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# Reply to Perkin et al.: Experimental observations demonstrate that ionic liquids form both bound (Stern) and diffuse electric double layers

Perkin et al. assert that ionic liquids (ILs) should behave as strongly dissociated (uncorrelated) electrolytes and use this premise to question our approach of implementing the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory in the analysis of our experimental observations (1). Perkin et al. also assert that the long-range attraction that we observed is inconsistent with the expectation that ILs should exhibit “strong electrolyte behavior” (1).

Our direct surface force measurements unambiguously demonstrate that  $[C_4mim][NTf_2]$  behaves as a weakly dissociated electrolyte, and we further show that DLVO theory can be used to quantitatively predict the (measured) electrostatic screening behavior of  $[C_4mim][NTf_2]$  at extended surfaces, provided that the effective ionic strength is properly defined (2). We expect these observations to be relevant to other aprotic ILs.

We think that Perkin et al. have misunderstood, and therefore misrepresented, the key finding of our publication by claiming that we conclude that ILs are liquids “consisting of ion pairs of which only a small fraction are dissociated” (1). Instead, we believe that the IL ions should not be viewed as forming exclusive pairs, where each cation is coordinated to one specific anion in the liquid. As stated in our paper, our work demonstrates that  $[C_4mim][NTf_2]$  behaves as “an effectively neutral, coordinated cation–anion network that exists in equilibrium with a small fraction of effectively dissociated ions”

(2), where the “effectively dissociated ions” can be considered as thermally excited defects within the “coordinated cation–anion network.” “Coordinated” refers to specific interactions that may be present, such as hydrogen bonding, in addition to the electrostatic interactions that govern the short-range ordering of the ions within the network.

Our framework is not based on the idea that ILs “consist of ion pairs.” Therefore, the assertion by Perkin et al. that “NaCl would be expected to be an ion-pair fluid” in the context of our framework (1) is incorrect. We also point out that the presence of a coordinated network of ions is inconsistent with the expectation by Perkin et al. that ILs should behave as strongly dissociated and, hence, uncorrelated electrolytes.

We conclude by noting that we discussed the differences between surface-bound layers of  $[C_4mim][NTf_2]$  ions at gold and mica surfaces in our paper, where we also related our results to previous experimental and theoretical work on ILs (2). Since the publication of our paper, we have become aware of two additional studies that have relevance to our work. Lauw et al. (3) found that surface-bound ion layers of a  $[NTf_2]$ -based IL are enriched in cations at gold electrode surfaces, even over a range of positive electrochemical biases. Richey et al. (4) found that “only a small fraction of the ions” in  $[C_2mim][NTf_2]$  contribute to the electrostatic screening of carbon electrode surfaces, “while the majority of the remaining ions

behave like neutral aggregates similar to a solvent.”

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**1** Perkin S, Salanne M, Madden P, Lynden-Bell R (2013) Is a Stern and diffuse layer model appropriate to ionic liquids at surfaces? *Proc Natl Acad Sci USA* 110:E4121.

**2** Gebbie MA, et al. (2013) Ionic liquids behave as dilute electrolyte solutions. *Proc Natl Acad Sci USA* 110(24):9674–9679.

**3** Lauw Y, et al. (2012) Structure of  $[C_4mpyr][NTf_2]$  room-temperature ionic liquid at charged gold interfaces. *Langmuir* 28(19):7374–7381.

**4** Richey FW, Dyatkin B, Gogotsi Y, Elabd YA (2013) Ion dynamics in porous carbon electrodes in supercapacitors using in situ infrared spectroelectrochemistry. *J Am Chem Soc* 135(34):12818–12826.

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The authors declare no conflict of interest.

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