Experimental Report HC- 1727

Adsorption of binary mixtures of immiscible molecules

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A new type of porous framework with immense technological potential has recently emerged, namely porous metal organic frameworks (MOFs). These three-dimensional networks can uptake significant amounts of methane, thus holding great promise as future energy storage systems. In particular they meet the US DoE target (180 times their own volume at 35 bar) for natural gas storage [1].
Samples in capillary tubes were previously equilibrated in the home laboratory with H_2O, methane and n-hexane vapours separately, and with organic – water vapour mixtures at different degrees of relative humidity. Two types of MOFs were investigated. In addition, two carbons of different pore size distribution were also measured, in order to investigate how the structure of the mixed adsorbate is affected when 1) the polar nature of the substrate is modified, and 2) the constraint of spatial confinement is relaxed.
The detailed analysis of the data is still ongoing. Figure 1 and 2 shows selected examples of the obtained response curves.

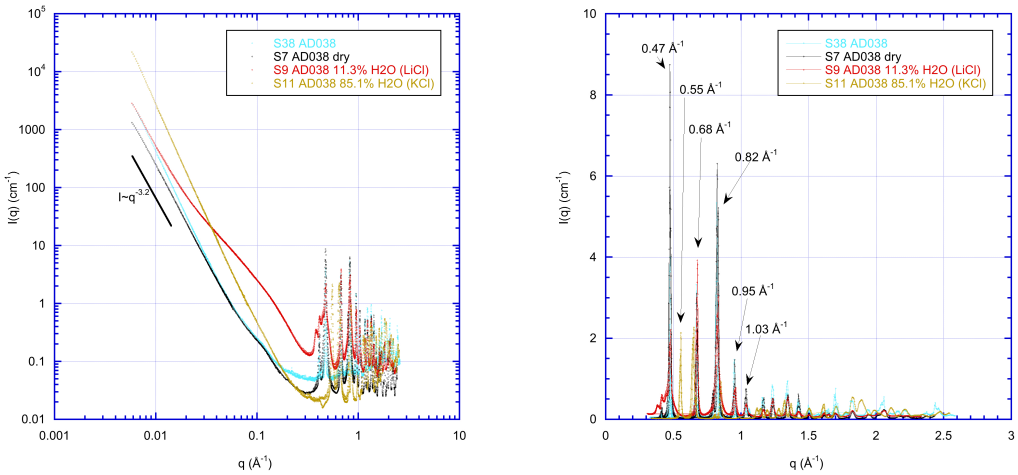

Figure 1. SAXS/WAXS (a) and WAXS (b) response of MOF *Type I* samples equilibrated at different levels of relative humidity.

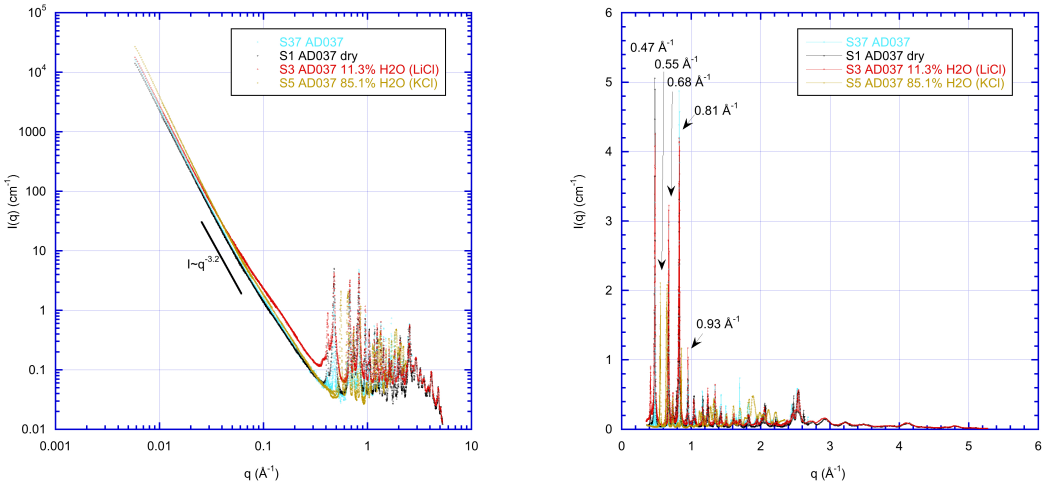

Figure 2. SAXS/WAXS (a) and WAXS (b) response of MOF *Type II* samples equilibrated at different levels of relative humidity.

Comparing the two types of MOFs we observe a difference in the SAXS regime. Beside the parallel shift at the dry samples there is a more pronounced knee in *Type I* sample at around 0.1 $Å^{-1}$, whereas the *Type II* sample looks rather featureless. The slope of 3.2 indicates surface scattering (rough surfaces). In the case of the non-dried samples a difference in the slope of the small angle regime can also be observed in *Type I*.

Concerning the WAXS signal, the major difference between the *Type I* and *Type II* is a peak at 0.74 $Å^{-1}$ that is present in the *Type II* sample (also in the dry one), but is absent from *Type I* (also from the dry one).

Concerning the water uptake of the two systems significant differences are observed: by exposing the two types of systems to the same conditions, *Type I* MOF shows significantly higher water uptake and greater structural change in the small angle region, whereas the SAXS response of the *Type II* system is almost unchanged.