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$_2$PPG$_3$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-$^+\text{NH}_3$-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 $^+\text{NH}_3$-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 $\text{NH}_2$-PPG$_3$-$\text{NH}_3^+$ resident in the interlayer (red) and the quaternary amine equivalent, $+(\text{CH}_3)_3$-PPG$_3$-$(\text{CH}_3)_3^+$ (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.