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Electronic Supplementary Information

Nanoconfined Ionic Liquids: effect of surface charges on flow and molecular layering

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1 SAM deposition on mica

Self-assembled monlayers of octadecyltriethoxysilane (OTE, 94% pure, ABCR Germany) were grafted on mica following a previously published protocole[1].

OTE was prehydrolyzed by dissolving 0.4470 g of silane in 50 mL of tetrahydrofuran (THF puriss. from Riedel-de Haen, Germany) containing hydrochloric acid at a concentration of 0.1 M. The solution was stirred at room temperature for 3 days. 2.5 mL of the prehydrolysis solution was then diluted in 50 mL of cyclohexane (puriss. grade, Riedel-de Haen), stirred for 30 min, filtered through a 0.2 μm PTFE membrane and brought to controlled temperature by immersion of the beaker in a thermoregulated dodecane bath. SAMs were formed by immersing the plasma-activated mica surfaces (see below) in this solution for 30s at 17°C. In order to achieve covalent grafting of the SAMs, mica surfaces were hydroxylated as follows. Two mica sheets were glued onto cylindrical lenses, cleaved with adhesive tape, transferred to the glass vessel of a plasma cleaning device, and exposed for 7 min to a plasma generated in water vapor, under a reduced pressure of 0.4 mbar. They were then immediately immersed in the silane solution.

We have checked the quality of the monolayers thus formed. The SAM-coated mica sheets were mounted in the SFA and brought into adhesive contact. The total thickness of these two monolayers in contact, measured by multiple-beam interferometry, was found to be 5.6± 0.2 nm, in good agreement with the thickness of densely-packed C_{18} SAM previously reported [1]. Besides, we have performed wetting and AFM measurements on flat mica samples silanized in the same batch as SFA samples. Wetting with water yielded contact angles of respectively 111° and 102° for advancing and receding, in excellent agreement with earlier measurements on dense and homogeneous SAM[1]. Tapping mode AFM scans of 5×5, 1×1 and 0.4×0.4 μm^2 further confirmed that the SAM surfaces were homogeneous and featureless, and as smooth as the underlying mica, with a rms roughness between 1 Å (0.4 μm scans) and 2.2 Å (5 μm scans).

2 Souce of imidazolium salts

[bmim][PF_6] (99.9% pure) was obtained from Solvionic (Toulouse, France) and used as received.

[bmim][BF_4] was synthesized, as follows, according to standard methods[2].

Synthesis of 1-butyl-3-methylimidazolium bromide

(bmimBr):

An excess of 1-bromobutane was slowly added to a stirred solution of 1-methylimidazole in ethyl acetate. The mixture was then heated at reflux for 24 h. The reaction was stopped when two phases were formed. The top phase, containing unreacted starting material in ethyl acetate, was decanted and discarded. The bottom phase contained the butylimidazolium bromide. The bottom phase was washed three times with ethyl acetate to remove any unreacted reagents (particularly 1-methylimidazole). Residual ethyl acetate was removed by heating (70°C) under vacuum (12 h). bmimBr was obtained as a colourless hygroscopic solid. The structure of the resulting salt was confirmed by 1H NMR spectroscopy (400 Mhz, $CDCl_3$, δ/ppm relative to TMS) = 0.94 (t, J=7.4 Hz, $NCH_2CH_2CH_2CH_3$); 1.35 (m, J=7.5 Hz, $NCH_2CH_2CH_2CH_3$); 1.88 (m, J=7.6 Hz, $NCH_2CH_2CH_2CH_3$); 4.10 (s, NCH_3); 4.31 (t, J=7.4 Hz, $NCH_2CH_2CH_2CH_3$); 7.41(s, CH(ring)); 7.52 (s, CH(ring)); 10.39 (s, CH(ring)).

Synthesis of 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF$_4$):

A solution of $NaBF_4$ in acetone was slowly added to a rapidly stirred solution of the prepared bmimBr. The mixture was stirred at room temperature for four days and then filtered through celite. Acetone was removed on a rotary evaporator. The resultant viscous liquid was dissolved in dichloromethane (CH_2Cl_2) and washed with small volumes of distilled water (3:1 v/v) until no precipitation of AgBr occurred in the aqueous phase on addition of a concentrated $AgNO_3$ solution. The CH_2Cl_2 was then evaporated. Traces of water and other volatile solvents were removed by freeze-drying just before starting the experiment. bmimBF$_4$ was obtained as a colourless, very viscous, hydrophilic liquid. The structures were confirmed by 1H and 13C NMR spectroscopy.

bmimBF$_4$: 1H NMR spectroscopy (400 MHz, D2O, δ/ppm relative to TMS) = 0.82 [t, J=7.4 Hz, $NCH_2CH_2CH_2CH_3$]; 1.21 [m, J=7.5 Hz, $NCH_2CH_2CH_2CH_3$]; 1.75 [m, J=7.6 Hz, $NCH_2CH_2CH_2CH_3$]; 3.79 [s, NCH_3]; 4.10 [t, J=7.4 Hz, $NCH_2CH_2CH_2CH_3$]; 7.34 [s, CH(ring)]; 7.35 [s, CH(ring)]; 8.60 [s, CH(ring)]; 13C NMR spectroscopy (300 MHz, D_2O, δ/ppm relative to TMS) = 15.37 [$NCH_2CH_2CH_2CH_3$] 21.52 [$NCH_2CH_2CH_2CH_3$]; 34.04 [$NCH_2CH_2CH_2CH_3$]; 38.35 [NCH_3]; 52.04 [$NCH_2CH_2CH_2CH_3$]; 124.97 [C(ring)]; 126.25 [C(ring)]; 138.60 [C(ring)]. ElectroSpray mass spectrometry (ESI positive): bmimBF$_4$, m/z=139.04 (bmim+).

3 Confinement of OMCTS by SAM-coated surfaces

We have performed the following control experiment in order to validate our results on RTILs confined between SAM-coated mica surfaces. After measuring quasi-static and dynamic $F_n(d)$ curves with [bmim][BF$_4$], the silanized mica surfaces were unmounted from the SFA, thouroughly rinsed with ultrapure water, ethanol and cyclohexane in order to remove the RTIL. After drying, they were installed back into the SFA and brought in adhesive contact. We checked that the total thickness of the two SAMs in contact was equal to that reported above. We then injected between the surfaces a droplet of the apolar octamethylcyclotetrasiloxane (OMCTS, purum grade, Fluka). The liquid was left to equilibrate at $T = 25°C$ for 6h, after which we measured a quasi-static approach curve. It can be seen on Fig. 1 that, in contrast to what we obtained for RTILs, (i) no adhesive interaction is observed upon approach of SAMs across OMCTS, and (ii) for $d \leq 4$ nm, repulsive forces build up while the film thickness decreases by steps of 0.7-0.8 nm, which is consistent with the short axis of the slightly oblate OMCTS molecule. This shows that OMCTS exhibits wall-induced layering when in contact with CH_3 terminated SAM, as it is also the case with bare mica[3]. After such a measurement, the SAM-coated surfaces were again unmounted, washed with cyclohexane, ethanol and water, dried, installed back in the SFA to check their thickness, and the static and dynamic measurements on [bmim][PF_6] reported in the communication were eventually performed.

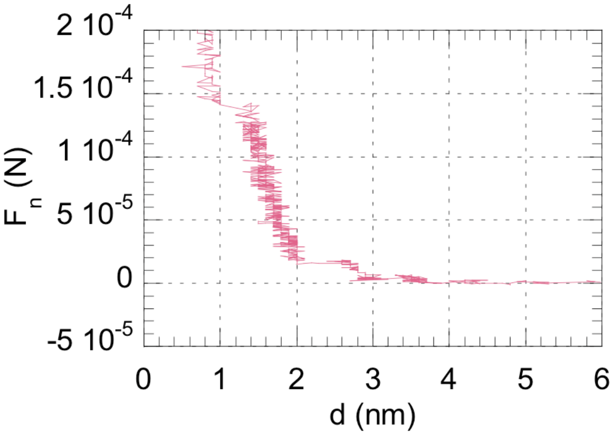

Fig. 1 $F_n(d)$ measured upon approach of SAM-coated mica across OMCTS.

References

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