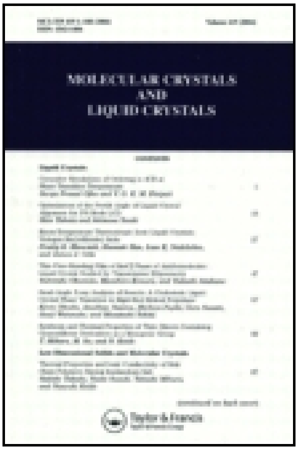

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Molecular Mechanics Simulations of Intercalates

Pavla Čapková [a] & Jiří Votinský [b]

[a] Faculty of Mathematics and Physics, Charles University, Ke Karlovu 3, 12116, Prague, Czech Republic

[b] Faculty of Chemical Technology, University Pardubice, Náměstí legií 565, 53210, Pardubice, Czech Republic

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Molecular Mechanics Simulations of Intercalates

PAVLA ČAPKOVÁ[a] and JIŘÍ VOTINSKÝ[b]

[a]*Faculty of Mathematics and Physics, Charles University, Ke Karlovu 3, 12116 Prague, Czech Republic and* [b]*Faculty of Chemical Technology, University Pardubice, Náměstí legií 565, 53210 Pardubice, Czech Republic*

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Intercalated layered structures of phyllosilicates, phosphates and graphite, have been analysed using molecular mechanics simulations (Cerius^2). The startegy of modelling was based on the experiment (x-ray diffraction, IR and Raman spectroscopy...). A generalizing overview of the structural characteristics is focused on the arrangement of guest species and on the stacking of layers. A classification scheme based on the ordering of the interlayer structure and mutual positions of the host and guest layers has been proposed as a result of the present structure analysis.

Keywords: molecular simulations; intercalates; phyllosilicates; phosphates

INTRODUCTION

The intercalation of layered structures is an intense area of material research aimed at the development of new materials with desirable physical and chemical properties [1-4]. Intercalation is an insertion of guest species into the interlayer space, which leads to the modification of properties via the modification of the interlayer structure, hence the understanding of the structure-property relationship is crucial for the design of new intercalates. Intercalation can be characterized as a positioning of known molecules into a known layered structure. Consequently the structure analysis of intercalates is usually focused to the determination of positions, orientations and arrangement of the guest molecules in the interlayer space and to determination of layer stacking. [5,6] Intercalated structures usually exhibit certain degree of disorder in their interlayer crystal packing and consequently in the layer stacking. As a consequence of this disorder, it is not possible to prepare single crystals of reasonable size for the diffraction analysis and the samples in such a disordered structures are available in a powder form only (intercalated smectites, vanadyl phospates etc..). The powder diffraction pattern, affected by the disorder, is in addition affected by the preferred orientation of disk-shaped particles. Consequently the conventional X-ray diffraction alone can not solve all the specific structural problems. In such a case molecular simulations represent very useful complementary tool in the structure analysis of intercalates.

Molecular simulations predict the crystal structure and properties using energy minimization [7]. The crystal energy in the molecular mechanics simulation is described by an empirical force field. The potential energy for an arbitrary geometry of a molecule or crystal structure is expressed as a superposition of valence (bonded) interactions and non-bonded interactions (i.e. Van der Waals, Coulombic and hydrogen bond). The valence interactions consist of bond stretch, bond-angle bend, torsion and inversion terms (for more details see for example [7]. Molecular mechanics simulations in *Cerius*^{2} modelling environment (Molecular Simulations Inc.) have been used to investigate the structures of vanadyl and zirconium phosphate intercalated with small organic molecules [8,9] and phyllosilicates intercalated with inorganic and organic guest species [5,10,11] and graphite, intercalated with tantalum chloride [12].

Clearfield [1] has appointed general rules for the process of intercalation. The process will occur if some concomitant factors are satisfied: (1) the host-guest interaction must be stronger than the mutual interactions of the guest molecules with themselves (if they constitute the liquid phase) or with the solvent molecules (if they are dissolved); (2) the surface of the layers of the host structure should possess active sites or groups, or a polar character, (3) the layers must allow the accommodation of the guest molecules, that means the weak interlayer bonding and no steric hindrance to the free diffusion of the guest molecules.

Intercalation of layered structures results in a system with a regular or irregular stacking of host and guest layers. The disorder on layer stacking may exhibit two characteristic features:

(1) First is a random stacking of two or more basal spacings corresponding to the host structure and intercalated structure with one or more guest layers between two host layers. (The multilayer arrangement of guest molecules is typical for the intercalation of water and has been observed in hydrated myoglobin crystals [13], hydrated phospholipids [14] and in $Na_{1/3}(H_2O)_yTaS_2$ system [15]).

(2) Second feature is the displacement disorder, that means the mutual shift of two successive host layers, caused by the insertion of a guest layer. This is the most usual disorder in intercalated layered structures.

One of the most interesting phenomena as to the layer stacking is the staging, observed in graphite intercalation compounds. Pure stage *n* is a periodic sequence of *n* host layers and one guest layer. (For a more detailed description of graphite intercalation compounds see for example [4]). During the process of intercalation and deintercalation the phase transition between stages occur. That means the real samples contain domains of pure stages with the phase boundaries of mixed stages, where the layer stacking is irregular [16,17]. Present work is focused to the interlayer crystal packing of guest molecules and displacement disorder of the host layers in dependence on the host-guest interaction and on the structural features of host layers and guest species.

STRATEGY OF MODELLING

Strategy of modelling, i.e. the building of the initial models, set up the energy expression, choice of the force field, conditions of energy minimization etc., was based on experiment. In present work we used the results of x-ray powder diffraction and vibrational (IR and Raman) spectroscopy to create the strategy of modelling. The initial models have been built using the known structure of host lattice and guest species. From the X-ray powder diffraction (XRPD) pattern of intercalate we obtained the basal spacing, the lattice parameter characterizing the structure of host layer and the information about the character of the structural disorder. The vibrational spectroscopy provide us with the information about the character of the host-guest interaction and about a possible distortion of host layers and guest species. Consequently experimental results allow us to define the "rigid units" in the initial model, (host layers and guest species), which can be treated as rigid bodies with non-bond mutual interactions during energy minimization. The rigidity of layers must be verified by experiment in each individual case. Then the energy calculations take into account the non-bond terms only, i.e. van der Waals interactions (VDW), Coulombic interactions (COUL), hydrogen bonding (H-B), and hydrostatic pressure. During the energy minimization, the rigid units can be translated and rotated and the unit cell parameters varied [10,11].

RESULTS AND CONCLUSIONS.

The results of modeling for various combinations of host structures and guest species led to the conclusions, allowing to appoint some general criteria for the crystal packing of intercalates as to the in plane arrangement of guest molecules and displacement disorder of host layers. The intercalated layered structures can be divided into four main groups:

1. Intercalates with disordered guest species in the interlayer and disordered layer stacking : DG-DLS (disordered guests, disordered layer stacking).
2. Intercalates with ordered interlayer guest structure and disordered layer stacking: OG-DLS (ordered guests, disordered layer stacking).
3. Intercalates with ordered interlayer guest structure and ordered layer stacking: OG-OLS (ordered guests, ordered layer stacking).
4. Intercalates with partially ordered guest structure and partially ordered layer stacking: POG-POLS. (Disorder in layer stacking in all mentioned cases in this paragraph means the displacement disorder).

Intercalates DG-DLS exhibit following characteristic features: the absence of a pronounced active sites on the host layers; very weak polar character of the host layers and guest species; the structure of guest species does not fit in the structure of host layers (see fig.1); the guest-guest interaction is comparable with host-guest interaction energy and guest molecules can create clusters [5] in the interlayer space. Examples: montmorillonites and hectorites intercalated with organic (tetramethylammonium [19]) and inorganic (Keggin cation [5,18]) species.

Intercalates OG-DLS can be characterized by the following features: the host layers do not posses a pronounced active sites allowing to anchor the guests at certain special positions. The repulsion in guest-guest interaction is strong enough to keep the two-dimensional order of guest species in the interlayer space. The in-plane structure of the guest layer is incommensurate with the structure of the host layer (see figure 2). Example: graphite, intercalated with tantalum chloride [12].

Intercalates OG-OLS consist of the host layers, which posses the striking active sites, where the guest species can be anchored by a certain well defined way, that means there is no disorder in the position and orientation of the guest molecules. The steric conditions in the interlayer space - i.e. the size and shape of guest molecules attached to the host layers - allow the regular stacking of the layers (see figure 3). Then the structure of intercalate posses the 3-dimensional periodicity [11] with a possible slight disorder in layer stacking [9]. Example: vermiculite, intercalated with tetramethylammonium and aniline [11] *and zirconium phosphate intercalated with ethanole* [9].

Intercalates POG-POLS posses active sites on the host layers, but the anchoring of guest molecules to the host layers may show certain degree of an orientational and/or positional disorder. This partial disorder in the interlayer structure leads to the partial disorder in layer stacking, where the diffraction pattern exhibits the predominant *00l* reflectins and only few very smoothed *hkl* reflections. Examples: vanadyl phosphate intercalated with ethanole [6] (see figure 4), propanole and butanole. Present structure analysis of intercalates is

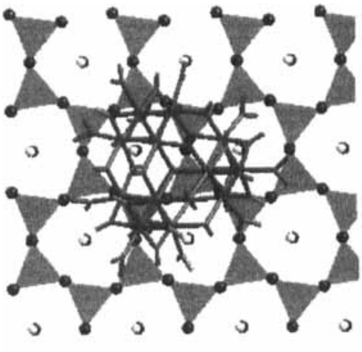

FIGURE 1 Keggin cation attached to tetrahedral sheet of montmorillonite

See Color Plate I at the back of this issue.

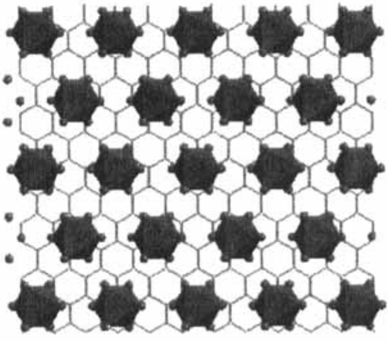

FIGURE 2 $TaCl_6$-octahedra arranged in graphite interlayer space

See Color Plate II at the back of this issue.

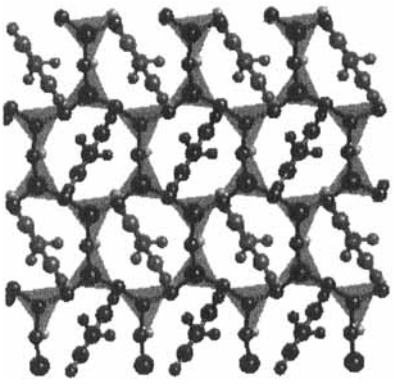

FIGURE 3 Aniline cations between adjacent tertrahedral sheets of vermiculite

See Color Plate III at the back of this issue.

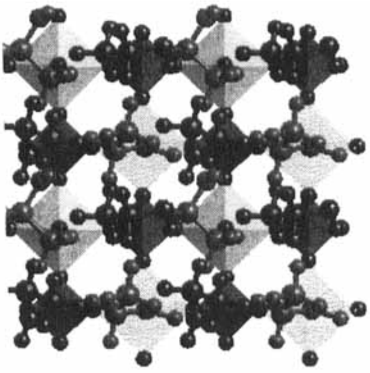

FIGURE 4 Bilayer arrangement of the etahanole molecules in $VOPO_4$

See Color Plate IV at the back of this issue.

based on molecular mechanics simulations, where the strategy of modelling was created using experimental results of X-ray diffraction and vibrational - IR and Raman spectroscopy. This structure analysis provide us with the detailed model of structure including the characterization of the disorder, the character of the host-guest interactions and the total sublimation energy.

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