Supplementary data

1. SFG experiment

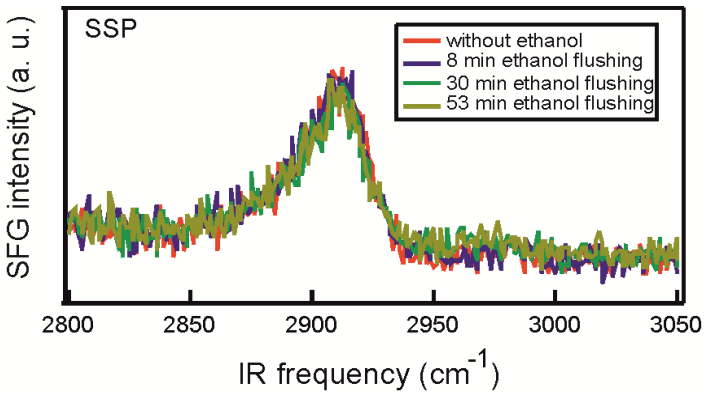

Figure 1. Sum-frequency spectrum (SSP polarization) of the PDMS-air interface without and with flushing of ethanol vapour over it.

Figure 1 depicts in red the sum-frequency spectrum for the PDMS-air interface. The spectrum consists of one peak at ~2910 cm^{-1}, assigned to the symmetric C-H stretch mode of the methyl groups (reference: Soft Matter 5 (2009) 3487). The asymmetric stretch mode at around 2970 cm^{-1} is only observed under PPP, PSS, and SPS polarization. Upon introducing ethanol vapour in the sample cell the SFG spectrum does not change: there is no vibrational resonance observed of ethanol both in the CH and OH (data not shown) spectral range. Also in PPP polarization no signals belonging to ethanol are observed. Clearly the ethanol does not stick to the hydrophobic PDMS surface.

2. The plot of h′/r defined by eqn. 19 versus different relative vapour pressures of ethanol.

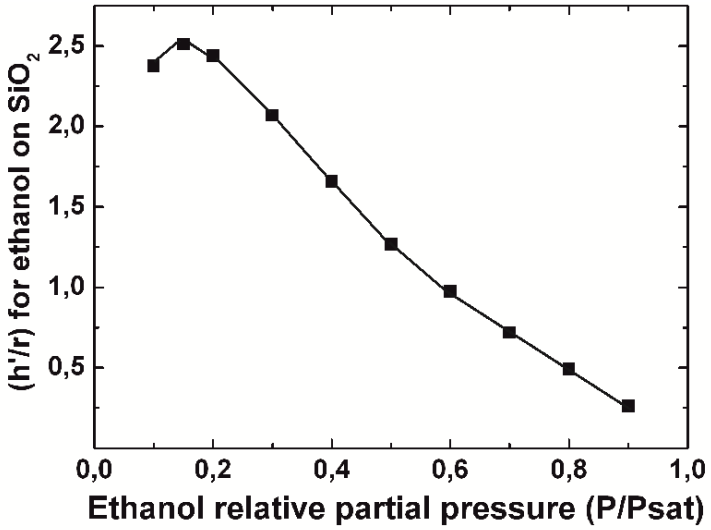

Figure 2. Ratio of ethanol physisorbed thickness (h') on SiO_2 surface (eq. 15) to ethanol meniscus radius (r) calculated from Kelvin equation at corresponding P/P_{sat} (eq. 2).

3. The values of meniscus radius as well as Laplace pressure at different relative vapor pressures of ethanol.

Table 1. P/P_{sat} – versus-meridional radius of meniscus and Laplace pressure

Ethanol P/P_{sat}	**Meridional radius of meniscus (nm)**
0.1	0.22
0.2	0.32
0.3	0.43
0.4	0.56
0.5	0.75
0.6	1.01
0.7	1.45
0.8	2.32
0.9	4.92
Ethanol P/P_{sat}	**Laplace pressure (MPa)**
0.1	99.864
0.2	68.656
0.3	51.093
0.4	39.232
0.5	29.293
0.6	19.970
0.7	15.152
0.8	9.470
0.9	4.465