry of the cation and anion in the liquid. When the volume fraction of ions is very small, their positions become less correlated (in particular when their thermal energy exceeds the Coulomb interaction between neighbours) and there is also more "freedom" to adopt Boltzmann-distributed local densities because solvent can act to fill the space. Then we expect, in the limit of low ion concentration, simple Debye–Hückel screening of the surface by the ions. The remaining space is filled by solvent molecules, and the templating effect of the surface causes them to occupy layers near the surface for several solvent-diameters distance. Since the ion layering has disappeared and solvent layering emerges, it becomes dominant in terms of the structure at the surface (as also measured in the SFB force measurement at low salt concentration).

Sichao Li remarked: I have done some similar experiments of ILs with PC. In Fig. 3 in the region with a smaller concentration of ILs, is the reason for the arrangement of dominant PC solvent layering because of the high dipole-moment of PC? As the PC is dipolar, is there a different participation/arrangement of ions for the positive charge density in Fig. 3?

Susan Perkin replied: We have studied the orientation of the PC dipole and its influence on the surface screening, and a fuller account can be found in the DPhil thesis of S. Coles.[1] For example, the integrated charge density away from the surface reveals aspects of how the PC dipole plays a substantial role in modifying the charge screening. Details of the structure at the positive electrode and the orientation of ions and solvent can be found in the thesis.[1]

1 S. Coles, DPhil thesis, University of Oxford, 2017.

Sichao Li asked: Since propylene carbonate (PC) is dipolar with a higher dipole moment, is there a difference in solvent layering arrangement with positive and negative charge density?

Susan Perkin replied: Qualitatively the behavior is the same at positive and negative surface charges, with small differences arising from the asymmetry of the PC and the asymmetry of the ions of the ionic liquid. The latter is more important; see also my comment to your previous question.

Vladislav Ivaništšev suggested: It might be a good idea to share the MD trajectories with the community for advanced analysis or additional simulations.

Susan Perkin answered: Thank you for this excellent suggestion, we will be happy to make the MD trajectories openly available. Colleagues interested in receiving the data are invited to correspond with us directly.

Leigh Aldous returned to discussion of the paper by Natalia Borisenko: As a comment, you observed a dramatic change at your interface after adding $SiCl_4$, which you attributed to the accumulation of $SiCl_4$ at the interface, which changed the force profile. But that requires a neutral species to accumulate at the charged electrode surface. So instead you may want to consider that the small amount of solute could be significantly changing the physicochemical properties of the ionic liquid, maybe even "lubricating" the movement of the ions.[1] So as a question, have you measured any bulk properties after adding your solutes, such as viscosity or diffusion coefficients?

1 Y. Meng, L. Aldous and R. Compton, *J. Phys. Chem. C*, 2011, **115**, 14334–14340.

Natalia Borisenko answered: We observe that increasing the concentration of $SiCl_4$ in ILs can change the nanostructure of the electrode/electrolyte interface (EEI). We would like to refrain from speculating that the neutral species of $SiCl_4$ can accumulate at the interface upon raising the concentration in the ILs. Furthermore, we have mentioned that $SiCl_4$–IL species can be present at the interface. Addition of solutes indeed changes the liquid structure and its transport behaviour.

We have not measured the transport properties of salts dissolved in ILs (*e.g.* viscosity and diffusion coefficients). We agree that these measurements might provide more information.

Simon Halstead communicated in relation to the paper by Susan Perkin: In the MD simulations in the manuscript (DOI: c7fd00168a) the relative permittivity was set to 1.6 to allow for polarisability. Could you explain/give a reference for this specific value? Also, is this value only for the ionic liquids you were investigating or a generic value?

Vladislav Ivaništšev communicated in reply: The permittivity is used to scale down the ionic charges by $\sqrt{(1/\varepsilon)}$.[1] The value of 1.6 corresponds to the scaling factor of 0.8. This is a typical value (± 0.1) commonly obtained in DFT calculations for charges from electrostatic potentials. For example, see our results for a set of 48 ionic liquids.[2] In molecular dynamics the use of polarizable force fields is preferred, yet the scaling is commonly used, especially when the focus is on the structure. For example, in coarse-grained and fully atomistic simulations of the interfacial structure in ionic liquids.[3,4]

1 C. Schröder, *Phys. Chem. Chem. Phys.*, 2012, **14**, 3089–3102.
2 K. Karu, A. Ruzanov, H. Ers, V. Ivaništšev, I. Lage-Estebanez and J. M. García de la Vega, *Computation*, 2016, **4**, 25.
3 K. Kirchner, T. Kirchner, V. Ivaništšev and M. V. Fedorov, *Electrochim. Acta*, 2013, **110**, 762–771.
4 V. Ivaništšev, S. O'Connor and M. V. Fedorov, *Electrochem. Commun.*, 2014, **48**, 61–64.

Millicent Firestone communicated in reply: By default, the effective fragment potential (EFP) method includes a polarization dampening factor of 0.6.[1] This factor is only applied to the polarization term and is included to facilitate convergence of the self-consistent procedure. The only attenuation factor applied to the static (full integer) charges is a very short range screening term due to the breakdown of the multipole expansion at short ranges. In this way we feel our

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simulations are consistent with the results of Schröder.[2] Additionally, the polarizabilities of only the SCN$^-$ ion are scaled by a factor of 0.65. This was done out of practical necessity, as without this scale factor the self-consistent polarization calculation would not converge.

1 I. Kaliman and L. Slipchenko, *J. Comp. Chem.*, 2013, **34**, 2284–2292.
2 C. Schröder, *Phys. Chem. Chem. Phys.*, 2012, **14**, 3089–3102.

Barbara Kirchner opened a general discussion of the paper by Toshiyuki Itoh: This is a very nice study, because with your varying functionalization you vary the speciation (how the ions interplay) and you introduce a kind of molecular liquid side to the ionic liquid. I'd like to ask you to speculate, on adding a lithium salt—the lithium ions usually coordinate to the anions—what would happen? Are the cations more occupied by the anions and allow the lithium ions to move faster as they are not coordinated, or *vice versa*? Could your electrolyte be working well, because the electrolyte leaves the lithium ions unbound? And what would you expect from nitrile-functionalized ILs?

Toshiyuki Itoh responded: Thank you for your question. It is well known that the coordination ability of both the FSA anion and TFSA anion is not strong. Therefore, we believe that Li ions can smoothly move in liquid electrolytes. However, unfortunately, we have not yet conducted a detailed investigation about this point. I offer my deep appreciation of your helpful comments. As you mentioned, the nitrile functional IL may work as a good electrolyte because the nitrile can coordinate to the lithium ion, but the nitrile group is generally not tolerable to a high voltage like the lithium ion battery. It is known that the dicyanide ion (DCA) ILs generally show low viscosity, for example, [bmim][DCA] shows 33.0 mPa s at 25 °C, which is lower than that of [bmim][Tf$_2$N](49.6 mPa s), see the ESI of ref. 1. However, there is no example of using the DCA salt IL as an electrolyte of Li ion batteries.

1 A. Harada, H. Yamaoka, S. Tojo, K. Watanabe, A. Sakaguchi, K. Kinoshita, S. Kishida, Y. Fukaya, K. Matsumoto, R. Hagiwara, H. Sakaguchi, T. Nokami and T. Itoh, *J. Mater. Chem. C*, 2016, **4**, 7215–7222.

Matthieu Gras commented: How did you define the electrochemical window of your ionic liquids? Don't you think that giving a maximum value in current density instead of giving the current would help scientists to have reproducible results?

Toshiyuki Itoh replied: Thank you for your question. Since many people use the electrochemical window of ILs for evaluation of an IL as an electrolyte, we investigated this property of our ILs. Linear sweep voltammetry (LSV) of neat ILs is the most convenient method to estimate the electrochemical window of the ILs. Therefore, the electrochemical analyses were performed at 298 K using a glassy carbon electrode as the working electrode, platinum wire as the counter electrode, and the Ag/AgNO$_3$ reference electrode. The scan rate was 50 mV s^{-1} and the redox potentials at which a 100 μA redox current was observed were defined as the threshold value of the electrochemical windows of the ILs. The reduction potentials E_{red} in the electrochemical windows were not significantly changed

among these ILs. On the contrary, the oxidation potentials E_{ox} in the electro-chemical windows depended on the structures of the ILs. For the details, see the ESI of our paper (DOI: c7fd00142h).

As you mentioned, the maximum current density value might be useful for the accurate evaluation of the ILs. However, LSV is easier to perform compared to the impedance analysis. We measured the conductivity of all the ILs (see Fig. 3 in our paper). Since the conductivities of the ILs are not high, the overall properties of the ILs as an electrolyte are significantly dependent on the current. Therefore, the electrochemical window has been used as an indicator of the electrochemical properties of the ILs.

William Wallace opened the discussion of the paper by Octavian D. Pavel: In your paper (DOI: c7fd00159b) you mentioned that there was no leaching of the metal, do you see any leaching of the ionic liquid in your final products?

Octavian D. Pavel replied: No leaching of the IL was found on analysis of the liquid samples *via* NMR.

William Wallace continued: The process you use is a batch process. Have you tried this with a flow process, and how would this change with the ionic liquid?

Octavian D. Pavel answered: The reactions were only examined under batch conditions, however, examination of a flow process would be of significant interest. This is the next step in our research and will provide important information on deactivation of the catalyst as well as the potential to develop a continuous oxidation process. The IL will potentially have an effect on the catalysis under flow conditions, in particular, the strength of the interaction with the surface of the catalyst and its solubility in the reaction solvent will determine the extent of IL leaching.

Christopher Hardacre opened the discussion of the paper by Robert G. Jones: When you co-adsorbed the SO_2 with the ionic liquid, was there any evidence of reaction of SO_2 with residual water forming acid?

Robert Jones responded: The experiments were carried out at 90 K so there is the possibility that water from the background vapour may have condensed onto the surface along with the ionic liquid and SO_2. However, due to the exposed tank of liquid nitrogen used to provide cryo-pumping for the line of sight mass spec-trometer, the vacuum chamber pumping speed for residual water was particularly high, so the partial pressure of water was in the low 10^{-10} mbar region. As the temperature programmed desorption (TPD) experiments commenced as soon as the coadsorbed surface of IL and SO_2 had formed (tens of minutes), the small pressure of water relative to that of the other components means a relatively small proportion (<1%) of water can have adsorbed in that time. If a reaction or inter-action had occurred between the adsorbed water and SO_2, we would have ex-pected to see some feature in the $m/z = 64$ (SO_2^+) TPD scan due to a cracking fragment of the reaction or interaction product. No other features were observed in the TPD except those described in the paper (DOI: c7fd00146k), so any reaction or interaction product with water is contained within the results of the SO_2

desorption behaviour. With hind-sight, it would have been useful to monitor the $m/z = 17$ and 18 (OH^+ and H_2O^+) signals during TPD, to see how much water, or water related material, came off, but this was not done.

Masayoshi Watanabe returned to discussion of the paper by Toshiyuki Itoh: It is interesting to see the introduction of oxygen atoms into the cationic structure of ionic liquids. When lithium salts are incorporated into conventional ionic liquids having [NTf$_2$] anions, the total charge of the lithium ion becomes negative by solvation of Li$^+$ by two [NTf$_2$] anions. The negative lithium charge causes a very low Li$^+$ transference number and sometimes falls to a negative value, which is not preferable for battery applications. If you introduce oxygen atoms that have strong coordinating properties to Li$^+$, Li$^+$ may be solvated by the cation and the total charge may also change. This is an interesting point in terms of the transport properties. However, the oxidation potential of the cation might be reduced because ether oxygen atoms start to oxidize at *ca.* 4 V *vs.* Li/Li$^+$. How do you think this would affect the applications for batteries?

Toshiyuki Itoh answered: I offer my deep appreciation for your helpful comments. I will consider these points in our future investigations.

Radha Gobinda Bhuin continued discussion of the paper by Robert G. Jones: You have mentioned three different states of acetone when acetone is covered with an ionic liquid (IL) layer. I would like to know how does the quantity of stabilised acetone change with the thickness of the IL layers and acetone layer? Does the quantity remain the same if you change the thickness of IL or acetone?

Robert Jones responded: The three different states of acetone were stabilised acetone (for desorption temperatures >140 K), destabilised acetone (for desorption temperatures less than the desorption temperature of pure acetone by itself) and desorption of pure acetone through cracks or empty pores in the overlying IL. The desorption features for destabilised and pure desorption through cracks are reproducible and were monitored as a function of coverage, as described in the paper. However the observed desorption features are narrower than expected for simple first or zero order desorption peaks. To simulate these peaks one of several very specific models, utilising precise kinetic parameters, would have had to be used. We feel that this would have conferred an unwarranted level of confidence in the particular model chosen and the kinetic parameters used. We therefore kept the description qualitative. For the stabilised acetone, the situation was simpler, and the desorption features could be simulated using a continuum of first order desorption peaks with increasing activation energies, corresponding to increasing interaction with the pore walls. Fig. 5B (DOI: c7fd00146k) shows the distribution of initial states as initial coverage *versus* activation energy E_a. The number of states for $45 \le E_a \le 57$ rises linearly with increasing IL coverage, *i.e.* as the IL gets thicker the number of pores increases proportionally and hence the number of states also increases. However the state for $E_a = 61$ kJ mol^{-1} increases markedly when the IL coverage increases from 20 to 34 monolayers. We have tentatively assigned this to the IL being able to rearrange at the higher IL coverage such that a highly corrugated layer of anions and cations can form, such that the acetone can then lie between the oppositely charged layers and hence be

particularly stabilised. At present this is speculation. However, ILs are thought to form such bi-layers at their surfaces at higher temperatures, when they are liquid, so putative formation of such a structure at approximately the glass transition temperature (190 K) is not an unreasonable assumption.

Radha Gobinda Bhuin remarked: What was the temperature of the ionic liquid evaporator during deposition and the deposition rate of ionic liquid on the surface?

Robert Jones answered: The ionic liquid evaporator was operated at 673 K and the IL deposition rate was a monolayer every few minutes. This rate varied somewhat over long periods but was relatively constant over a few days/weeks. The IL coverage for a particular experiment was always calibrated by desorbing the IL at the end of the experiment and determining the coverage from the desorption peak area.

Radha Gobinda Bhuin opened a general discussion of the paper by Simon Purcell: Why is oxygen atom scattering sensitive to the alkyl chain of ionic liquids but not the aromatic heterocyclic ring of ionic liquids?

Simon Purcell replied: Hydrogen abstraction by ground state atomic oxygen will only occur if there is enough energy along the reaction coordinate to surmount the potential energy surface (PES) barrier. For hydrocarbons, the kinetically determined activation energies, which are closely related but not identical to the PES barrier heights for hydrogen abstraction by $O(^3P)$, are typically 19 kJ mol^{-1} for secondary CH bonds and 29 kJ mol^{-1} for primary CH bonds.[1] In the reactive-atom scattering with laser-induced fluorescence detection (RAS-LIF) experiments reported in our paper, laser photolysis of NO_2 at 355 nm is used to prepare $O(^3P)$ atoms with a laboratory-frame translational energy distribution that has a mean of 16 kJ mol^{-1} and an (asymmetric) spread of 25 kJ mol^{-1} (FWHM). With this translational energy distribution, abstraction from secondary CH bonds is highly favoured over abstraction from primary CH bonds. The lower reactivity of primary CH bonds was also observed directly in RAS-LIF experiments on deuterium-labelled alkylthiolate SAMs.[2] Given that sp^2 CH bonds on the cation imidazolium ring have homolytic bond dissociation energies approximately 100 kJ mol^{-1} greater than those of primary and secondary CH bonds,[3] which will correlate with substantially higher barrier heights, it is highly unlikely that hydrogen abstraction from CH bonds of the imidazolium ring make any significant contribution to the detected OH signal.

1 M. A. Tesa-Serrate, B. C. Marshall, E. J. Smoll Jr, S. M. Purcell, M. L. Costen, J. M. Slattery, T. K. Minton and K. G. McKendrick, *J. Phys. Chem. C*, 2015, **119**, 5491–5505.
2 C. Waring, P. A. J. Bagot, M. W. P. Bebbington, M. T. Raisanen, M. Buck, M. L. Costen and K. G. McKendrick, *J. Phys. Chem. Lett.*, 2010, **1**, 1917–1921.
3 M. A. Tesa-Serrate, E. J. Smoll Jr, L. D'Andrea, S. M. Purcell, M. L. Costen, D. W. Bruce, J. M. Slattery, T. K. Minton and K. G. McKendrick, *J. Phys. Chem. C*, 2016, **120**, 27369–27379.

José Nuno Canongia Lopes resumed discussion of the paper by Robert G. Jones: Different setups were used for acetone and the other two small

molecules (you either mix the two components or have one atop the other). Why are these setups different?

Robert Jones replied: The aim of the desorption experiments was to investigate the interaction of the small molecules with the ionic liquid. Initial experiments, described in the paper, had shown that if acetone was adsorbed at 90 K on top of a layer of ionic liquid, then some of the acetone would diffuse down into the ionic liquid and become stabilised by it, but most of the acetone desorbed before it could diffuse down to interact with the IL. By depositing the acetone first, and then depositing the ionic liquid on top of it, the acetone was forced to diffuse through the ionic liquid, and hence interact with it, before it could desorb. The desorption behaviour of the acetone was found to be consistent with the IL forming a highly porous structure under these conditions, so the model used is that of interaction with a porous structure. We then realised that even more intimate mixing could be achieved if we coadsorbed the ionic liquid and small molecules. This was done for SO_2 and water resulting in a surface which is best considered as a random matrix of one molecule with the other. In this second setup there is no pre-formed porous structure within the ionic liquid, so the kinetics look rather different. However, the interactions between the small molecules and the IL will be of similar nature in both cases. It would definitely have been useful to study at least one system using both setups. Unfortunately we simply did not think of doing that at the time. Hind-sight is always perfect.

José Nuno Canongia Lopes added: I think it is hard to make comparisons and obtain meaningful conclusions with such different starting conditions. What if the acetone procedure was used for water?

Robert Jones responded: A valid point which has been partially answered above. If the water had been adsorbed first, below a layer of porous IL, then it, like the acetone, would have been forced to move through a pre-formed porous structure. We would have expected it to become somewhat stabilised and possibly destabilised by the ionic lined and octyl chain lined pores respectively. For excess water, we would have expected to see pure water desorption through cracks or empty pores, but with the added complication of the phase change within the pure water layer as the temperature rose during desorption. Such experiments would have given a clearer idea of how the water interacted with a surface (the walls of the pores) for comparison with the acetone behaviour. Unfortunately we did not do these experiments. The coadsorption experiments that were carried out, by contrast, showed that an enormous amount of water can be slightly stabilised by an IL when it is distributed through the water matrix. This would not have been apparent using the pre-formed porous structure experiment. So the two set ups are not directly comparable, but they have led to a rather broader understanding.

José Nuno Canongia Lopes returned to discussion of the paper by Simon Purcell: You focused your paper on the C_2 plus C_{12} mixtures. However you also mention mixtures of C_6 with two different anions. Apparently there is a concentration at the surface of the NTf_2 anion. Do you reach this conclusion based on the apparent depletion of chains at the surface caused by the larger volume of the anion?

Simon Purcell answered: This is correct. Based on our previous oxygen atom scattering experiments and MD simulations on neat ILs with the same chain length but with a series of anions of systematically increasing volume ($[BF_4]^-$, $[OTf]^-$, $[NTf_2]^-$), $[NTf_2]^-$ gave the lowest OH yields, implying that the alkyl chains are less exposed at the surface.[1] We conclude from the $[C_6mim][BF_4]_{(1-x)}[NTf_2]_x$ mixture measurements that the excess depletion of the OH signal below the linear, stoichiometric trend is caused by a decreased density of alkyl chains at the surface. This, in turn, is the result of the greater preference of the larger-volume $[NTf_2]^-$ anion to occupy the surface.

1 M. A. Tesa-Serrate, B. C. Marshall, E. J. Smoll, Jr., S. M. Purcell, M. L. Costen, J. M. Slattery, T. K. Minton and K. G. McKendrick, *J. Phys. Chem. C*, 2015, **119**, 5491–5505.

José Nuno Canongia Lopes clarified: In other words, the experimental deviations from a linear trend implicitly show that the NTf_2 anion goes more to the surface than BF_4?

Simon Purcell replied: Correct.

Florian Maier commented: As discussed after your talk, I raised the issues that in your $[C_2C_1Im][Tf_2N]_{(1-x)} : [C_{12}C_1Im][Tf_2N]_{(x)}$ mixtures, the surface enrichment of the $[C_{12}C_1Im]^+$ cations found by your group is—to some extent—in contradiction to our own angle-resolved X-ray photoelectron spectroscopy (ARXPS) data (see Fig. 5 and text, Maier *et al.*[1]). Indeed, there is no contradiction after having re-read your article carefully and revised our own work again (that is the good thing about discussions!). We stated that the surface is not *dominated* by $[C_{12}C_1Im]^+$ cations due to the lack of pronounced surface enrichment effects in such ways that the minority long-chained cations represent the majority species.[1] Your sentence on page 18, "only an isolated report using ARXPS has suggested an absence of non-stoichiometry surface segregation for related mixed long and short chain systems", was not the intended result in this reference. We clearly stated that "from our experimental ARXP spectra we can unambiguously rule out a surface that is solely dominated by one component of the mixture" which is also what you found for a small $[C_{12}C_1Im][Tf_2N]$ content. In our work, however, it is clearly seen that the composition of the surface layer is, on average, similar to a $[C_4C_1Im][Tf_2N]$ IL (red curve in Fig. 5b)[1] instead of the nominal $[C_3C_1Im][Tf_2N]$ on average as expected for the $[C_2C_1Im][Tf_2N]_{(0.9)} : [C_{12}C_1Im][Tf_2N]_{(0.1)}$ mixture employed in our experiment. $[C_4C_1Im][Tf_2N]$ would correspond to $[C_2C_1Im][Tf_2N]_{(0.8)} : [C_{12}C_1Im][Tf_2N]_{(0.2)}$. Thus, we also found about two times more $[C_{12}C_1Im][Tf_2N]$ (relative surface enrichment by a factor of about two), which is still less than your findings for the mixtures close to 0.1 mol% $[C_{12}C_1Im][Tf_2N]$ but is not ideal mixing behaviour. Due to the enhanced surface sensitivity of your method, the difference can be easily understood. I would thus like to ask you to re-adapt your above statement on our work and take it even more as a confirmation of your findings.

1 F. Maier, T. Cremer, C. Kolbeck, K. R. J. Lovelock, N. Paape, P. S. Schulz, P. Wasserscheid and H. P. Steinrück, *Phys. Chem. Chem. Phys.*, 2010, **12**, 1905–1915.

Simon Purcell responded: We are of course pleased that your revised analysis of your earlier ARXPS data[1] leads to a conclusion that is compatible with our RAS-

LIF results. We note also that your result for the surface tension of 33.6 mN m^{-1} at the single mole fraction of $x = 0.1$, quoted in the same work, is compatible with the data we show in Fig. 3 of our paper (DOI: c7fd00175d). We are reassured that the available data therefore all points qualitatively towards there being surface enrichment of the C_{12} chains. It would indeed be interesting to have more extensive ARXPS, and perhaps also time-of-flight secondary-ion mass spectrometry (TOF-SIMS) or high-resolution Rutherford backscattering (HRBS), measurements on a wider range of compositions to test further the extent of quantitative agreement.

1 F. Maier, T. Cremer, C. Kolbeck, K. R. J. Lovelock, N. Paape, P. S. Schulz, P. Wasserscheid and H. P. Steinruck, *Phys. Chem. Chem. Phys.*, 2010, **12**, 1905–1915.

Ramesh Gardas asked: We often use air–liquid or N_2 gas–liquid interfaces. Why in your work did you try a vacuum–liquid interface for the surface tension measurements?

Simon Purcell replied: The surface tension measurements were conducted in air. Only the RAS-LIF measurements were conducted in near-vacuum (in practice, under a low pressure of NO_2, the O atom precursor), which is an essential feature of the method. However, the vapour pressures of the ionic liquids are extremely small at the relevant temperatures, so it is not clear that the composition of the interface would be sensitive to the nature of the phase above the liquid.

Ramesh Gardas remarked: Prior to measuring the surface tension of IL mixtures by the pendant drop method, how is the mixing of 2 ILs done to obtain a homogeneous mixture of ILs, especially when you use viscous ILs?

Simon Purcell responded: The ILs were mixed using a magnetic stirrer and stored under N_2 for some time (usually days) before the measurements. The IL mixtures showed no problems with miscibility; visually, they appear to be a single homogeneous phase and there was no observed time dependence of the measured surface tension (or the RAS-LIF results, with which they are consistent).

Ramesh Gardas returned to discussion of the paper by Toshiyuki Itoh: Compared to IL **2** (2 ether oxygens, 89 mPa s), IL **7** (3 ether oxygens, 95 mPa s) should have low viscosity? Would both of them have similar water content? Did you observe any correlation between the number of ether oxygens in the IL *vs.* viscosity?

Toshiyuki Itoh answered: Thank you for your question. When I was asked this question, I replied that we measured the viscosity using ILs that had water contents of less than 700 ppm. I offer my apologies that this answer was incorrect. I forgot that we replaced the instrument with a new one last year and my students measured the viscosity under flowing argon gas to avoid water absorption during the measurement process. The results reported in our paper were those of ILs of which the water contents were less than 50 ppm. Table 1 shows the results of the viscosity of compound **6** with different water contents (entries 6 and 7). As shown in the results, the water content indeed influences the viscosity, though no difference was observed at 90 °C (entries 6 and 7).

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Table 1 Viscosity of ILs at different temperature conditions[a]

Entry	IL[b]	Viscosity at 35 °C (cP)	Viscosity at 90 °C (cP)	Water content (ppm)
1	**1**	134.5	13.1	9.0
2	**2**	66.2	7.68	48.5
3	**3**	63.2	8.73	11.7
4	**4**	95.4	10.9	18.2
5	**5**	82.8	10.2	49.0
6	**6**	63.7	8.92	31.2
7	**6**	57.7	8.97	163
8	**7**	54.4	7.76	23.2
9	**7** + LiTf$_2$N (5 : 1)	148.2	13.6	23.2
10	**7** + LiTf$_2$N (10 : 1)	91.3	10.4	23.2

[a] All measurements were conducted under flowing argon gas using the BrookField DV2T instrument. [b] Please refer to the manuscript (DOI: c7fd00142h) for structures of the ILs.

Radha Gobinda Bhuin continued discussion of the paper by Robert G. Jones: Did you try depositing acetone on top of the ionic liquid? If so, what do you observe? If not, what do you expect?

Robert Jones replied: We initially attempted to adsorb acetone onto several layers (oligolayers is perhaps a useful description) of ionic liquid at room temperature but no absorption of acetone was detectable on subsequent temperature programmed desorption. We then attempted to absorb acetone into the solid IL glass (formed by cooling the IL liquid from room temperature) at 90 K, but no absorption occurred, the acetone simply formed multilayers on the glass surface. This is described in Section 3.2.2 of the paper (DOI: c7fd00146k). We then adsorbed acetone onto the IL snow (formed by depositing the IL at 90 K) at 90 K and this did allow acetone to penetrate into the porous structure and interact with the IL. This is described in Section 3.2.3 of the paper. We then adsorbed the acetone below the IL snow, as described above and in the paper, to force the acetone to enter the IL structure and interact with it before desorbing.

Radha Gobinda Bhuin commented: How is the destabilised acetone peak related to the thickness of the ionic liquid? Is it possible to calculate the diffusion rate of acetone at a particular temperature?

Robert Jones responded: As noted above in my response to your first question, the stabilised peak behaved in a way that was analysable using a rather simple and general model, so that was done. However, the behaviour of the destabilised acetone peaks has only been discussed qualitatively as explained earlier. By fitting a sufficiently detailed model to the experiments, specific kinetic parameters, including those of the diffusion rate of the acetone inside the pores, could have been extracted, but these parameters would be highly sensitive to the original assumptions used for the model. We did not feel that such an analysis would be believable and did not attempt it.

James Wishart returned to discussion of the paper by Toshiyuki Itoh: During the discussion it came up that the water contents of the ionic liquids reported in this study are on the order of 800 ppm. While I understand the difficulty of drying ionic liquids with ether groups, 800 ppm of water is enough to alter their physical properties, for instance reducing their observed viscosities. Based on a survey of the literature on the effects of water content, including this paper,[1] I developed a general rule for my laboratory that physical characterization of ionic liquids should be done only when the water content is below 300 ppm, where I would expect the viscosity deviation to be less than 1%. Water contents in the range of 800 ppm could result in a few percent deviation in various physical properties and it would be desirable if you could report the exact water contents of each ionic liquid you report so that the likelihood of property deviation could be individually assessed.

1 J. A. Widegren, A. Laesecke and J. W. Magee, *Chem. Commun.*, 2005, 1610–1612.

Toshiyuki Itoh answered: Thank you for your comments. When I was asked this question, I replied that we measured the viscosity using ILs that had water contents of less than 700 ppm. I offer my apologies that this answer was incorrect. I forgot that we replaced the instrument with a new one last year and my students measured the viscosity under flowing argon gas to avoid water absorption during the measurement process. The results reported in our paper were those of ILs of which the water contents were less than 50 ppm. I show the results of the viscosity of compound **6** which has different water contents (Table 1, entries 6 and 7). As shown in the results, the water content indeed influenced the viscosity, though no difference was observed at 90 °C (entries 6 and 7).

Ruth Lynden-Bell continued discussion of the paper by Robert G. Jones: You refer to ionic liquid snow. What is the nature of this material and how do you know it is "snow"?

Robert Jones responded: A good question. The description is driven by the experimental observations. Fig. 2 in the paper (DOI: c7fd00146k) shows the TPD of acetone adsorbed onto the carbon covered Au surface at 90 K. It exhibits the simple zero order desorption kinetics expected for multilayer adsorption. Almost identical desorption behaviour was observed for acetone adsorbed on IL glass showing again that simple multilayers of acetone are formed, with desorption complete by 135 K (the TPD curves can be found in ref. 1.) However, when the IL was deposited on top of multilayers of acetone at 90 K, the desorption behaviour was very different (Fig. 4 in the paper), with highly structured desorption peaks replacing the single zero order peak of pure acetone desorption, and new desorption peaks stretching up to 200 K. The simplest explanation consistent with this behaviour is that the IL liquid has formed a porous structure through which the acetone must move before desorbing from the surface. The quantity of acetone that interacts with the porous IL is consistent with a very high surface area, so we have used the term "snow" to connote a material where the voids, or pores, are of approximately the same dimension as the solid material, explaining the high surface area. As far as we are aware, no other studies have been undertaken to determine the porosity of such IL snows. Studies combining scanning

tunnelling microscopy and quartz crystal microbalance measurements could be used to determine porosity, as they have been for thin films of metal halides.[2]

1 M. Buckley, PhD thesis, University of Nottingham, 2016.
2 H. Kim and A. H. King, *J. Mater. Res.*, 2007, **22**, 2012–2016.

Christopher Hardacre asked: Do you observe the same melting transition of the IL irrespective of the conditions applied?

Robert Jones replied: The temperature programmed desorption technique used here is unable to detect a glass transition temperature or a melting transition except, rather indirectly, by inference from a change in desorption peak position or peak intensity. Therefore we are unable to say anything regarding transitions apart from the observation of an increase in the relative concentration of the most stabilised acetone desorption peak at 190 K, which we think may be due to the IL passing through the glass transition temperature. X-ray photoelectron spectroscopy (XPS) can detect glass and melting transitions of ILs rather more clearly, as the solid is insulating while the liquid is ionically conducting, leading to a difference in apparent binding energy. For multilayer of pure [OMIM] [BF$_4$] snow on clean Cu(111),[1] the F 1s peak started to shift on heating to 190 K, due to the IL becoming more electrically conductive. XPS experiments in the future would be able to detect changes in transition temperature caused by absorbed material within the IL.

1 K. L. Syres and R. G. Jones, *Langmuir*, 2015, **31**, 9799–9808.

Christopher Hardacre commented: Are there any structural changes that can be detected by LEED?

Robert Jones responded: Low energy electron diffraction (LEED) studies were not carried out in this work. In previous work we have tried to observe LEED patterns from the surfaces of bulk ionic liquid samples at room temperature and from adlayers of ionic liquids on metal crystal surfaces at both room and low temperature, but we have never observed any level of diffraction pattern, not even diffuse ring structures. The effect of the electron beam (≈ 1 μA in 1 mm^2 on the surface) is to damage the IL within a few seconds (as evidenced by XPS or ultraviolet photoelectron spectroscopy). It is possible that such electron beam damage may be sufficiently fast that the inherent diffraction pattern due to the surface of the IL is not seen. Studies using an amplified LEED apparatus with incident beams in the nA region, so as to almost eliminate electron beam damage, may show some degree of surface order, as one might expect from an ionic liquid. As far as we are aware, no LEED patterns have been observed by any other research group.

Barbara Kirchner returned to general discussion of the paper by Simon Purcell: In general if you go from the bulk to the surface (bulk-vacuum) in an ionic liquid, you obviously observe more ion pairing. The choice of your systems showed in the simulations that depending on the mole fraction you had more alkyl side chains at the surface. I was wondering if your ion pairing at the surface is disrupted when the side chain aggregation occurs?

Simon Purcell answered: Our simulations were designed to examine static snapshots of the vacuum–liquid surface structure in $[C_2mim]_{(1-x)}[C_{12}mim]_x[Tf_2N]$ mixtures. In this dataset, there is little structural evidence to suggest that the polar network at the vacuum–liquid interface is strongly perturbed as the mole fraction of $[C_{12}mim]^+$ is varied from 0 to 1. For example, consider the radial distribution function (RDF) between the unique carbon atom of the imidazolium ring in near-surface cations and the nitrogen atom of the $[Tf_2N]^-$ anion (Fig. 4). There is very little change in the relative intensity and lineshape of the 1st and 2nd nearest-neighbour peaks as a function of $[C_{12}mim]^+$ mole fraction. This observation is consistent with our work on the vacuum–liquid surface structure of 1-alkyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide and 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids as a function of the alkyl chain length.[1] We found that XY RDFs between oppositely charged polar units of near-surface ions do not show dramatic changes with alkyl chain length. Future work may explore the dynamic properties of the near-surface polar network (*e.g.*, ion cage lifetimes) to search for evidence of ion pairing.

1 M. A. Tesa-Serrate, E. J. Smoll Jr, L. D'Andrea, S. M. Purcell, M. L. Costen, D. W. Bruce, J. M. Slattery, T. K. Minton and K. G. McKendrick, *J. Phys. Chem. C*, 2016, **120**, 27369–27379.

John Slattery added: This is a comment, as we performed the synthesis of the ILs used in this work. I am fairly confident that we can exclude the possibility of siloxane impurities, which may indeed be surface active, as we do not use grease during the syntheses of these liquids. It is possible, however, that low volatility
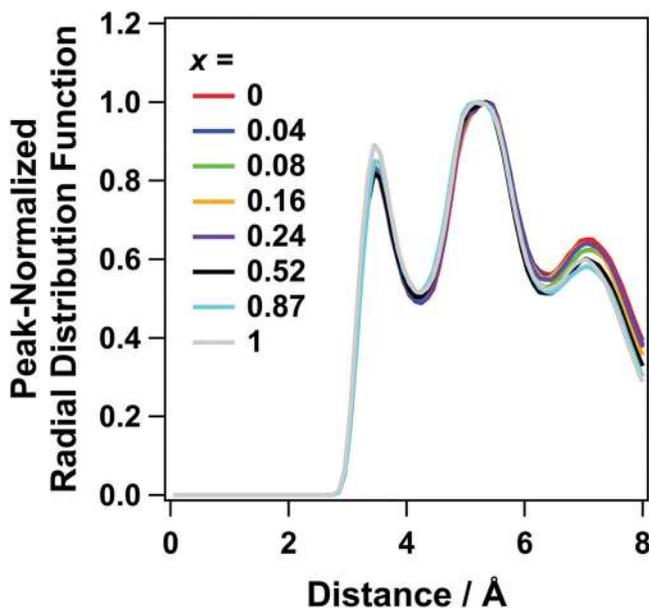

Fig. 4 Radial distribution function between oppositely charged ions in the near-surface polar network of $[C_2mim]_{(1-x)}[C_{12}mim]_x[Tf_2N]$ mixtures as predicted by MD simulations. Ion distance is measured between the unique imidazolium carbon in $[C_2mim]^+$ and $[C_{12}mim]^+$ cations and the nitrogen atom of $[NTf_2]^-$ anions.

alkyl halides (*e.g.* dodecylbromide) might be present in very small quantities that we cannot detect. We take care to remove volatiles such as these after the synthesis by heating gently under a vacuum of around 10^{-3} to 10^{-4} mbar for prolonged periods and they are not detected by the analyses that we perform after the synthesis. In addition, the Edinburgh group heat the samples under even higher vacuum prior to their experiments, so there is another chance to remove volatiles. So our feeling is that the chance of these impurities being present in sufficient quantities to affect the results is low.

Margarida Costa Gomes continued discussion of the paper by Octavian D. Pavel: You claim that the difference in solubility between oxygen, nitrogen and argon can explain the differences in the performance of your catalyst. Even if the Henry's law constants you present at 70 °C seem quite different (KH = 1854 bar for O_2; 3064 bar for N_2; 2707 bar for Ar), they reflect a relatively small difference in the mole fraction solubility at a partial pressure of gas equal to 1 bar ($x = 5.4 \times 10^4$ for O_2; 3.3×10^4 for N_2; 3.7×10^4 for Ar). Do you think that this small difference in solubility is the only explanation for the behaviour of your catalyst using a feed of O_2 in Ar when compared with a feed of O_2 in N_2?

Octavian D. Pavel responded: Indeed, the gas solubility plays an important role in conversion. We have also considered several other properties, but this was the only one offering a rational explanation. Its effect has also been demonstrated in additional experiments including those reported previously.[1] In that manuscript the variation of the gas solubility in $[C_4C_1im][NTf_2]$ *vs.* the gas mixture composition at 70 °C has been shown.

1 O. D. Pavel, P. Goodrich, L. Cristian, S. M. Coman, V. I. Pârvulescu and C. Hardacre, *Catal. Sci. Technol.*, 2015, **5**, 2696–2704.

Margarida Costa Gomes asked: Have you looked to other explanations, rather than the difference in gas solubility, to explain the increase in the conversion of 1-butanethiol when you use argon instead of nitrogen in your gas feed?

Octavian D. Pavel replied: Thank you for this question. Indeed, two other effects have been taken into consideration: (i) the change in the chemisorption of the substrates in the presence of the inert gases, and (ii) the change in thermal conductivity by the dilution gases at the reaction temperature. Finally, we had neither experimental nor theoretical support for these effects.

Seiji Tsuzuki returned to discussion of the paper by Toshiyuki Itoh: I have two comments. The first one concerns the effects of ether oxygens introduced to the cation on the transport properties. The DEME cation (*N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium) is another ether oxygen-introduced cation. The ether oxygen atom of the DEME cation also enhances the diffusion of ions in the ionic liquid and decreases the viscosity. The introduction of oxygen to the per-fluoroalkyl chain of the perfluoroalkyltrifluoroborate anion also enhances the diffusion of ions. These results show that the ether oxygen atom plays important roles in determining the transport properties of ionic liquids. Unfortunately,

however, it is not well understood how the ether oxygen atom affects the transport properties.

My second comment concerns the interaction between Li^+ and the ether oxygen atom in the cation. I have studied the interaction of Li^+ and $DEME^+$ cations. Although the Li^+-$DEME^+$ complex has a local energy minimum structure in which the Li^+ has contact with the ether oxygen atom of $DEME^+$, this structure is less stable than the isolated Li^+ and $DEME^+$. On the other hand the interaction of Li^+ with the TFSA anion increases the stability of the complex. The $DEME^+$-Li[TFSA] complex, in which the Li atom of the Li[TFSA] complex has contact with the ether oxygen atom of $DEME^+$, is more stable than the isolated $DEME^+$ and Li[TFSA] complexes. I believe that at least one TFSA anion has contact with Li^+ in the mixture of the ether oxygen-introduced cation-based ionic liquid and Li[TFSA] salt studied in this work. Therefore, I believe that the Li^+ interacts with the ether oxygen atoms of the cation in the mixture.

Toshiyuki Itoh responded: I offer my deep appreciation for these helpful comments. I will consider these points in our future investigations.

Leigh Aldous stated: You have measured the viscosity of the pure ionic liquids; could you comment on what happened to the viscosity when the lithium salt was added to the ionic liquid?

Toshiyuki Itoh replied: Thank you for your question. We have measured the viscosity of a mixture of IL 7 with $LiTf_2N$. Please see Table 1 (entries 8–10). As shown in this table, increased viscosity was observed when $LiTf_2N$ was added to this IL.

Johan Jacquemin asked: Could you tell us the amount of lithium salt which could be added into these ILs? Could you quantify the impact of Li salt added on the physical properties of IL-based electrolytes?

Toshiyuki Itoh answered: We measured the viscosity of mixtures of $LiTf_2N$: IL 7. Please see entries 9 and 10 in Table 1. The addition of an increased amount of $LiTf_2N$ increased the viscosity of the solution.

Leigh Aldous resumed discussion of the paper by Robert G. Jones: Coming back to the discussion on melting points, were you able to discern between the different phases, *e.g.* solids, gels and liquids, inside the cell?

Robert Jones replied: In these experiments we did not use a cell. The sample was a carbon covered Au(111) crystal surface with an area of about 1 cm^2, on which the ionic liquid and small molecules were deposited prior to temperature programmed desorption. As noted above in my first response to Christopher Hardacre, TPD is unable to provide information on different phases except by indirect inference.

Leigh Aldous continued: I wonder if you could convert your instrument to run differential scanning calorimetry (DSC)? That way you might be able to discern phase transitions.

Robert Jones responded: An interesting idea. In DSC a macroscopic quantity of material is heated such that the energy involved in the phase transition can be matched by electrical energy in the dummy crucible, thus providing a measurement of the enthalpy change involved. In our case, the "crucible" is a gold crystal of about 2 g with a surface area of about 1 cm^2, and for acetone the maximum coverage used was 35 monolayers on this surface. Using the surface density of acetone given in the paper, 35 monolayers corresponds to 2.4×10^{-8} mol of acetone, which (using the highest energy desorption state of 61 kJ mol^{-1}) would absorb 1.4×10^{-3} J during desorption. The sample temperature change would be too small to detect experimentally so this would not be a viable method for DSC using our type of sample. However, if the "crucible" were reduced in mass, by using a self supporting thin metal film, then its temperature change would become detectable and DSC would become possible. Work carried out by David King into single crystal adsorption calorimetry[1] shows how low mass substrates can be used to measure heat changes for very small quantities of surface materials.

1 W. A. Brown, R. Kose and D. A. King, *Chem. Rev.*, 1998, **98**, 797–832.

William Wallace commented: The ionic liquids you use are pure. Have you looked into mixing them with water or another molecular solvent and seeing how this would affect the catalytic activity?

Octavian D. Pavel responded: The ILs were deposited on the catalyst surface using a mixture with an organic solvent and thereafter the organic was evaporated to form the catalyst. We have not looked at using water as the second phase to deposit the IL but it would also be removed on evacuation to a large extent. The residual water may be higher than that in the original IL due to the effect of confinement in the pore. This water may influence the solubility of the reactants in the IL as well as the nature of the active site with increased levels of surface hydroxyls. It is not clear how this would affect the catalytic activity but it is likely to be strongly dependent on the active metal and the support used.

Johan Jacquemin continued discussion of the paper by Toshiyuki Itoh: Did you compare the physical properties of the selected ILs with those already published in the literature? Could you then highlight, for example, the effect of the number of oxygen atoms in the cation (imidazolium, pyrrolidinium, *etc.*) on these properties?

Toshiyuki Itoh replied: All our ether-functionalized piperidinium salt ILs are new ILs. To the best of our knowledge, no physical properties of these ILs have been reported. Although [PP1,6][Tf$_2$N] was found in a patent, no physical properties of this IL have been reported.

Johan Jacquemin asked: Why did you choose this type of cation? Why not imidazolium or other types?

Toshiyuki Itoh responded: We initiated this study for the development of an appropriate electrolyte for lithium-ion batteries with the Si electrode. To this aim, we tested three types of ILs, *i.e.*, 1-ethyl-3-methylimidazolium ([emim]), N-methoxyethoxymethyl-N-methylpyrrolidinium (PY1MEM), and N-methoxyethoxy-methyl-N-methylpiperidinium ([PP1MEM] bis(fluorosulfonyl)amide ([FSA]) and

found that [PP1MEM][FSA] gave the best results, though there was only a small difference between the pyrrolidinium and piperidinium salts. During this study, we further found that smooth Li cation transfer was accomplished even using a piperidinium salt which has a mono-ether functional substituent, though the best efficiency was obtained when [PP1MEM][FSA] was used as the electrolyte. Inspired by these results, we decided to systematically synthesize piperidinium salts that have an ether functional moiety and evaluated their physical properties.

Johan Jacquemin queried: The stability of your ILs (Electrochemical Window) against a lithium electrode is an important matter to take into consideration for Li-ion battery applications. Is this not an issue in your work?

Toshiyuki Itoh responded: We used IL **2** as an electrolyte for the Li ion battery with Si electrode in a collaboration with Professor Sakaguchi in our department.[1] I heard that our IL was stable under their experimental conditions.

1 K. Yamaguchi, Y. Domi, H. Usui, M. Shimizu, K. Matsumoto, T. Nokami, T. Itoh and H. Sakaguchi, *J. Power Sources*, 2017, **338**, 103–107.

Vladislav Ivaništšev commented: We have worked on a method for predicting the viscosity of ionic liquids. We have applied it to the presented set of seven ionic liquids and succeeded to identify those with lower viscosity. It is challenging to continue with similar sets synthesized by the same group and measured under the same (dry) conditions.

1 K. Karu, A. Ruzanov, H. Ers, V. Ivaništšev, I. Lage-Estebanez, J. M. García de la Vega, *Computation*, 2016, **4**, 25.

Toshiyuki Itoh responded: I offer my deep appreciation for your helpful comments. I will consider the results reported in your paper in our future investigations.

I replied that we measured the viscosity using ILs that had water contents of less than 700 ppm. I offer my apologies that this answer was incorrect. I forgot that we replaced the instrument with a new one last year and my students measured the viscosity under flowing argon gas to avoid water absorption during the measurement process. The results reported in our paper were those of ILs of which the water contents were less than 50 ppm. I show the results of the viscosity of compound **6** which has different water contents (Table 1 entries 6 and 7). As shown in the results, the water content indeed influenced the viscosity, though no difference was observed at 90 °C (entries 6 and 7).

Leigh Aldous returned to discussion of the paper by Octavian D. Pavel: You mixed your support and IL in a 1 : 1 weight ratio; is there a reasoning behind that? Is that optimised?

Octavian D. Pavel replied: In these studies, the IL : catalyst ratio has not been optimized but it is an important variable to study as the IL can modify the effective concentrations of the substrates and intermediates at the active sites as discussed in ref. 1. This variable will be examined in future studies.

1 M. Sobota, M. Happel, M. Amende, N. Paape, P. Wasserscheid, M. Laurin and J. Libuda, *Adv. Mater.*, 2011, **23**, 2617–2621.

Leigh Aldous commented: Can you comment on what your SCILL looked like? For example, was it initially a free-flowing powder which became "sticky"?

Octavian D. Pavel answered: Following deposition of the IL, the catalyst becomes less free flowing. However, this did not result in any issues associated with stirring and dispersing the catalyst in the reaction solvent.

Ryan Clark returned to discussion of the paper by Robert G. Jones: You attribute the stabilisation and destabilisation to the porous structure. Would you expect a similar porous structure to form when using a shorter chain?

Robert Jones replied: As the chain length attached to the imidazolium gets shorter, the anion as a whole becomes more compact and less likely to leave pores between the ion pairs when they adsorb randomly onto the substrate at 90 K. So we might expect smaller pore sizes, and hence less porosity as a whole, for shorter chain lengths such as in $[EMIM]^+$, 1-ethyl-3-methylimidazolium. It is worth noting that metal halides such as LiF and MgF_2,[1] when condensed from the vapour onto glass at homologous temperatures (substrate temperature/metal halide melting point) of <0.3, achieve linear porosity values of >30% even though the anions and cations are spherical and the ion pairs are of high symmetry. We might reasonably expect a relatively high porosity from the larger and less symmetrical imidazolium cation even with short chains. For chains longer than octyl the porosity would probably increase somewhat, but the increase in porosity would be associated with the alkyl chains and hence be destabilising rather than stabilising. Given that the $[BF_4]^-$ in this work is of high symmetry, swapping this for a larger and more asymmetric anion such as $[Tf_2N]^-$, $[(CF_3SO_2)_2N]^-$ may also increase the porosity, but now it would be the stabilising pores that are increased in size.

1 H. Kim and A. H. King, *J. Mater. Res.*, 2007, **22**, 2012–2016.

Matthew Addicoat continued discussion of the paper by Toshiyuki Itoh: You spent time tying to correlate calculated properties of the single cation with viscosity, but viscosity means molecules sliding past each other, and is therefore fundamentally a property of an ensemble of molecules. Seeing as you are only changing the tails of your cations, wouldn't considering how two cations stack, specifically the interaction between the tails, give you a better indication and perhaps even supply a physical explanation for the changes in viscosity?

Toshiyuki Itoh answered: I offer my deep appreciation for your helpful comments. I agree with your opinion. I will consider your comments in our future investigations.

Christopher Hardacre asked: Your work has concentrated on piperidinium-based ionic liquids. Can you offer some ideas about whether pyrrolidinium or azepinium-based ionic liquids may perform better for battery applications?

Toshiyuki Itoh replied: We initiated this study for the development of an appropriate electrolyte for the lithium-ion batteries with the Si electrode. Our basic idea is that the introduction of the methoxyethoxymethyl group on the cationic part may contribute to smooth Li ion transfer to the Si cathode, because the surface of the Si cathode is covered with the cationic part of the IL, which may prevent absorption of the Li cation into the electrode (Fig. 5). To this aim, we tested three types of ILs, *i.e.*, 1-ethyl-3-methylimidazolium ([emim]), *N*-methoxy-ethoxymethyl-*N*-methylpyrrolidinium (PY1MEM), and *N*-methoxyethoxymethyl-*N*-methylpiperidinium ([PP1MEM] bis(fluorosulfonyl)amide ([FSA]) and found that [PP1MEM][FSA] gave the best results, though there was only a small difference between the pyrrolidinium salt and piperidinium salt. During this study, we further found that smooth Li cation transfer was accomplished even using a piperidinium salt which has a mono-ether functional substituent, though the best efficiency was obtained when [PP1MEM][FSA] was used as the electrolyte. Inspired by these results, we decided to systematically synthesize piperidinium salts that have an ether functional moiety and evaluated their physical properties.

Seiji Tsuzuki stated: The cause of the difficulty to elucidate the relationship between structures of ions and the transport properties of ionic liquids is that several factors affect the transport properties of ionic liquids. One factor is the size of ions. If the alkyl chain length of the cation is increased, the diffusivity of ions decreases and the viscosity increases. This means that the size of ions is an important factor determining the transport properties. Another factor is the shape of ions. The diffusion of ions in quaternary ammonium-based ionic liquids is slower than that in imidazolium and pyridinium-based ionic liquids, even if the sizes of cations are nearly identical. The plate-shaped imidazolium and pyr-idinium enhance the diffusion compared with bulky quaternary ammonium. This
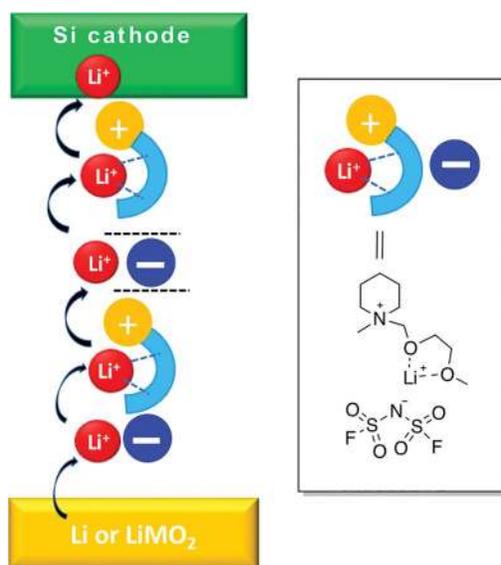

Fig. 5   Initial working hypothesis of the IL-type electrolyte for Li ion batteries with the Si electrode.

shows that the shape of the ions is important for the transport properties. The third factor is the magnitude of the attraction between the cations and anions. Although the TFSA anion is larger than the BF_4 and CF_3SO_3 anions, the diffusion of ions in TFSA-based ionic liquids is faster than that in the BF_4 and CF_3SO_3-based ionic liquids. Analysis of the interaction energy by *ab initio* calculations show that the interaction between TFSA anions with cations is weaker than the interactions of BF_4 and CF_3SO_3. This shows that the magnitude of the attraction between cations and anions is also important. The fourth factor is the conformational flexibility of ions. We can artificially increase the barrier of internal rotation in MD simulations by changing torsional parameters in the force field used for the simulations. If the rotation of the C–N bond connecting the alkyl group and imidazolium ring is fixed by increasing the barrier height, the calculated self-diffusion coefficients of ions decrease significantly. This shows that conformational flexibility of ions is important for the transport properties. In addition, other factors such as the effects of ether oxygen atoms introduced to the ions affect the transport properties. Many factors affect the transport properties. This would be the cause of the difficulty to predict the transport properties of ionic liquids from ion structures.

Toshiyuki Itoh responded: I offer my deep appreciation for the helpful comments. I will consider these points in our future investigations.

James Wishart commented: In reference to the comments about lengthening oligoether chains providing more opportunities for hydrogen bonding, thus leading to higher viscosities with increasing number of ether segments, that may be highly case-dependent. For example, we have found that lengthening the chains in a series of 1-R-1-methylpyrrolidinium NTf_2 (R = CH_2–CH_2OCH_3, $CH_2CH_2OCH_2CH_3$, $CH_2CH_2OCH_2CH_2OCH_3$, $CH_2CH_2OCH_2CH_2OCH_2$–CH_3, and $CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_3$) ionic liquids results in very little increase in viscosity.[1] As opposed to the imidazolium case where there is a monotonic increase,[1] hydrogen bonding may be less of a factor in the pyrrolidinium case.

1 S. I. Lall-Ramnarine, M. Zhao, C. Rodriguez, R. Fernandez, N. Zmich, E. D. Fernandez, S. B. Dhiman, E. W. Castner and J. F. Wishart, *J. Electrochem. Soc.*, 2017, **164**, H5247–H5262.

Leigh Aldous returned to discussion of the paper by Robert G. Jones: You use Au(111) as your surface, but are you restricted to a certain kind of surface? Does it have to be a metal, or can it vary more widely?

Robert Jones replied: The substrate surface can be of any material that is vacuum compatible, provided it is sufficiently thermally conductive to avoid any temperature variations across the surface, which would invalidate the TPD analysis. We used a carbon contaminated Au(111) surface which does not react with the ionic liquid or the small molecules, and where the heat of physisorption of the adsorbates is similar in magnitude to their inherent heats of vaporisation. This ensured that the behaviour of the IL and small molecules was dominated by their inherent interactions and not by interactions with the substrate. Using atomically clean substrates opens up the possibility of reaction with the surface, which would be interesting in its own right but would complicate the behaviour. It

also opens up the possibility of the substrate influencing the structure adopted by the adsorbates either during adsorption or during desorption, *e.g.* epitaxial growth. This could lead to very different types of porosity (*e.g.* long tubes) which would strongly affect the desorption behaviour of the adsorbate.

Leigh Aldous said: You use a focal point to measure one section of the surface. Have you considered having two metal electrodes and polarising them, for example with a battery? Would polarising the interface perhaps make it easier or harder to desorb the ionic liquid?

Robert Jones responded: I think the very interesting idea that you are suggesting here is the effect of a potential difference across the depth of the adsorbate layer, and how that would influence the desorption. Simply applying a voltage to a substrate in a vacuum, relative to the chamber walls at earth potential, establishes an electric field of volts per cm, or possibly volts per mm if an earthed plate is quite close to the sample surface. However, such fields are too weak to cause any change in chemical behaviour such as desorption, so simply applying different potentials to adjacent surfaces a few mm from each other in a vacuum produces no change in chemical behaviour. Fields of the order of volts per Å are required to alter chemical behaviour and these can only be generated by having an electrode very close to the sample, such as in a scanning tunnelling microscope (STM), or a high electric field due to curvature of the surface, as in field electron microscopes (FEMs) or field ion microscopes (FIMs), or in an electrochemical cell where such fields are generated between the working electrode and the bulk electrolyte some tens of Å away. The STM is vacuum compatible but the area where electric field exists is (probably) too small for any desorption to be detectable mass spectrometrically. In FEMs and FIMs, molecules on the tip can be desorbed directly by the applied electric field and detected mass spectrometrically, but TPD is not usually used. The electrochemical cell is not (at the present time) vacuum compatible and it has a semi-infinite condensed phase above the surface, making TPD impossible. So at present there is no obvious way of generating the necessary electric field, at an extended surface, so that the effects could be measured by TPD. Were such an electric field to be established through an adsorbate layer, one would expect the molecules to be stabilised by alignment of their dipoles with the field, which would increase the activation energy for desorption, while individual anions and cations would become stabilised or destabilised depending on whether the field was tending to move them towards the substrate, or towards the vacuum. A difference of 1 V Å^{-1} corresponds to 96 kJ mol^{-1} for a singly charged species over 1 Å, so a field strength of 10 mV Å^{-1} between two adsorbed species 10 Å apart (perpendicular to the surface) would change their relative desorption energies by $\approx 10 \text{ kJ mol}^{-1}$ which would be very easily measured by TPD.

Shraeddha Tiwari continued discussion of the paper by Simon Purcell: It has been mentioned that the interfacial behaviour of ionic liquid mixtures (as inferred from the RAS-LIF measurements) is analogous to Henry's law at low mole fractions and Raoult's law at high mole fractions. These are thermodynamic notations applied to ideally dilute or ideal solutions. How far is it technically correct to apply these analogies to ionic liquid mixtures?

Simon Purcell answered: The analogy was only intended loosely and not to be taken to be technically exact, because distinct physical systems are being described. One significant difference, for example, is that the surface layer in ionic liquid mixtures has a finite capacity to accommodate one of the cations, whereas there is no similar restriction for molecules in the vapour phase above a binary liquid mixture. Nevertheless, we believe that the generality of our qualitative analogy is interesting and may prove useful in interpreting the surface enrichment of specific ions in ionic liquid mixtures. The applicability of Henry's Law in a conventional liquid implies that the mixing is being driven by enthalpy, where it is energetically favourable to expel the solute from the bulk into the gas phase. This gives insight into C_2/C_{12} mixtures in our paper (since there are corresponding bulk measurements also available[1,2]). At low bulk mole fractions, x, the $[C_{12}mim]^+$ cation in the bulk is in a fairly polar environment with only small numbers of small sized $[C_{12}mim]^+$ aggregates around to offer an accommodating environment. Therefore there is an energetic drive for the $[C_{12}mim]^+$ cation to occupy the surface. At medium x, the bulk forms percolated polar and non-polar domains; the energy cost of a $[C_{12}mim]^+$ cation remaining in the bulk is correspondingly decreased, reducing the propensity to occupy the surface and hence the deviation away from stoichiometry. At high x, the observation of Raoult's law-type behaviour suggests an entropic mixing where, on average, the energetics of a $[C_{12}mim]^+$ cation joining the bulk or the surface are the same.

1 C. P. Cabry, L. D'Andrea, K. Shimizu, I. Grillo, P. Li, S. Rogers, D. W. Bruce, J. N. Canongia Lopes and J. M. Slattery, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00167c.
2 D. W. Bruce, C. P. Cabry, J. N. Canongia Lopes, M. L. Costen, L. D'Andrea, I. Grillo, B. C. Marshall, K. G. McKendrick, T. K. Minton, S. M. Purcell, S. Rogers, J. M. Slattery, K. Shimizu, E. Smoll and M. A. Tesa-Serrate, *J. Phys. Chem.* B, 2017, **121**, 6002–6020.

Masayoshi Watanabe commented on the paper by Toshiyuki Itoh: It is well known that the ether structure is not compatible with 4 V-class cathodes such as LiCoO$_2$, which is the most widely used cathode material in lithium ion batteries. Such a cathode is charged to at least 4.2 V *vs.* Li/Li$^+$ in the charging process. Ether oxygen atoms decompose at potentials higher than 4 V. If ionic liquids are designed to be applied in lithium battery systems we need to be careful about the oxidation.

Morgan L. Thomas resumed general discussion of the paper by Robert G. Jones by communicating: In the experimental section of this interesting manuscript, you stated that "acetone, water and SO$_2$ were dosed into the chamber *via* a leak valve from a separately pumped gas line, the pressure being measured with an ion gauge". Could you please provide the approximate pressure observed during this dosing/deposition process?

Robert Jones communicated in reply: Pressures in the range 2×10^{-8} to 5×10^{-7} mbar were used for dosing acetone, SO$_2$ and H$_2$O molecules at 90 K for times of up to several hundred seconds. The TPD experiments for the pure compounds from the substrate were used to identify the exposures (pressure $\times$ time) in mbar s needed to form one monolayer of each. For acetone it was then straightforward to calculate the time required for a particular pressure (often 1×10^{-7} mbar was used) to achieve a particular coverage of acetone. For SO$_2$ and H$_2$O where co-adsorption with the IL was used, the IL evaporator required a fixed

length of time to deposit the required coverage of IL, so the applied pressure of the SO_2 or H_2O gas was adjusted such that in that time the necessary pre-determined exposure was achieved. As all dosing was carried out at 90 K we are confident that the sticking probability was 1.0 for all vapours impinging on the surface, and hence surface coverages were proportional to exposure at all times.

Morgan L. Thomas also communicated: There has been much discussion in the literature about the mechanism and possible specific nature of interactions between CO_2 and ILs. It would be of interest, if it is experimentally possible, to study the interaction (*i.e.* TPD profiles and desorption activation energies) of CO_2 co-deposited with various ILs using this compelling technique.

Robert Jones communicated in reply: We agree that TPD studies of the inter-actions of CO_2 with ionic liquids would be useful. However, the line of sight mass spectrometry (LOSMS) used for the present and previous studies utilised liquid nitrogen (77 K) as the cryopumping agent, and at this temperature CO_2 is not effectively pumped, preventing any study of CO_2/IL coadsorption using LOSMS for TPD. Recently we have constructed a new LOSMS with cryopumping at 40 K using a closed cycle helium refrigerator which does effectively pump CO_2. We have used this low temperature LOSMS to carry out TPD studies of CO_2 coadsorbed with 1-octyl-3-methylimidazolium tetrafluoroborate, $[C_8C_1Im][BF_4]$, and 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_8C_1Im][Tf_2N]$). The results will be published soon.

Andrew Abbott opened the discussion of the Concluding Remarks paper by Philip Jessop: This is an excellent summary of the future directions and needs of ionic liquids. You are correct that the next generations for ionic liquids need to focus on more environmentally benign liquids but I think we should also high-light that no green technology has so far been adopted which is more expensive that the technology it is replacing, so the cost of the liquid is imperative.

Philip Jessop replied: Thank you for your comment. Yes, the price is crucial too. Fortunately if we can make the synthesis shorter and greener, then the ionic liquid is also likely to be cheaper. Not guaranteed, of course, but possible. A worthy goal to work towards!

John Holbrey said: One of the challenges in bringing rigorous life cycle analysis into materials development at an early stage is that the "goal posts" are always changing. This means that we do tend to see life cycle assessment (LCA) reports that highlight issues with materials (ionic liquids in this context) that the community has already moved largely away from. Not withstanding this, there certainly is a great merit in implementing key aspects of LCA right from the beginning of development.

Philip Jessop responded: Indeed. We need the LCA folks and the research chemists working side by side, so that new information from the researchers is passed on to the LCA folks promptly, and findings from the LCA folks are passed to the researchers equally promptly, so that we researchers can modify our projects or our liquids accordingly. Also, as you suggested, even if researchers don't have an

active collaboration with an LCA expert, being aware of LCA and some of its key findings can help us design our liquids and our projects better from the start.

John Slattery asked: There are a number of fields at the moment that are heavily promoting their work as being green or sustainable. In many cases this might be based on a single metric (*e.g.* the use of more earth-abundant metals in catalysis in preference to platinum-group metals) and there often isn't even a qualitative consideration of the full life cycles of the existing and new processes. How can we get more communities to consider their systems carefully before labelling them as green or sustainable to avoid over-selling this aspect of their work?

Philip Jessop answered: This is an important but difficult question. So many fields of research in the area of green or sustainable chemistry have been hurt by misleading or insufficiently demonstrated claims of green-ness. It's not a problem of outright dishonesty but more a lack of education. Researchers who are experts in their own fields (catalysis or solvents or whatever) are attracted by this new selling-point and wish to incorporate it into their papers and their research, but they lack the knowledge of how to properly demonstrate (or even think about) green-ness or sustainability. We need to get the message out to all such researchers that it is insufficient to use a single metric (such as mass efficiency of a reaction or earth-abundance or an element) to support a claim that a new technology is green. A multifaceted discussion of the pros and cons of the new technology *versus* the incumbent technology is needed. It's best exemplified by the concept of Life Cycle Thinking, which is a non-quantitative comparison of the new and old technologies on each of several kinds of environmental impacts. But how can we spread this word to all researchers? That's the hard part. Frankly, I don't know how to spread the word efficiently, but Perspectives papers written for the journals in different fields, discussing this need, may be the best approach at present.

Doug MacFarlane asked: Given all of the electrochemical applications of ionic liquids and the resultant extended life cycle of the devices that they support, and thereby the reduction in fossil fuel use that they allow, is the life cycle analysis sophisticated enough to take these broad impacts into consideration?

Philip Jessop responded: Yes. LCA comparisons are based upon a common deliverable. For example, if we're thinking about battery-powered cars *vs.* gasoline-powered cars, one would declare a common deliverable to be, for example, transporting one person for 40 km every day for a year. If we assume that a gasoline powered car would last for x years, then the cost of making, maintaining and disposing of the car would be amortized over those x years and only $1/x$ of that cost would be allocated to the 1 year in question. Thus if a battery-powered car would last longer (*e.g.* y years), or an ionic liquid-containing battery-powered car would last longer, then that would be taken into account in the calculation. The pollution involved in gasoline production and gasoline burning would be counted against the gas-powered car while the pollution involved in electricity production would be counted against the battery-powered cars. I hope that helps.

Sefik Suzer asked: Thank you very much for the comprehensive overview of the past, present and future developments related with mostly chemical aspects of

ionic liquids. However, there is an ever-increasing use of ILs for electronic materials and device applications, where the volume involved might be very small, but the impact might be very significant, if successful. My comment/question is, how do you, or anybody in the audience, conceive the future developments in these fields?

Philip Jessop replied: While I am not the best person to forecast specific developments in ILs for those applications, I can suggest that applications like that are the best examples for a future in which ILs can contribute to a greener and more sustainable future. Because ILs at present are environmentally and economically costly to make, they need to be used in fields where the volume is low, the impact is high, and their unusual properties make them excel. Applications involving energy storage or increased energy efficiency, if ILs would have better performance over more conventional materials, could have environmental benefits so large that they would completely offset the negative impact of IL production. This is an exciting area of active research and very promising for demonstrating the value of ILs in a greener economy.