Electronic Supplementary Material (ESI) for Energy & Environmental Science

Supporting Information

The supporting information contains hydration energy profiles, the results of which are referred to in the manuscript, The hydration energy profiles are for clay-molecular cation systems: $NH_2PPG_3{}^+NH_3^+$, $^+NH_3$-PPG_9-NH_3^+, NH_2-PEG_3-NH_3^+, NH_2-PMG_3-NH_3^+ and the quaternary amine $^+(CH_3)_3$-PPG_3-$(CH_3)_3^+$. See figure captions in the supporting information for additional information about the hydration energy profiles of these cations.

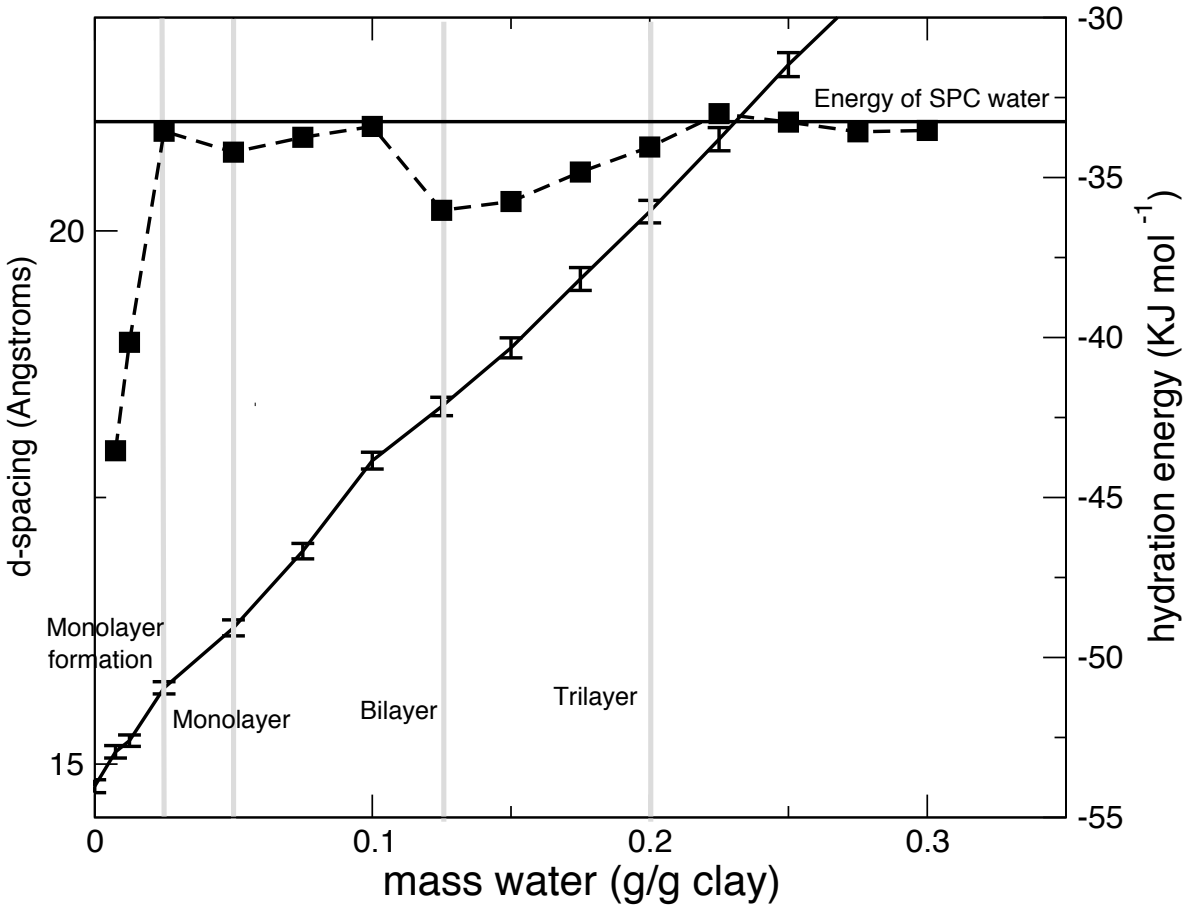

Figure 1: *d*-spacings and discrete hydration energies of montmorillonite with NH_2-PPG_3-NH_3^+ resident in the interlayer. The reference states used in eq. 2 are indicated by the grey solid vertical lines. As we assume complete cation exchange, there are twice as many organic molecules in the interlayer than for the montmorillonite-$^+NH_3$-PPG_3-NH_3^+ system, and approximately the same organic mass in the interlayer as for NH_2-PPG_6-NH_3^+. The hydration energies are very similar to that of $^+NH_3$-PPG_6-NH_3^+, indicating that the amount of organic PPG backbone for the diamine molecules in the interlayer is important.

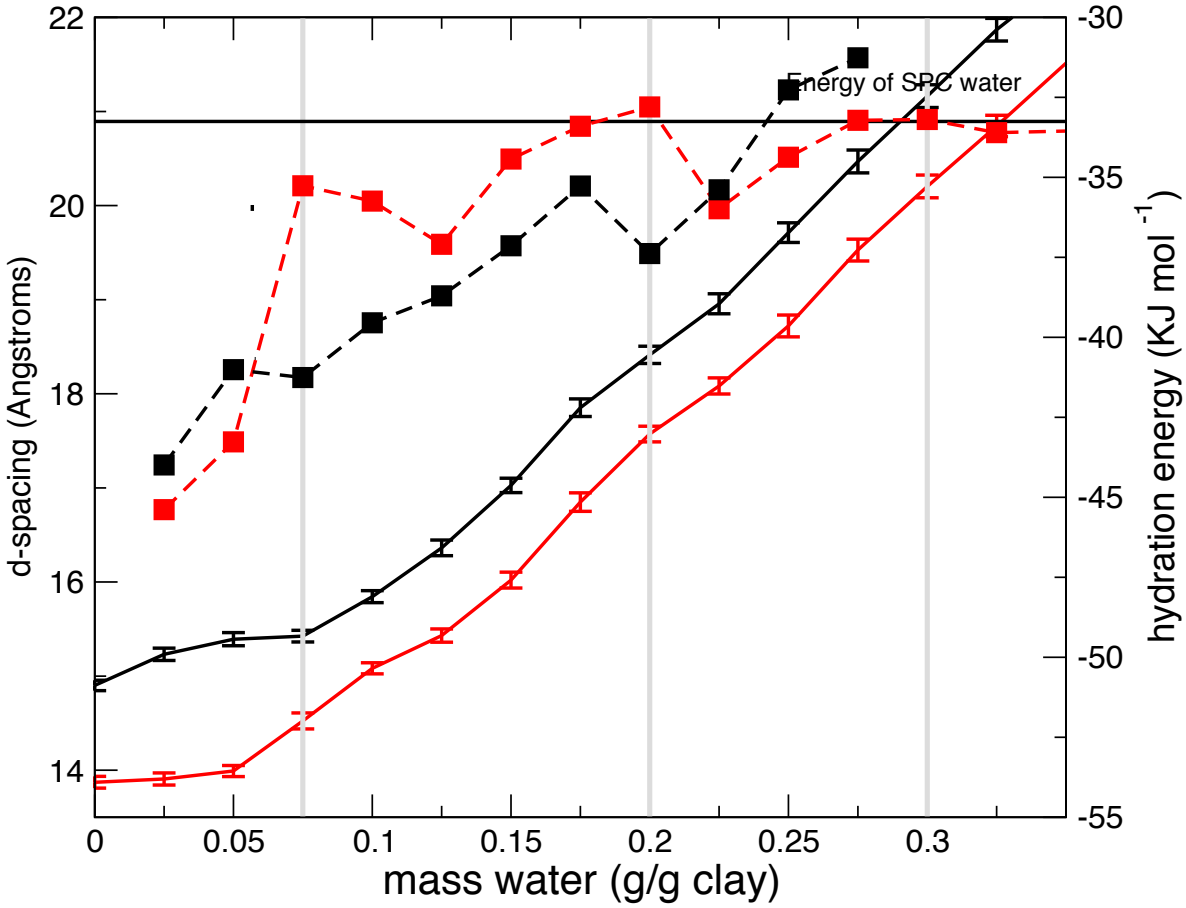

Figure 2: *d*-spacings and discrete hydration energies of montmorillonite with NH_2-PPG_3-NH_3^+ resident in the interlayer (red) and the quaternary amine equivalent, $^+(CH_3)_3$-PPG_3-$(CH_3)_3^+$ (black). The reference states used in eq. 2 are indicated by the grey solid vertical lines. We see that for the same backbone, the additional layer spacing due to the extra methyl groups cause a decrease in swelling inhibitor performance.

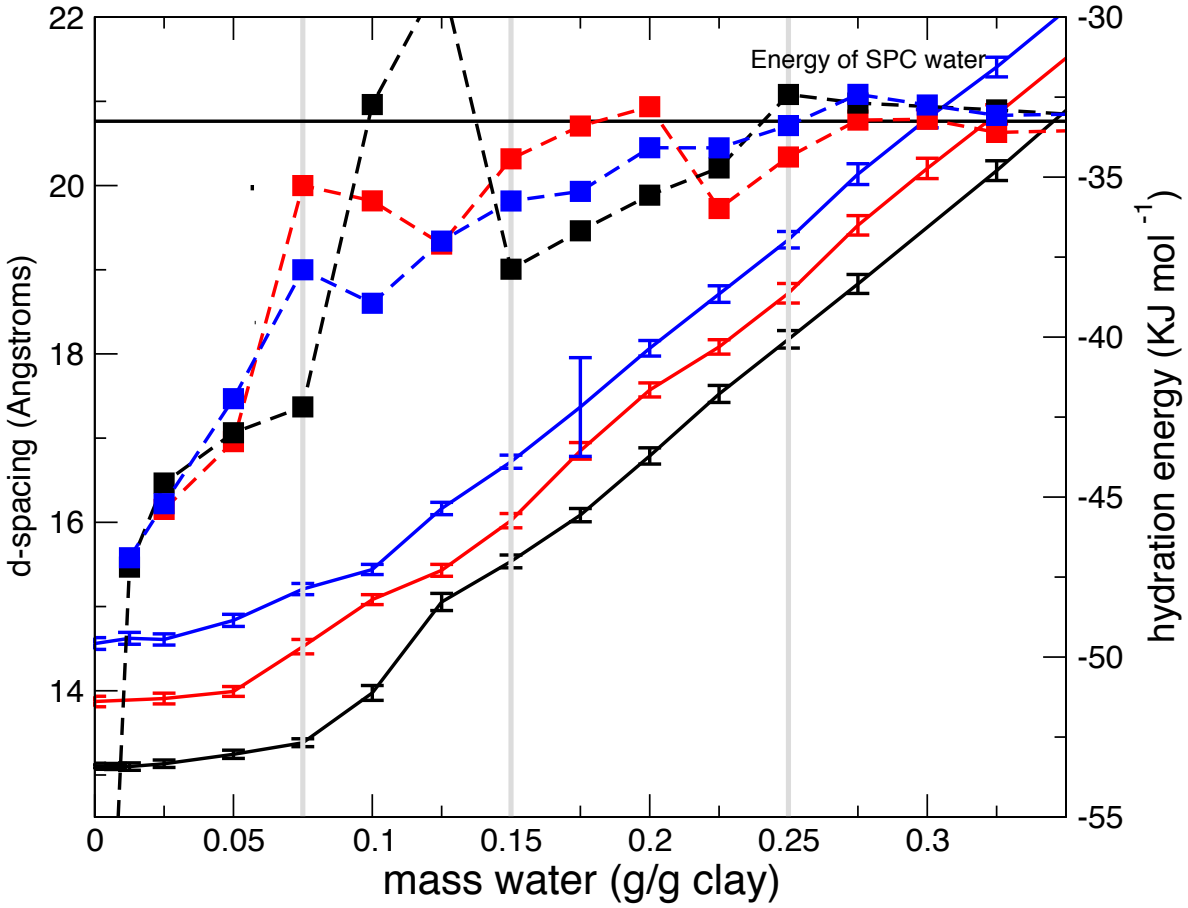

Figure 3: *d*-spacings and discrete hydration energies of montmorillonite with NH_2-PEG_3-NH_3^+ resident in the interlayer (black), NH_2-PPG_3-NH_3^+ (red) and NH_2-PMG_3-NH_3^+ (blue).The reference states used in eq. 2 are indicated by the grey solid vertical lines. The increase in hydrophobicity of the backbone increases the swelling inhibition but at progressively higher water contents.