

IMMOBILIZATION OF 1,10-PHENANTHROLINE BY MONTMORILLONITE AND SAPONITE – DFT STUDY

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This work provided molecular-level insight into the adsorption and intercalation of organic molecules into layered structures of clay minerals and investigated interactions between 1,10-phenanthroline (*phen*) and the layered clay minerals montmorillonite and saponite using density functional theory (DFT) method for the solid state. *Phen* is a planar heteroaromatic bidentate ligand containing two nitrogen donor atoms and is widely used in coordination chemistry¹. Since dispersion interactions act in these hybrid systems, the D3 scheme for their correction was employed. The main objective was to characterize the structural, energetic, and vibrational properties of the resulting hybrid systems and to identify the interactions responsible for their stabilization. Representative models *phen* associated with both clay minerals were constructed and subsequently geometrically optimized. Their structural stability was evaluated based on calculated intercalation energies, with particular attention to hydrogen bonds. First-principles molecular dynamics (FPMD) was used for the examination of vibrational properties of the studied systems by analysis of the projected densities of states², focusing on *phen* functional groups. Differences in structural stability of the studied hybrid systems based on the two different clay minerals were associated with their distinct structural characteristics. In particular, the trioctahedral structure of saponite, compared with the dioctahedral structure of montmorillonite, favoured the formation of a more energetically stable hybrid system with *phen* ($-569 \text{ kJ}\cdot\text{mol}^{-1}$ and $-290 \text{ kJ}\cdot\text{mol}^{-1}$, respectively). The results show that the stability of the studied systems is governed by a combination of strong electrostatic interactions, weak hydrogen bonds, dispersion forces, and π - π interactions (Fig.1).

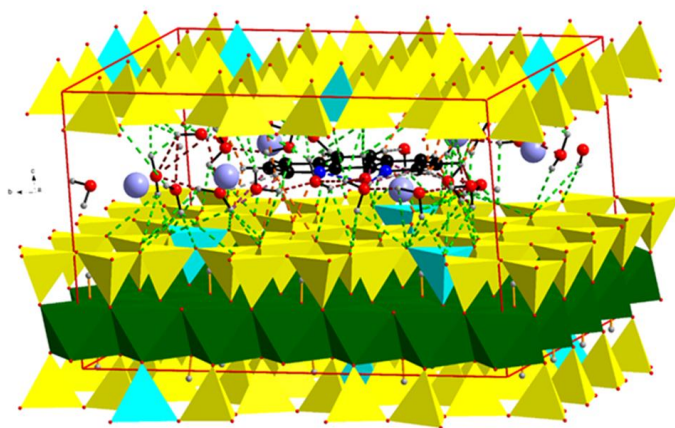


Fig.1 Preferred hybrid system: *phen-sap* and its interlayer space featuring hydrogen bonds.

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