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Modeling in Structure Analysis of Vanadyl Phosphate Intercalated with 1-Alkanols

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Abstract Molecular mechanics simulations supported by X-ray powder diffraction measurements have been used to investigate the structure of vanadyl phosphate intercalated with 1-alkanols $C_nH_{2n+1}OH$ for n = 2, 3, 4. Modeling revealed the specific features and differences in arrangement of alkanol molecules with different chain length, depending on the relation between the parameters of active sites network and size of guest molecules. This result enabled us to explain the irregularities in dependence of basal spacing on the chain length. The comparison of experimental d_{exp} and calculated d_{calc} values of basal spacing showed the good agreement of modeling with x-ray powder diffraction. While we obtained $d_{calc}(Univ) = 13.05$ Å for vanadyl phosphate-ethanol using the Universal force field (d_{exp}=13.17 Å), for vanadyl phosphate-propanol and vanadyl phosphate-butanol better agreement with experiment was obtained using the Tripos force field. In the case of vanadyl phosphate-propanol the calculated basal spacing $d_{calc}(Tripos) = 14.49$ Å, compared with an experimental value of d_{exp}=14.36 Å. For vanadyl phosphate-butanol $d_{calc}(Tripos) = 17.71$ Å and d_{exp}=17.90 Å.

Keywords Vanadyl phosphate-alkanol intercalates, Molecular mechanics, Structure analysis

Introduction

Vanadyl phosphate- and zirconium phosphate-alkanol intercalates may be considered as very good starting materials for the intercalation of other polar organic molecules. [1,2]

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Previous X-ray diffraction studies of vanadyl phosphate-alkanol intercalate [3] revealed irregularities in basal spacing increments depending on the alkyl chain length. Comparing the experimental basal spacing for $VOPO_4$-ethanol d = 13.17 Å, $VOPO_4$-propanol d = 14.36 Å and $VOPO_4$-butanol d = 17.90 Å, one can see that one additional carbon atom causes the increment of basal spacing $\Delta d = 1.19$ Å in the case of propanol and 3.54 Å in the case of butanol. In the present work we have used molecular mechanics simu-

lations in the *Cerius²* [4] modeling environment to investigate the structure of VOPO₄-alkanol intercalates and to explain the irregularities in the dependence of basal spacing on the number of carbon atoms *n* in the alkyl chain for *n* = 2, 3, 4.

Alkanol intercalates of vanadyl phosphate exhibit a certain degree of disorder in the arrangement of guest molecules and in layer stacking. Thanks to this disorder, it is almost impossible to prepare a single crystal of reasonable size for diffraction analysis. Powder diffraction patterns affected by the disorder are in addition influenced by the strong preferred orientation of disk-shaped particles. As a result of this disorder we can see on the diffraction pattern predominant *00l* reflections and only a few broad *hkl* reflections and thus the information content of such a powder pattern is very limited. It is evident that using this diffraction data we are not able to solve the structure with the conventional structure analysis based on diffraction only. In such a case molecular simulations represent very useful complementary tool for investigation of these structures. However, from powder diffraction we can obtain the basal spacing and from the character of the pattern we can indicate the type and the degree of disorder. All this information is useful for the strategy of modeling.

Experimental basis for the strategy of modeling

Vanadyl phosphate dihydrate was prepared by boiling a mixture of V_2O_5 in diluted H_3PO_4 under reflux for 14 hours [5]. The product was filtered and washed with distilled water several times. The yellow solid was dried in ambient air at room temperature. The intercalation compounds of 1-alkanols with $VOPO_4$ were obtained by suspending microcrystalline $VOPO_4 \cdot 2H_2O$ in dry liquid alcohol. The reaction mixture was placed in a 15 ml glass flask equipped with a reflux condenser and put into a waveguide of a microwave generator with stirring and heating and exposed to a microwave field for 10 minutes [6,7]. After cooling, the solid product formed was filtered off and dried at room temperature under nitrogen. The content of guests in intercalates was determined by the thermogravimetric method.

The powder diffraction measurements were carried out using a HZG-4 powder diffractometer with CuKα radiation (Ni filter), the CuKα2 intensities were removed from the original data. Silicio powder was used as external standard. In order to suppress the preferred orientation of crystallites, the following procedure was applied: A piece of a flat glass serving as a sample holder was coated with silicon grease and then sprinkled with finely ground powder of $VOPO_4 . 2H_2O$. Vapors prepared by bubbling dry nitrogen through liquid alcohol were blown on the sample. The whole process of intercalation was continually checked by X-ray diffraction.

The measured diffraction patterns are shown in Figures 1a - c for ethanol (a), propanol (b) and butanol (c). The experimental values of basal spacings are summarized in Table 2. As one can see in Figures 1a - c, the basal reflections *00l*

are dominant in diffraction pattern thanks to two main circumstances:

• In spite of the special preparation of powder samples for diffraction measurements, there is still a certain degree of preferred orientation present in these samples.

• The *hkl* and *hk0* reflections are broad and smoothed thanks to the displacement disorder in VOPO₄ layer stacking.
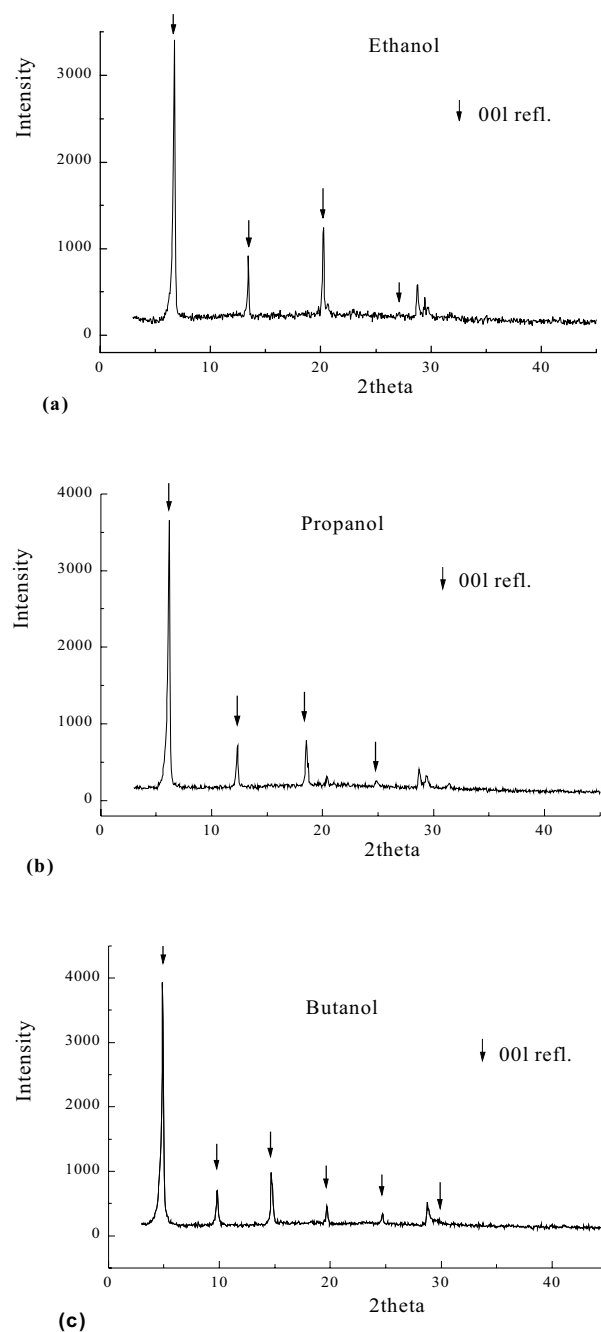

Figure 1 *X-ray powder diffraction pattern of ethanol (**a**), propanol (**b**) and butanol (**c**). Basal reflections* 00l *are marked by arrows*

In all three diffraction patterns we can observe one strong *200* reflection at the same position (2θ ~ 28.73 Å), showing that the $VOPO_4$ lattice parameter of the host structure ~ 6.21 Å did not change during intercalation.

Strategy of modeling

The initial models of intercalates $VOPO_4 \cdot 2C_nH_{2n+1}OH$ (for n = 2, 3, 4) were built using the known structure data of the host compound vanadyl phosphate dihydrate $VOPO_4 \cdot 2H_2O$. This structure was determined by Tietze [8] and refined by Tachez et al. [9] as tetragonal, space group *P4/n*, *a = b =* 6.215 Å, *c* = 7.403 Å and *z* = 2. The host structure of $VOPO_4 \cdot 2H_2O$ consists of infinite sheets of VO_6 octahedra and PO_4 tetrahedra linked by shared oxygen atoms [8,9]. One water molecule W_1 is attached with its oxygen atom to vanadium to complete the VO_6 octahedron. The second water molecule W_2 is hydrogen-bonded to PO_4 oxygen atoms and to the first water molecule W_1. During the intercalation process, the water molecules are replaced by 1-alkanol molecules in the interlayer space.

The strategy of modeling is described in details in [10,11]. Our previous IR and Raman spectroscopic study of $VOPO_4$-ethanol intercalates [12] and the fact that interlayer water can be replaced by alkanol molecules reversibly led us to the two basic assumptions:

• assumption of rigid layers and rigid guests during the energy minimization and

• consideration of the non-bond host-guest interactions

The assumption of rigid layers is also supported by the diffraction data, which show the same $VOPO_4$ layer lattice parameter 6.21 Å for the host structure and alkanol intercalates. Taking into account the non-bond host-guest interactions only, we neglect the weak bond interaction between the vanadium and alkanol-oxygen atom. Our previous structure analysis of vanadyl phosphate-ethanol intercalate showed that this approximation can cause a discrepancy between the experimental and calculated basal spacing, which is within the limits of experimental error. The Crystal Packer Module in the Cerius[2] modeling environment can be used for minimization of the total non-bond interaction energy. Crystal Packer is a computational module which estimates the total sublimation energy and packing of molecular crystals. Energy calculations in Crystal Packer take into account the non-bond terms only, i.e. van der Waals interactions (VDW), Coulombic interactions (COUL), hydrogen bonding (H-B), internal rotations and hydrostatic pressure. The asymmetric unit of the crystal structure is divided into fragment-based rigid units. Non-bond (VDW, COUL, H-B) energies are calculated between the rigid units. During the energy minimization, the rigid units can be translated and rotated and the unit cell parameters varied. In the initial model five rigid units have been assigned to one unit cell: $VOPO_4$ layer and four $C_nH_{2n+1}OH$ molecules.

For VDW we used the well known Lennard-Jones functional form, with the arithmetical radius combination rule. A non-bond cut-off distance for the VDW interactions was 10.0 Å. Van der Waals parameters from Universal [13] and Tripos
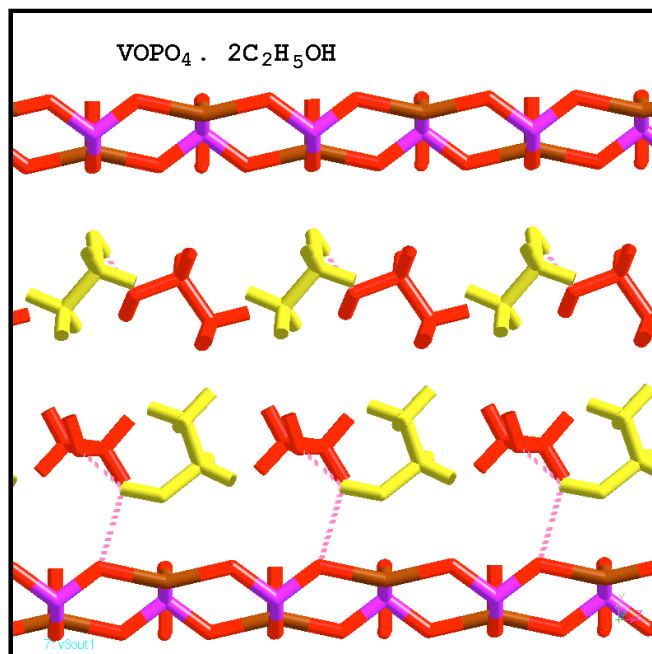

Figure 2 *Side view of the arrangement of ethanol molecules in the interlayer space of $VOPO_4$. Yellow ethanol molecules are attached to vanadium (brown)*
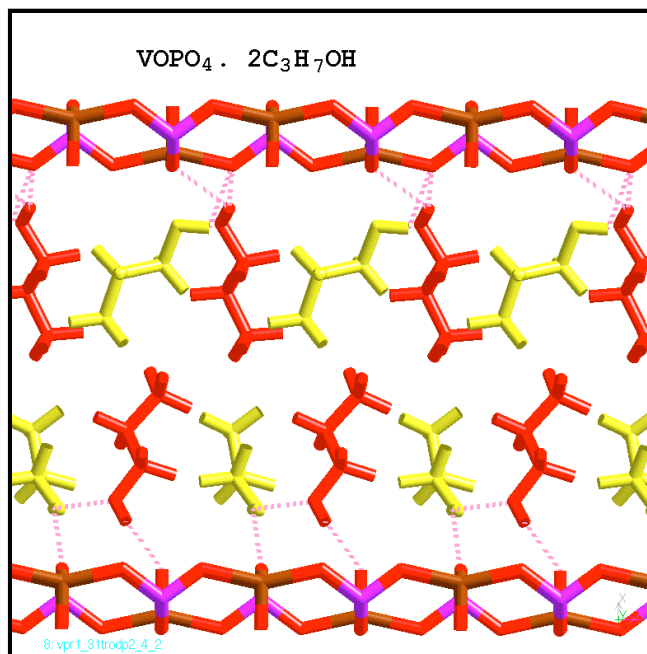

Figure 3 *Side view of the arrangement of propanol molecules between $VOPO_4$ layers (Colors as in Figure 2)*
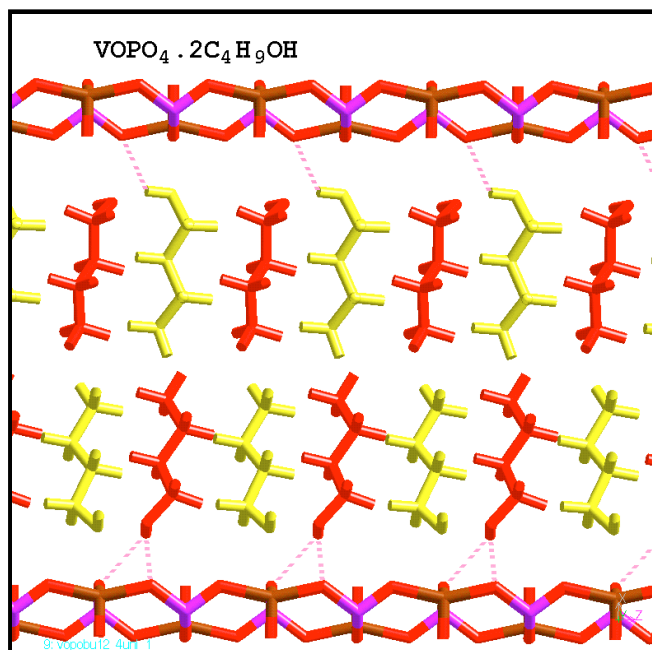
Figure 4 *Side view of the arrangement of butanol molecules between VOPO$_4$ layers (Colors as in Figure 2)*

Figure 5 *Fragment of the VOPO$_4$-propanol structure showing the attachment of propanol molecules to the host layer. The propanol anchored at vanadium **1** and propanol **2** is hydrogen bonded to the anchored propanol and to VOPO$_4$ layer oxygen atoms. Hydrogen bonds are marked with dotted pink lines.*

force fields [14] have been used and the results were compared with experimental data. The hydrogen bond term was a CHARM-like angle dependent potential, with Dreiding coefficients [15]. The Ewald summation method [16] was used to calculate the Coulombic energy in a crystal structure. The Ewald sum constant was 0.5 Å^{-1}. The minimum charge taken into the Ewald sum was 0.00001e. All atom pairs with separation less than 12 Å were included in the real-space part of the Ewald sum and all reciprocal-lattice vectors with lengths less than 0.5 Å^{-1} were included in the reciprocal part of the Ewald summation. Charges in crystals are calculated in Cerius^2 using the QEq-method (Charge equilibrium approach). This method is described in details in the original work [17]. A series of initial models with a slightly different positions and orientations of the guest molecules were built with ethanol, propanol and butanol. Several preliminary minimization cycles with and without external pressure 20 kbar have been performed at the beginning of the final minimization procedure to approach the global minimum. The modified Newton algorithm has been used for energy minimization.

Results and discussion

The bilayer arrangement of 1-alkanol molecules between VOPO$_4$ layers calculated for ethanol, propanol and butanol is shown in Figures 2, 3 and 4. One half from the total number of alkanol molecules is anchored with their oxygen atoms to VOPO$_4$ layers at vanadium, to complete the VO$_6$ octahedra.
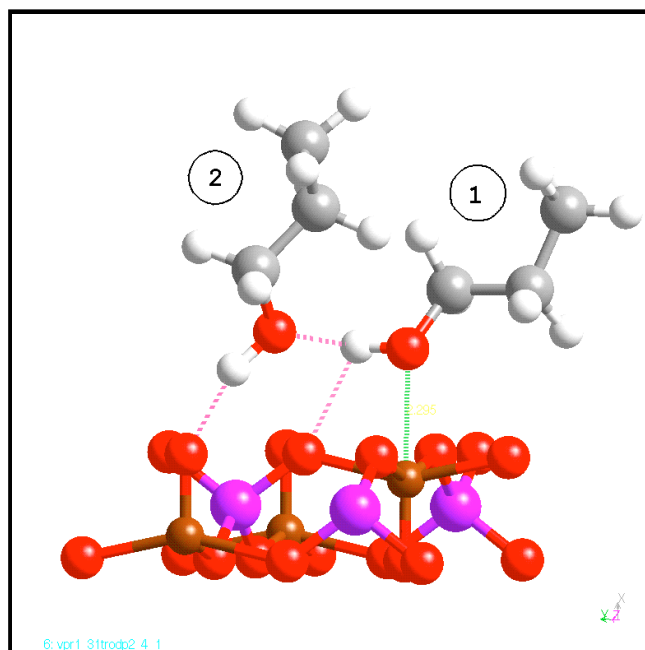
The rest of alkanol molecules is hydrogen bonded to the anchored alkanol molecules and/or to the PO$_4$ oxygen atoms. There is no regular hydrogen bond network in VOPO$_4$-alkanol intercalates. Figure 5 illustrates the attachment of the alkanol molecules to VOPO$_4$ layers, showing the fragment of structure

VOPO$_4$·2C$_3$H$_7$OH where one propanol molecule (**1** in Figure 5) is anchored at vanadium and the second one (**2**) is hydrogen bonded to the first one and to VOPO$_4$ oxygen atoms. The series of minimized models for ethanol-, propanol- and butanol-intercalate with nearly the same total sublimation energy and with slightly different orientations of guest molecules with respect to layers showed the disorder in arrangement of alkanol molecules in the interlayer space and disorder in layer stacking.

The cylindrical visualization mode in Figures 2 - 4 enables us to compare the orientation of alkanol molecules with respect to VOPO$_4$ layers. In case of VOPO$_4$-ethanol and VOPO$_4$-propanol one can see that the alkanol molecules anchored at vanadium (yellow in Figures 2 - 4) and alkanol molecules which are hydrogen bonded (red in Figures 2 - 4) have significantly different tilting angle to VOPO$_4$ layers. The tilting angle ϕ is defined as the angle between the O-C$_T$ line (Oxygen-terminal carbon atom line) and basal plane of VOPO$_4$ layer. On the other hand for VOPO$_4$-butanol intercalate one can see in the Figure 4 that the tilting angles of the two alkanol molecules are not as different as in Figures 2 and 3. Taking

Table 1 *The limits of tilting angles* ϕ *between the alkanol chains and basal plane of the VOPO$_4$ layer, the range of tilting angles* $\Delta\phi$ *and the average value of tilting angles* ϕ_{av} *for the three intercalates: VOPO$_4$-ethanol, VOPO$_4$-propanol and VOPO$_4$-butanol; n is the number of carbon atoms in the alkanol chain;* Δz *is the difference between the lowest cartesian z-coordinate in the upper guest layer and highest z-coordinate in the lower guest layer (z - perpendicular to layers),* Δz *characterizes the partial overlap of guest layers.*

Intercalant in VOPO$_4$	n	Limits of ϕ (°)	$\Delta\phi$ (°)	ϕ_{av} (°)	Δz (Å)
Ethanol	2	3.9 – 80.1	76.2	42.0	1.4
Propanol	3	41.0 – 71.1	30.1	56.0	0.48
Butanol	4	61.9 – 83.3	21.4	71.6	0.74

into account the whole series of minimized models for all three intercalates, we summarize in Table 1 the limits of tilting angles ϕ, the range of tilting angles $\Delta\phi$ and the average values of tilting angles ϕ_{av} (averaged over all minimized models and alkanol molecules **1** and **2**).

To characterize the mutual position of two adjacent guest layers, we show in the last column of Table 1 the guest layer distance Δz, calculated as the difference between the lowest Cartesian z-coordinate in the upper guest layer and the highest z-coordinate in the lower guest layer (z - perpendicular to layers). This value of Δz characterizes the mutual distance or overlap of guest layers in the interlayer of VOPO$_4$. One can see that this difference is lowest in the case of propanol guest molecules $\Delta z = 0.48$ Å. This means the upper and lower guest layers are partially overlapping (taking into account the VDW

radii). This overlap contributes to the highest interlayer density for this intercalate.

The packing density in one guest layer adjacent to the host layer is shown in Figures 6 - 8 for the three intercalates investigated. This projection onto the basal plane illustrates the steric conditions for the arrangement of guest molecules. In VOPO$_4$ layers the active sites are vanadium atoms. These active sites create a square network with the lattice parameter 6.21 Å. This lattice parameter enables the wide range of tilting angles ϕ in the case of ethanol molecules. One characteristic feature observed in the arrangement of ethanol and propanol molecules is the substantially different tilting angle between the neighboring alkanol molecules. In the case of butanol, the tilting angles ϕ between the neighboring alkanol molecules are not so different, as one can see from Table 1
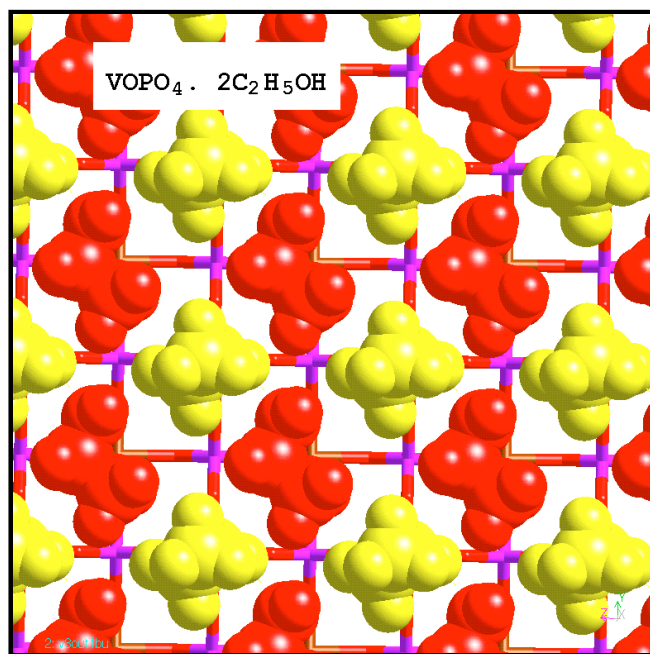

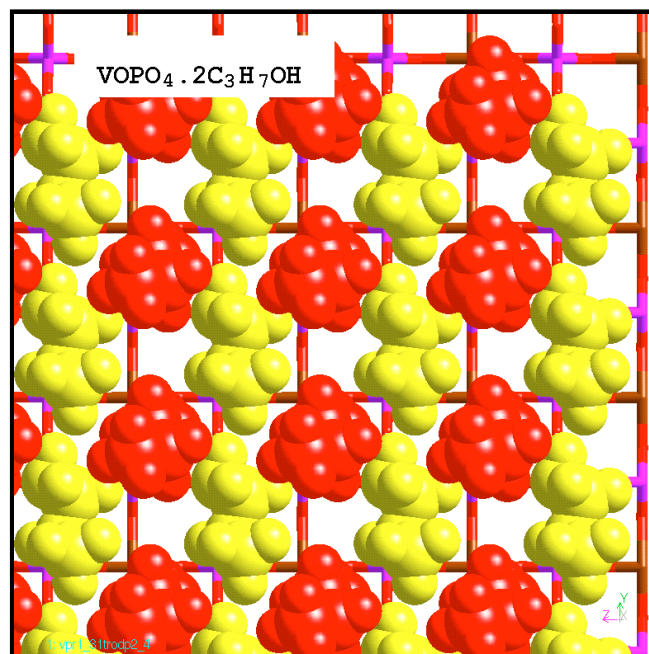**Figure 6** *The upper view of the ethanol layer attached to VOPO$_4$ layer*

Figure 7 *The upper view of the propanol layer attached to VOPO$_4$ layer*

Table 2 *Comparison of experimental basal spacing d_{exp} and those calculated using the Tripos d_{exp} and Universal force fields d_{Univ}. In the last column are the interlayer densities g_{int} for VOPO$_4$ – ethanol, VOPO$_4$ – propanol and VOPO$_4$ – butanol; n is the number of carbon atoms in the alkyl chain.*

Intercalant in VOPO$_4$	n	d_{exp} (Å)	d_{Trip} (Å)	d_{Univ} (Å)	g_{int} (g·cm^{-3})
Ethanol	2	13.17	12.75	13.05	0.86
Propanol	3	14.36	14.49	15.00	0.98
Butanol	4	17.90	17.71	18.12	0.93

and Figure 8, due to the relatively dense packing of butanol molecules within one guest layer.

Table 2 summarizes the experimental (d_{exp}) and calculated basal spacings using the Tripos (d_{Trip}) and Universal force fields (d_{Univ}) and the interlayer density (g_{int}), calculated for the experimental basal spacing. As one can see in Table 1, in the case of the VOPO$_4$-propanol intercalate with maximum interlayer density, we obtained the best agreement between experimental and calculated basal spacing using the Tripos force field. On the other hand, for VOPO$_4$-ethanol intercalate with the lowest interlayer density, the best agreement with experiment has been obtained using the Universal force field.

Conclusions

Summarizing the results we can see that the irregular increment of basal spacing with increasing number of carbon atoms in the alkyl chain is accompanied with the anomalous course of interlayer density g_{int} and guest layer distance Δz in dependence on the chain length. In the case of bilayer arrangement of guest molecules, the interlayer density and the basal spacing of intercalates are governed by the molecular packing within one guest layer and by the mutual distance (or overlap) of two adjacent guest layers. The arrangement of molecules within the guest layer is a result of competition between the host-guest and guest-guest interactions, affected by the distribution of active sites in the host layer. The present modeling results show that the relationship between the parameters of the active sites network and the size and shape of the guest molecules is an important factor governing the structure of intercalates.

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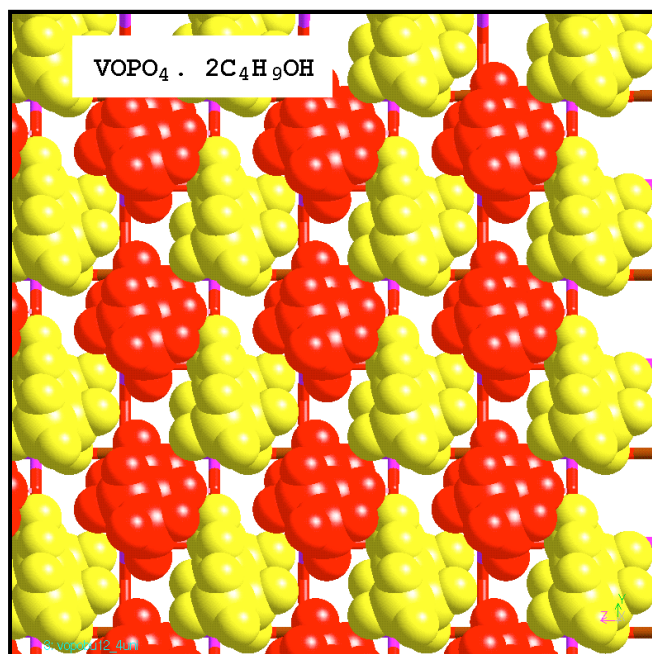

Figure 8 *The upper view of the butanol layer attached to VOPO$_4$ layer*

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