Quantized Friction across Ionic Liquid Thin Films

Electronic Supporting Information

Materials: $[C_4C_1Pyrr][NTf_2]$ was synthesized according to existing literature methods[1] at Imperial College London. The liquid was not treated by column chromatography, since this has been shown to introduce particulate impurities[2]. Ionic liquids were thoroughly washed with water then dried *in vacuo* (10^{-2} mbar, 70 °C) for 24 hours prior to injection into the SFB apparatus. Karl Fischer titration showed the water levels were <50 ppm prior to injection. SFB friction measurements were carried out using ~100 μL of ionic liquid suspended between two freshly cleaved and atomically smooth (step-free) muscovite mica sheets and at T = 22±1°C. The oscillatory normal forces provide strong evidence for the dry and clean nature of the ionic liquid; these are seen to disappear upon introducing humidity to the environment. The data in Fig. 1**d** was measured over 5 different experiments (different pairs of mica sheets and different ionic liquid samples), and at multiple contact spots on the mica for each experiment.

Determination of the load and adhesion friction coefficients: Linear fits to the measured $F_{S,k}$ and F_N data (Fig. 1d) for each i were used to obtain μ^i (gradient) and $F_{S,k}$ at F_N =0 (intercept). d^i, the distance between an anion layer and the adjacent cation layer, as obtained from the half the distance between adjacent minima in the oscillatory force law (Fig. 1c), and F_{adh} was measured from the force required to pull apart the surfaces (minima of the oscillations in Fig. 1c). R was measured from the optical interferometry. K was calibrated by applying much larger normal forces and the corresponding large flattened area measured in the interference fringes was fitted using the JKR equation. The values used to then calculate α^i using Eq. 1 (and the associated propagated errors) are shown below.

i	μ^i	error	F_{adh} (μN)	error	F_S at F_N=0	error	d^i (nm)	error	A_0(μm^2)	α^i	error
9	**0.082**	0.008	12.28	3.07	1.22	0.37	0.50	0.05	12.76	**0.18**	0.13
7	**0.125**	0.006	25.32	6.33	7.96	0.57	0.45	0.05	20.67	**0.22**	0.09
5	**0.172**	0.008	52.71	13.18	28.67	1.35	0.45	0.05	33.71	**0.23**	0.08
3	**0.812**	0.090	99.67	24.92	49.79	2.59	0.50	0.05	51.54	**0.15**	0.09

[1] M. A. Ab Rani *et al.*, Physical Chemistry Chemical Physics **13** (2011).

[2] F. Endres, S. Z. El Abedin, and N. Borissenko, Z. Phys. Chem. **220** (2006).