LETTER

Is a Stern and diffuse layer model appropriate to ionic liquids at surfaces?

According to a recent article in PNAS by Gebbie et al., ionic liquids (ILs) should be considered as dilute electrolyte solutions, consisting of ion pairs of which only a small fraction are dissociated (1). This claim is based upon measurements of weak attractive forces between a mica surface and a gold surface across ILs, attributed to double-layer attraction. From the decay length of the attractive force (10–13 nm), an effective free-ion concentration is deduced by fitting to a modified Derjaguin–Landau–Verwey–Overbeek (DLVO) theoretical expression. However, the overwhelming evidence from the thermodynamic and transport properties of similar ILs is that they are not composed of neutral ion pairs with simple dissociation equilibria, and, as such, the DLVO framework is inappropriate. Rather, the liquid should be considered as strongly dissociated with ions interacting to varying extents with several nearby counterions (2, 3). The authors support their assertion of weak dissociation by calculating the binding energy of an ion pair, relative to isolated ions in a dielectric medium. However, they do not contrast this with the energetics of a dense, locally charge-ordered ionic melt that is the likely state of the fluid. In the same limited framework, NaCl would be expected to be an ion-pair fluid.

The novel aspect of the experiments is the ability to fix the electrical potential of the gold surface; a monotonic, long-range attraction is observed. The result is surprising because, based on the expected strong electrolyte behavior of the liquid, the surface charge should be screened at relatively short distances. At potentials where the gold surface is expected to be negatively charged, only a weak, potential-independent attractive force is observed by Gebbie et al. (1), who attributed it to compensation of the gold surface charge by absorbed cations. However, the mica surface carries a similar negative surface charge and is presumed to be incompletely screened.

Previous surface force apparatus (SFA) experiments, with two equivalent, flat, negatively charged mica surfaces have shown a strongly oscillatory force (4). This oscillatory structure is consistent with the strongly layered ion densities found in ILs at flat surfaces of metallic and nonmetallic character in diffraction and atomic force microscopy (AFM) experiments and computer simulations. Gebbie et al. (1) explain that they are unable to resolve the oscillatory structure because their gold surfaces are not atomically smooth. However, if, as assumed by Gebbie et al., the adsorbed layers at the mica surface are unable to completely screen the surface charge, the conventional SFA experiments with equally charged mica surfaces should have seen a monotonic repulsive force at separations larger than the range of surface layering—this has not been seen in SFA experiments by four separate groups (4). Colloid-probe AFM experiments measuring interactions against potential-controlled gold surfaces, with similar resolution to Gebbie et al. (F/R, ∼0.01 mN/m) and over a wider potential range, also did not reveal any long-range forces beyond the oscillatory structure (5).

The picture of ionic liquids proposed by Gebbie et al. (1) is bold and intriguing. However, there are, at present, too many unresolved inconsistencies with the whole volume of related observations. This means that the main conclusions of the paper, as conveyed in figure 3 of ref. 1, should be considered as premature.

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