



## 2-Alkanol Intercalated VOPO<sub>4</sub> and NbOPO<sub>4</sub>: Structure Modeling of Intercalate Layers

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### Abstract

Intercalates of VOPO<sub>4</sub>·2H<sub>2</sub>O and NbOPO<sub>4</sub>·3H<sub>2</sub>O with a homologous series of 2-alkanols (from 2-propanol to 2-undecanol) were prepared and characterized by X-ray powder diffraction, thermogravimetric analysis, and IR spectroscopy. A method for structure modeling of the intercalate layers is described and possible arrangements of alkanol carbon chains in the intercalates are discussed. A bimolecular packing of the guest molecules in the interlayer space was proposed as the most plausible with regard to the determined interlayer distance and stoichiometry.

### Introduction

Vanadyl and niobyl phosphates form a number of intercalation compounds with molecular guests having a Lewis base character [1]. The intercalations of, for example, aliphatic and aromatic amines [2–7], heterocycles [8–10], carboxylic acids and their derivatives [11–13], aliphatic alcohols and diols [14–19], and ketones [20] have been investigated.

The reaction of solid VOPO<sub>4</sub>·2H<sub>2</sub>O with liquid or molten solid 1-alkanols and 1,ω-alkanediols in a microwave field leads to intercalation compounds with the composition VOPO<sub>4</sub>·2C<sub>n</sub>H<sub>2n+1</sub>OH (*n* = 2–18) or VOPO<sub>4</sub>·C<sub>n</sub>H<sub>2n</sub>(OH)<sub>2</sub> (*n* = 2–10) [16]. The structure of all polycrystalline layered complexes retains the original layers of (VOPO<sub>4</sub>)<sub>∞</sub>. The molecules of alcohols are placed between the host layers in a bimolecular arrangement, being anchored to them by donor-acceptor bonds between the oxygen atom of the OH group and the vanadium atom as well as by hydrogen bonds. The molecules of diols, on the other hand, using similar bonds, form, in a monomolecular arrangement, bridges linking the adjacent layers of the host. The aliphatic chains of both intercalated alcohol and diol molecules have an *all-trans* configuration and their axes are perpendicular to the host layers. Similar complexes of niobyl phosphate and arsenate with 1-alkanols and 1,ω-alkanediols have been studied [17]. In this case, the aliphatic chains of both guest types are slightly tilted to the host layers.

Much attention has been paid to compounds containing vanadium and phosphorus for their possibility to be used as catalysts in oxidative hydrocarbon reactions. The composition and the morphology of the precursors of these catalysts are shown to be controlled by the choice of the alcohol selected to carry out the dehydration and reduction

of VOPO<sub>4</sub>·2H<sub>2</sub>O [21]. Precursors prepared from 1-alkanols comprise VOHPO<sub>4</sub>·0.5H<sub>2</sub>O crystals for which the (220) reflection is virtually the only feature of the diffraction pattern, whereas precursors prepared from 2-alkanols give VOHPO<sub>4</sub>·0.5H<sub>2</sub>O for which the (001) reflection is the dominant feature of the diffraction pattern. This indicates that the two sets of alcohols produce precursor crystals with distinctly different morphologies. 3-Pentanol and 3-hexanol show identical behavior to the corresponding 2-alkanol, however, use of 3-octanol leads to the exclusive formation of VO(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>. The differences in boiling point of the various alcohols are not considered to be important since the range of boiling points for each carbon number is relatively small. It is possible that the alcohols are incorporated in the structure of the precursor and so there may be a steric factor associated with the structure of the alcohol playing the main role.

This paper presents the results of intercalation of 2-alkanols into vanadyl and niobyl phosphates.

### Experimental

#### Preparation

Vanadyl phosphate dihydrate and niobyl phosphate trihydrate were synthesized as previously described [22, 23]. The intercalates of both hosts with 2-alkanols were prepared by reintercalation reactions. The solid propanol intercalated hosts [16, 17] were prepared in a first step and used as a starting material for the reactions with alcohols. The intercalates of VOPO<sub>4</sub> were obtained by contact of 0.35 g VOPO<sub>4</sub>·2C<sub>3</sub>H<sub>7</sub>OH with a mixture of 4 mL of 2-alcohol and 5 mL of toluene. The intercalates of NbOPO<sub>4</sub> were prepared by suspending 0.4 g NbOPO<sub>4</sub>·2C<sub>3</sub>H<sub>7</sub>OH in 5 mL of dry

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liquid alcohol. The reaction mixtures were exposed to a microwave field for about 10 min. The solid products formed were filtered off. All samples for X-ray diffraction analyses were left with a small residue of the respective alcohol to avoid hydrolysis. The samples for TG-DTA and elemental analyses were washed with dry toluene and dried in dry nitrogen at room temperature.

### Analyses

The TGAs of the intercalates were performed with a Derivatograph MOM (Hungary), the measurements being carried out in the temperature interval of 30–600 °C in air at a heating rate of 5 °C/min. The weight of the samples was 100 mg. In some cases the composition was controlled by elemental analysis (C, H).

### Diffraction measurements

The powder data of the intercalates with a minor surplus of the guest alcohol were obtained with an X-ray diffractometer (HZG-4, Germany) using  $\text{CuK}\alpha 1$  radiation ( $\lambda = 1.54051 \text{ \AA}$ ) with discrimination of the  $\text{CuK}\beta$  by a Ni-filter. The  $\text{CuK}\alpha 2$  intensities were removed from the original data. Silicon ( $a = 5.43055 \text{ \AA}$ ) was used as internal standard. Diffraction angles were measured from  $1.5^\circ$  to  $37^\circ$  ( $2\theta$ ).

### IR spectral measurements

Infrared spectra of the solid intercalates were measured in Nujol suspensions in the region of  $4000\text{--}400 \text{ cm}^{-1}$  using a Perkin-Elmer 684 spectrometer.

### UV VIS reflectance spectra

A dual-beam JASCO V570 UV-VIS-NIR spectrometer equipped with an integrating sphere attachment ISN-470 was used for the measurements of diffuse reflectance spectra.

### A method for structure modeling of the intercalate layers

The aim of the structure modeling is to find the most effective and plausible arrangements of the guest molecules in the interlayer space of the host agreeing with the experimental data. Both host layers lie in the plane perpendicular to the  $z$  axis, in the mutual distance of  $c$ . Firstly, a compact arrangement of the guest molecules was constructed and the layers of the host were then attached to it. The whole process can be described in the following points:

(1) Fictitious coordinates of atoms of 2-alkanol molecules were calculated in an orthogonal coordinate system so that the molecules had configurations discussed further. The oxygen atom of the OH group was placed at the origin of the coordinates. Initially, the chain axis (a line connecting centers of the C—C bonds) was chosen to be parallel with the  $z$  axis. The bond lengths  $l_{\text{CC}} = 1.537 \text{ \AA}$ ,  $l_{\text{CO}} = 1.40 \text{ \AA}$ ,  $l_{\text{CH}} = 1.05 \text{ \AA}$  and angles  $\angle \text{CCC} = 112.6^\circ$ ,  $\angle \text{OCC} = 106.2^\circ$  and  $\angle \text{HCH} = 109^\circ$  were used for the calculation of the atomic coordinates [24, 25].

- (2) The chain was tilted to the layer plane at a chosen angle  $\alpha$  by its rotation in the  $xz$  plane. Similarly, the chain was oriented in the direction of the diagonal of the tetragonal lattice by rotation in the  $xy$  plane.
- (3) The coordinates of the neighboring 2-alkanol molecules anchored to the same layer were generated by translation of the original molecule by the  $a$  parameter in the direction of the  $x$  and/or  $y$  axes.
- (4) The chains were then oriented in the  $xy$  plane (every chain was rotated by an angle  $\beta$  around its OR atom) so that the space was most effectively filled with the guest molecules and the distances between the hydrogen atoms of the neighboring chains were greater than  $2.4 \text{ \AA}$  (two van der Waals radii of hydrogen).
- (5) The coordinates of the atoms of the molecules anchored to the upper host layer were obtained from the coordinates of the molecules anchored to the lower layer by inversion and then translation.
- (6) The coordinates of the chains of the molecules anchored to the upper host layer were translated so that they approached the lower layer of the molecules and the space was most fully and most homogeneously filled with the guest. Simultaneously, the distance between two hydrogen atoms of the  $\text{CH}_3$  and  $\text{CH}_2$  groups could not be distinctly less than  $2.4 \text{ \AA}$ .
- (7) The  $l_{\text{O1O2}}$  distance between oxygen atoms of the guest molecules anchored to the lower and upper host layer was obtained as a simple difference between the  $z$  coordinates of these two oxygen atoms. The  $l_{\text{V-OR}}$  length of the bond between vanadium and oxygen of the alkanol molecule was calculated from the equation

$$c = l_{\text{layer}} + l_{\text{O1O2}} + 2 \cdot l_{\text{V-OR}} \quad (1)$$

where  $c$  is the basal spacing of the intercalate and  $l_{\text{layer}}$  is the thickness of the  $(\text{VOPO}_4)_\infty$  layer defined as a distance between two sheets of the vanadium atoms in the layer ( $1.28 \text{ \AA}$ ) [26].

- (8) The vanadium atoms of the lower and upper host layers were placed at the distance  $-l_{\text{V-OR}}$  and  $+l_{\text{V-OR}}$ , respectively, from the oxygen atoms of the alkanols in the direction of the  $z$ -axis. The  $x$  and  $y$  coordinates of the vanadium atoms are the same as those for the corresponding coordinated oxygen atoms of the guest molecules. The positions of other atoms of the host layers were then calculated using known structure parameters [26]. Finally, all atoms were shifted so that the vanadium atom of the lower layer has coordinates of  $[0, 0, 0]$ .

## Results and discussion

### Preparation and characterization of intercalates

Only 2-propanol can be intercalated directly into vanadyl phosphate dihydrate. The intercalates of vanadyl phosphate with longer 2-alkanols and all intercalates of niobyl

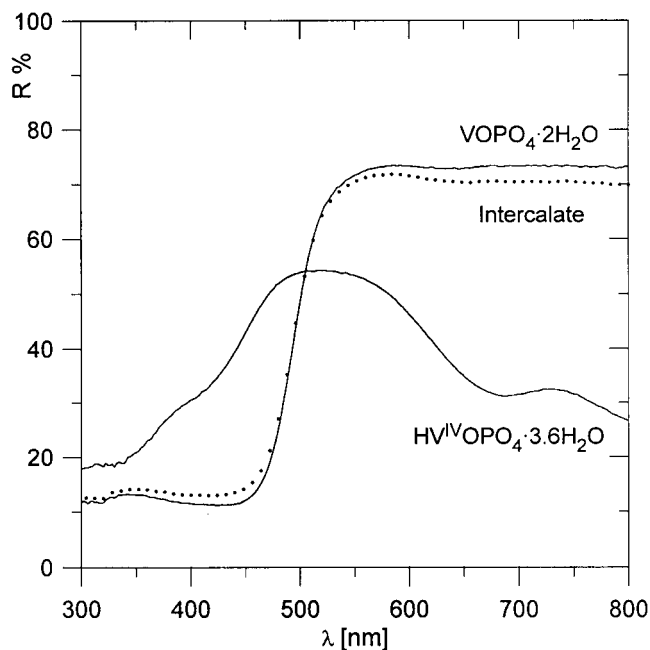


Figure 1. UV VIS reflectance spectrum of 2-octanol intercalated  $\text{VOPO}_4$  together with the spectra of  $\text{V}^{\text{V}}\text{OPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{HV}^{\text{IV}}\text{VOPO}_4 \cdot 3.6\text{H}_2\text{O}$ .

phosphate had to be prepared by substitution of these 2-alkanols for 1-propanol in 1-propanol intercalates of both hosts. The intercalates of  $\text{VOPO}_4$  were obtained from a mixture of the corresponding alcohol and toluene because  $\text{VOPO}_4 \cdot 2\text{C}_3\text{H}_7\text{OH}$  dissolves in pure alcohol. The intercalates of vanadyl phosphate are yellow. The valence of vanadium in the products was confirmed by their UV VIS reflectance spectra. The spectrum of 2-octanol intercalated  $\text{VOPO}_4$  is given in Figure 1 together with the spectra of  $\text{V}^{\text{V}}\text{OPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{HV}^{\text{IV}}\text{VOPO}_4 \cdot 3.6\text{H}_2\text{O}$  [27]. As can be seen from the figure, the spectrum of the intercalate is similar to that of  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ , which indicates that no significant reduction of vanadium (V) occurs during intercalation. Attempts to prepare intercalates with 3-heptanol, 3-octanol and 4-octanol were not successful.

The intercalates prepared were crystalline solids and their diffractograms showed a series of sharp (00 $l$ ) reflections. As an example, the diffractograms of 2-octanol intercalated  $\text{VOPO}_4$  and  $\text{NbOPO}_4$  are given in Figure 2. The  $a$  parameter of the tetragonal lattice was determined from the diffraction lines (110) and (200) and from (200) for niobyl and vanadyl phosphates, respectively. The values found for the  $a$  and  $c$  lattice parameters are presented in Table 1. The results of thermogravimetry for all complexes together with several checking analyses of carbon and hydrogen content showed that the intercalates of 2-alkanols (except 2-propanol and 2-butanol) have the stoichiometric quotient  $x = 0.99 \pm 0.07$ , hence their composition most probably corresponds to the formula  $\text{MOPO}_4 \cdot \text{C}_n\text{H}_{2n+1}\text{OH}$  ( $M = \text{V}, \text{Nb}$ ). The stoichiometric quotient found for the 2-propanol and 2-butanol intercalates is higher (see Table 1).

Infrared spectra were measured to elucidate interactions between the guest molecules and the host lattice. The valence vibration band of the  $\text{M}=\text{O}$  group ( $M = \text{V}, \text{Nb}$ ) in

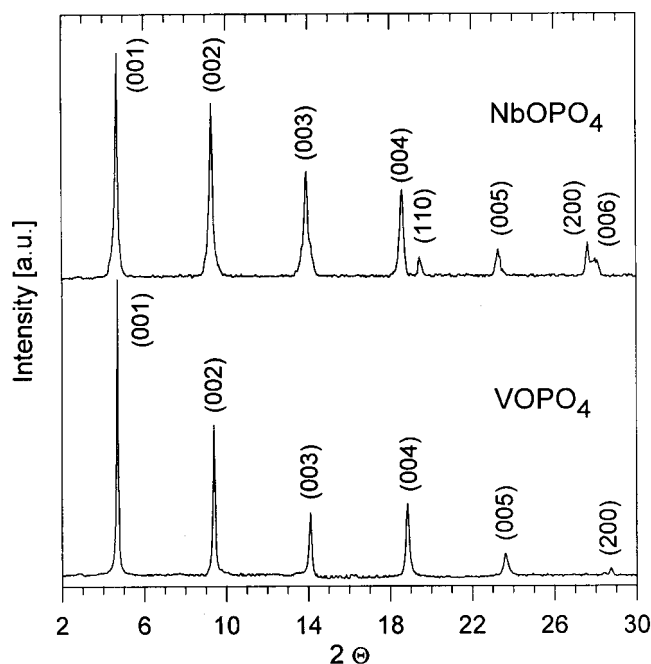


Figure 2. The diffractograms of 2-octanol intercalated  $\text{VOPO}_4$  and  $\text{NbOPO}_4$ .

Table 1. Lattice parameters and content  $x$  of 2-alkanols in the intercalates

2-alkanol	$\text{VOPO}_4$			$\text{NbOPO}_4$		
	$a[\text{\AA}]$	$c[\text{\AA}]$	$x$	$a[\text{\AA}]$	$c[\text{\AA}]$	$x$
2-propanol	6.22	13.12	1.45	6.47	13.63	1.50
2-butanol	6.21	14.02	1.20	6.46	14.32	1.17
2-pentanol	6.22	15.60	1.05	6.47	16.07	0.99
2-hexanol	6.20	16.83	0.95	6.46	17.16	1.07
2-heptanol	6.21	17.85	0.98	6.46	18.18	0.98
2-octanol	6.21	18.84	0.93	6.47	19.15	0.93
2-nonanol	6.20	19.87	1.04	6.46	20.10	1.01
2-decanol	6.22	20.76	1.01	6.47	21.13	0.85
2-undecanol	6.22	22.17	0.97	6.46	22.52	1.10

this type of compound is sensitive to the donor ability of the ligand which coordinates the metal atom at the position opposite to the oxygen atom [8, 28]. In the case of phosphates, this band is overlapped by the intense bands of the  $\text{PO}_4$  tetrahedron. Therefore an IR spectrum of the  $\text{NbOAsO}_4$  intercalate with 2-hexanol was measured. The  $\nu(\text{Nb}=\text{O})$  vibration in this intercalate was observed at  $1005 \text{ cm}^{-1}$ . This indicates that the donor-acceptor bond between an oxygen atom of 2-alkanol and the niobium atom is probably weaker than in the case of  $\text{NbOAsO}_4 \cdot 4\text{H}_2\text{O}$  ( $998 \text{ cm}^{-1}$ ) [6], the intercalates of 1-alkanols [17] or anhydrous  $\text{NbOAsO}_4$  [29]. Several broad bands in the region from  $3600$  to  $3100 \text{ cm}^{-1}$  were found, which could be assigned to a valence vibration of the OH group affected by the interaction of the alcohol with the host lattice.

The  $\text{MOPO}_4$  intercalates with 2-alkanols are distinctly less stable than that with 1-alkanols [16, 17]. The former are very quickly decomposed in humid air (with relative humid-

Table 2. Parameters of straight lines calculated from the dependences of the basal spacings on the number of carbon atoms in the guest chains and angles  $\alpha_1$  and  $\alpha_2$  for 'pseudomonomolecular' and bimolecular arrangements, respectively

	Slope [ $\text{\AA}$ ]	y intercept [ $\text{\AA}$ ]	$R^2$	$\alpha_1$	$\alpha_2$
VOPO <sub>4</sub>	1.107	9.94	0.997	59.9	25.6
NbOPO <sub>4</sub>	1.101	10.32	0.997	59.4	25.5

ity of 50%) being completely hydrated to VOPO<sub>4</sub>·2H<sub>2</sub>O or NbOPO<sub>4</sub>·3H<sub>2</sub>O within several minutes. The thermal stability of the intercalates studied is also very low in comparison with the 1-alkanol intercalates, for instance the NbOPO<sub>4</sub> intercalate with 2-hexanol is decomposed at a temperature as low as 40 °C.

#### Structural model of an intercalate layer

To the best of our knowledge, a total structure of an intercalate containing organic molecules with aliphatic chains has not been determined yet. The main reason is that no monocrystal of such an intercalate has been prepared. Diffractograms of polycrystalline samples usually have a turbostratic structure so that the structure of the intercalate could not be solved by a refinement from the X-ray powder data. Nevertheless, an angle  $\alpha$  under which aliphatic chains of the guest molecules are tilted to the plane of the host layer can be found from the X-ray powder data. It is presumed that the straight chains of the guest have the *all-trans* configuration with all carbon atoms lying in the same plane [30]. The value of  $\alpha$  is determined from the increment of the basal spacing given by the prolongation of the guest chain by one carbon atom ( $\Delta c/\Delta n$ ) according to the relationship

$$\alpha = \arcsin \left( \frac{1}{m} \cdot \frac{\Delta c/\Delta n}{\Delta h/\Delta n} \right), \quad (2)$$

where  $m$  is a number of the guest-molecule layers in the interlayer space of the intercalate and  $(\Delta h/\Delta n) = 1.279 \text{ \AA}$  is an increment of the chain length per one carbon atom presuming that the chains are perpendicular to the host layers [16].

A dependence of the basal spacing of the intercalates studied on the number of carbon atoms in the chain is given in Figure 3. The dependence is linear (Table 1) except for the 2-propanol and 2-butanol intercalates. Therefore, these intercalates were excluded from the following linear regression computations. The slope ( $\Delta c/\Delta n$ ) and the y intercept of the linear dependence are given in Table 2 together with the correlation coefficient.

It is obvious from the value of the stoichiometric coefficient ( $x = 1$ ) and IR spectra that there is one oxygen atom of the OH group (OR atom) complementing one coordination polyhedron of V or Nb. Completing one distorted VO<sub>6</sub> octahedron can be achieved in two different ways: (i) alkyl chains are interdigitated in the interlayer space so that the increment of  $\Delta c/\Delta n$  corresponds to the addition of one C—C bond ( $m = 1$ ) to the guest system and a 'pseudo-

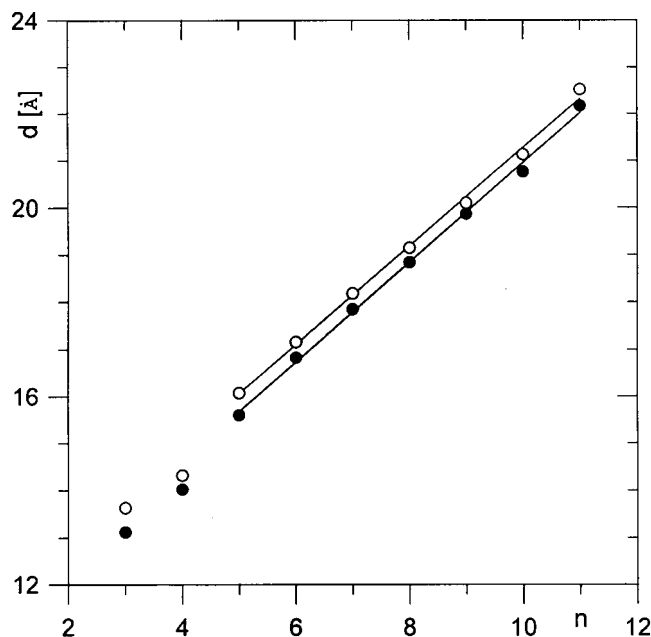


Figure 3. Basal spacing  $d$  of the VOPO<sub>4</sub> (closed circles) and NbOPO<sub>4</sub> (empty circles) intercalates with 2-alkanols as a function of the number  $n$  of the carbon atoms in the chain of the guest molecules.

monomolecular' arrangement of the guest molecules in the interlayer space of the intercalate is formed. (ii) The alkyl chains are tilted more than in the former case and they are deposited in a bimolecular manner ( $m = 2$ ). The angles  $\alpha_1$  and  $\alpha_2$  for both these cases are given in Table 2 and the problem will be discussed later in more detail.

It also follows from the stoichiometry that the distance between oxygen atoms of the guests anchored to the same layer is given by the distance between metal atoms in the host layer, that is, by the  $a$  parameter of the tetragonal lattice. The alkyl chains are arranged so as to fill the interlayer space most homogeneously. Taking into consideration the steric requirements of 2-alkanol molecules, their chains must be placed so as to avoid mutual collisions of their hydrogen atoms, that is, at a distance greater than twice the value of the van der Waals radius of hydrogen ( $2 \times 1.2 \text{ \AA}$ ). These requirements relatively strictly determine the mutual positions of the chains provided that the chains take the energetically most convenient *all-trans* configuration [30]. The van der Waals width of this chain is then calculated as  $2 \times (l_{\text{CH}} \cdot \sin 54.5^\circ + 1.2) = 4.12 \text{ \AA}$ .

To achieve an as close as possible arrangement of the alkyl chains, the hydrogen atoms of the methylene groups in one chain fit into bends in a zigzag-shaped backbone of the neighboring chain. The periodical arrangement of the alkyl chains is then formed (Figure 4) with a periodicity (i.e., a distance between the axes of the chains) of at least  $\Delta l_{90} = 4.09 \text{ \AA}$ . When the chains are tilted to the layer at an angle  $\alpha$  lower than  $90^\circ$ , the distance  $\Delta l_{\text{FG}}$  between functional groups anchored to the host layer should be greater than  $4.09 \text{ \AA}$  (see Figure 5). In that case, only certain values of  $\alpha$  are possible to retain the closest packing of the neighboring chains and these  $\alpha$  values are given by expressions

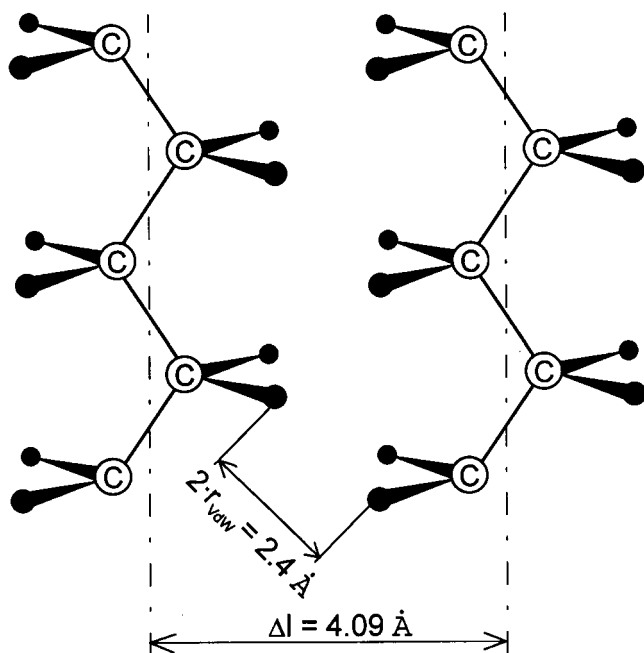


Figure 4. The most closely packed arrangement of the *all-trans* aliphatic chains.

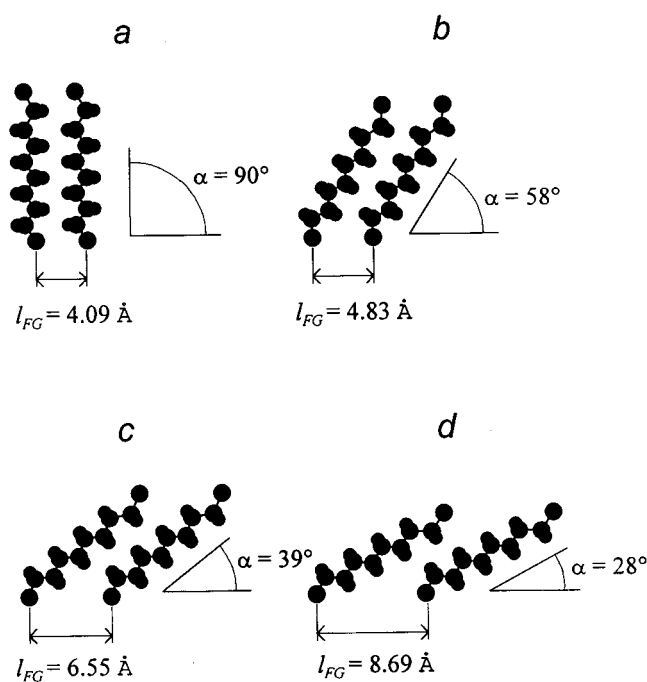


Figure 5. Inclinations of the carbon chain axes governed by the close packing of the chains.

$$\tan \alpha = \frac{\Delta l_{90}}{2 \times n \times 1.279} \quad (3)$$

$$\Delta l_{FG} = \frac{\Delta l_{90}}{\sin \alpha} \quad (4)$$

where  $n$  is an integer. Therefore, for  $n = 0$ ,  $\alpha = 90^\circ$ , for  $n = 1$ ,  $\alpha = 58.0^\circ$  and  $\Delta l_{FG} \geq 4.83 \text{ \AA}$ , for  $n = 2$ ,  $\alpha = 38.7^\circ$  and  $\Delta l_{FG} \geq 6.55 \text{ \AA}$ , and for  $n = 3$ ,  $\alpha = 28.1^\circ$  and  $\Delta l_{FG} \geq 8.69 \text{ \AA}$ . Regarding the values of the  $a$  parameter and  $a\sqrt{2}$  diagonal of the tetragonal lattice of vanadyl

or niobyl phosphate, only the values of  $\alpha$  close to  $58$  and  $28^\circ$  are possible.

As follows from the modeling in the series of ethanol, propanol, and butanol intercalates [31, 32], these alcohols with shorter chains are arranged in a different way from the alcohols with longer chains (1-pentanol to 1-octanol) [16]. The possible explanation is that the hydrophobic interactions between carbon chains of the shorter alcohols are so weak that they are insufficient to build up an arrangement as seen with longer alcohols. Therefore, the axes of the shorter chains are more tilted to the layers compared to longer alcohols. This is a general phenomenon observed for alcohols with small number of carbon atoms in the chain [32, 33]. Analogously, the arrangement of 2-alkanols with short chains (2-propanol and 2-butanol) is different from that for longer 2-alkanols as indicated by the different composition of the corresponding intercalates. Structural models for arrangements of 2-alkanols (from 2-pentanol to 2-undecanol) are proposed and discussed in the following part of the paper for the intercalates of vanadyl phosphate. Similar intercalates of isostructural niobyl phosphate should be governed by the same principles.

#### Structural model of 'pseudomonomolecular' arrangement of 2-alkanols

The proposed alternatives of the 'pseudomonomolecular' arrangement of 2-octanol are given in Figure 6 as projections to the  $xz$  plane. In all these alternatives, the axis of the aliphatic chain is tilted to the host layer at  $60^\circ$ . In all cases, the C2 to C8 carbon atoms are in the *all-trans* configuration and the alternatives differ in the positions of methyl (C1 carbon atom) and hydroxyl groups. The axes of the chains are directed along the  $x$  axis (i.e., the  $y$  coordinate is the same for all C2 to C8 atoms in one chain). The distance between neighboring chains both in the  $x$  and  $y$  directions is the same and equal to the lattice parameter  $a = 6.21 \text{ \AA}$ . The oxygen atoms of the hydroxy groups of alcohols complement the sixth coordination position of the vanadium atoms in the host layer. The chain of 2-octanol anchored to the upper layer of  $(\text{VOPO}_4)_\infty$  is shifted along the  $y$  axis by  $a/2 = 3.1 \text{ \AA}$  and interdigitated among four alcohol chains anchored to the lower host layer. The position of this chain is in agreement with the condition for mutual positions of  $\text{CH}_2$  groups of different chains as discussed earlier. The atoms of these chains shifted by  $a/2$  in the  $y$  direction are drawn as open circles in Figure 6.

The arrangement depicted in Figure 6a has the whole aliphatic chain in the *all-trans* configuration and the OR oxygen atom is out of the carbon atoms plane. Two other models proposed (Figures 6b and 6c) include these oxygen atoms in the *all-trans* configuration and the C1 methyl group is out of the O—C2—C8 plane.

The position of the 2-octanol chain which is anchored to the upper layer of  $(\text{VOPO}_4)_\infty$  is sterically determined by four chains anchored to the lower  $(\text{VOPO}_4)_\infty$  layer allowing us to estimate  $l_{V-OR}$ . The  $l_{O_1O_2}$  distances obtained from their  $z$  coordinates are drawn in Figures 6a–c. The values of  $l_{V-OR}$  calculated from Equation (2) are 3.73, 2.05, and 3.23  $\text{\AA}$  for

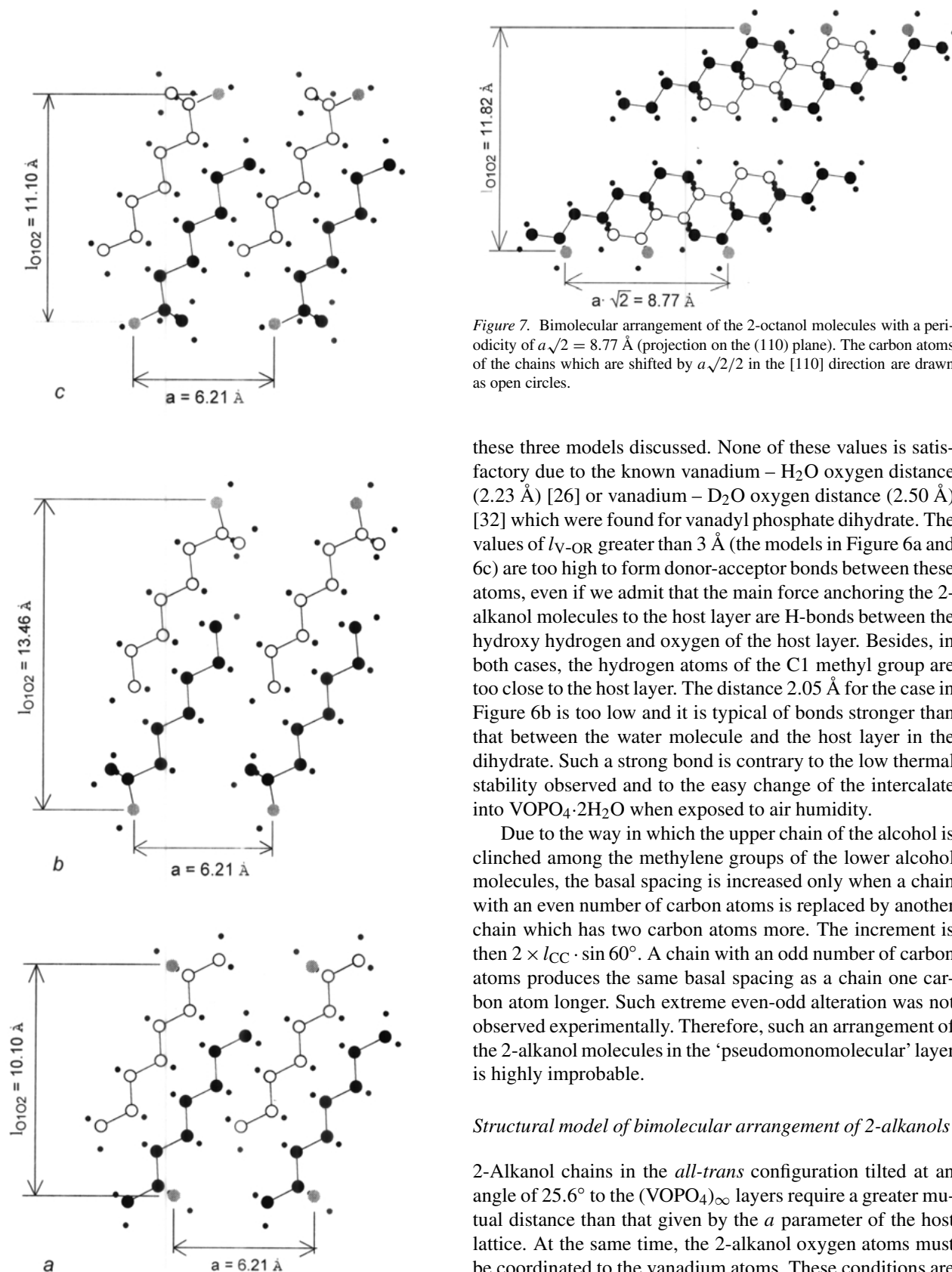


Figure 6. Three ways of the ‘pseudomonomolecular’ arrangement of the 2-octanol chains with a periodicity of  $a = 6.21 \text{ \AA}$  (projection on the  $xz$  plane). The carbon atoms of the molecules lying at a distance of  $y = \pm a/2$  are drawn as open circles.

Figure 7. Bimolecular arrangement of the 2-octanol molecules with a periodicity of  $a\sqrt{2} = 8.77 \text{ \AA}$  (projection on the (110) plane). The carbon atoms of the chains which are shifted by  $a\sqrt{2}/2$  in the [110] direction are drawn as open circles.

these three models discussed. None of these values is satisfactory due to the known vanadium –  $\text{H}_2\text{O}$  oxygen distance ( $2.23 \text{ \AA}$ ) [26] or vanadium –  $\text{D}_2\text{O}$  oxygen distance ( $2.50 \text{ \AA}$ ) [32] which were found for vanadyl phosphate dihydrate. The values of  $l_{V-OR}$  greater than  $3 \text{ \AA}$  (the models in Figure 6a and 6c) are too high to form donor-acceptor bonds between these atoms, even if we admit that the main force anchoring the 2-alkanol molecules to the host layer are H-bonds between the hydroxy hydrogen and oxygen of the host layer. Besides, in both cases, the hydrogen atoms of the C1 methyl group are too close to the host layer. The distance  $2.05 \text{ \AA}$  for the case in Figure 6b is too low and it is typical of bonds stronger than that between the water molecule and the host layer in the dihydrate. Such a strong bond is contrary to the low thermal stability observed and to the easy change of the intercalate into  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  when exposed to air humidity.

Due to the way in which the upper chain of the alcohol is clinched among the methylene groups of the lower alcohol molecules, the basal spacing is increased only when a chain with an even number of carbon atoms is replaced by another chain which has two carbon atoms more. The increment is then  $2 \times l_{CC} \cdot \sin 60^\circ$ . A chain with an odd number of carbon atoms produces the same basal spacing as a chain one carbon atom longer. Such extreme even-odd alteration was not observed experimentally. Therefore, such an arrangement of the 2-alkanol molecules in the ‘pseudomonomolecular’ layer is highly improbable.

#### Structural model of bimolecular arrangement of 2-alkanols

2-Alkanol chains in the *all-trans* configuration tilted at an angle of  $25.6^\circ$  to the  $(\text{VOPO}_4)_\infty$  layers require a greater mutual distance than that given by the  $a$  parameter of the host lattice. At the same time, the 2-alkanol oxygen atoms must be coordinated to the vanadium atoms. These conditions are fulfilled when the chains are arranged along the diagonal of the tetragonal lattice, i.e., the chains lie in the (110) plane at a distance of  $8.77 \text{ \AA}$ . A bimolecular arrangement of the 2-octanol chains as a projection to the (110) plane is given in Figure 7. The molecules with the atoms drawn as open circles lie in a parallel plane shifted by half of  $a\sqrt{2}$ .

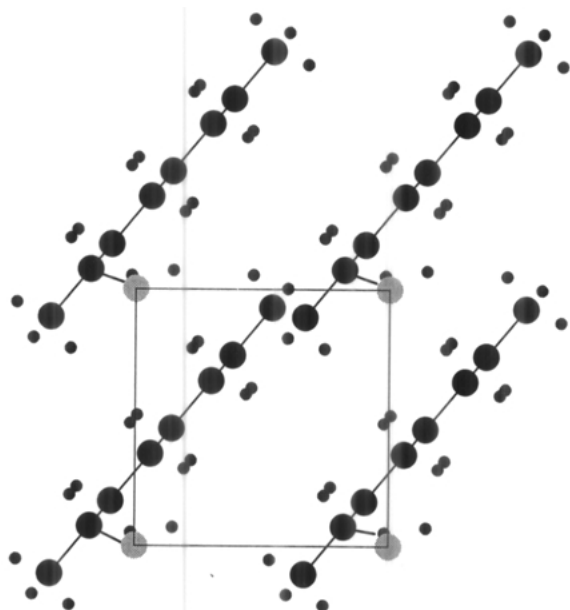


Figure 8. Arrangement of the 2-octanol molecules in the tetragonal lattice of the host (projection on the (001) plane).

As shown earlier, the van der Waals width of an *all-trans* chain is 4.12 Å. If the chains were parallel to the diagonal of the host tetragonal lattice, an empty gap of 0.26 Å would be formed between them. The space between 2-alkanol molecules can be filled when the molecules deviate by an angle  $\beta$  from the diagonal in the  $xy$  plane. For 2-octanol, the space is best filled when the guest molecules deviate by 5° from the diagonal. The projection of the 2-octanol molecules anchored to the  $(\text{VOPO}_4)_\infty$  layer on the  $xy$  (001) plane is given in Figure 8 with the host tetragonal lattice drawn as a square.

The bimolecular arrangement of the 2-octanol molecules in the space between the  $(\text{VOPO}_4)_\infty$  layers is formed so that one layer of the 2-octanol molecules anchored to the lower host layer is near the second layer of the molecules anchored to the upper host layer and oriented in an opposite direction. The distances between hydrogen atoms of both 2-octanol layers cannot be shorter than twice the van der Waals radius of the hydrogen atoms and both 2-octanol layers must be as close as possible at the same time. By using the experimentally found value of  $l_{\text{O}_1\text{O}_2}$  in Equation (2), the distance between vanadium and the R—OH oxygen is  $l_{\text{V-OR}} = 2.87$  Å.

The positions of the terminal methyl groups in the aliphatic chains are influenced by the even-odd character of these chains. For an even number of carbon atoms in the chain, the methyl groups jut from the alcohol plane. These methyl groups of both alcohol layers can interdigitate, thus decreasing the basal spacing of the intercalates with an odd number of carbon atoms in the alcohols. Nevertheless, an even-odd alternation resulting from such consideration was not experimentally observed. Therefore, a certain disorder in the arrangement of the alcohol molecules in the interlayer space can be presumed which does not allow both neighboring corrugated planes of the guest molecules to be fitted together.

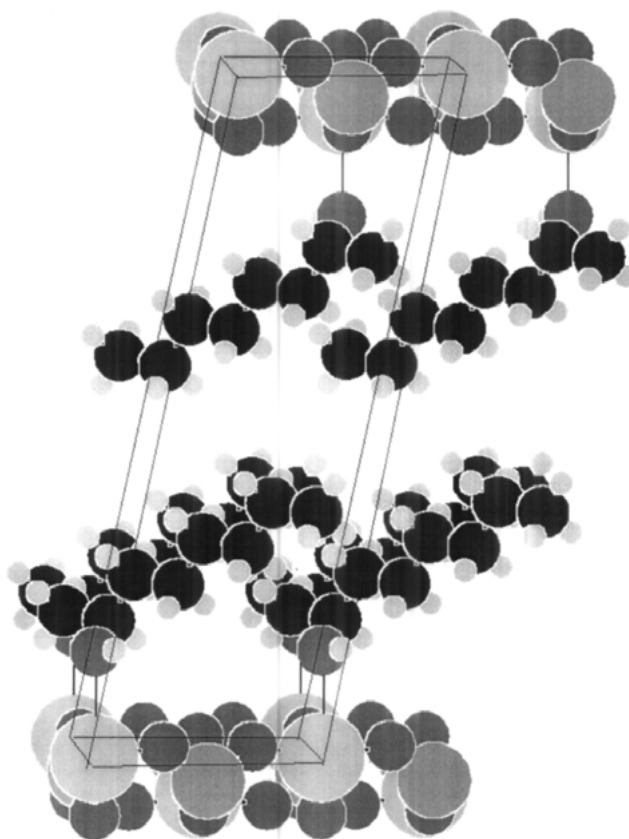


Figure 9. The layer of the  $\text{VOPO}_4$  intercalate with 2-octanol.

The experimental  $l_{\text{V-OR}}$  distance indicates very weak donor-acceptor bonds because the length of this bond is greater than that found for the  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  bonds in  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  [26] and  $\text{VOPO}_4 \cdot 2\text{D}_2\text{O}$  [34], respectively. This explains the extremely low stability of the  $\text{MOPO}_4$  intercalates with 2-alkanols in air where, at usual humidity (r.h. around 50%), the 2-alkanol molecules are replaced with water within a few minutes. Even the presumed H-bond of the hydroxy hydrogen to the oxygen atoms of the host layers is not strong enough to ensure sufficient anchoring of the 2-alkanol molecules.

The layer of the intercalate depicted in Figure 9 is formed by a triclinic unit cell with  $a = b$  and  $\gamma = 90^\circ$ . Taking into account a symmetrical arrangement of the lower and upper parts of the bimolecular layer, the 2-alkanol molecules can be oriented to the host layer in eight ways which differ in the angle between the alkanol chain axis and the  $x \equiv a$  axis. Presuming that the guest molecules are deposited in different orientations in every interlayer space of the host, the host layers must be mutually shifted in the  $a$  and  $b$  directions. These shifts cause a loss of periodicity in the arrangement of atoms; nevertheless, when the interlayer distance is retained, a turbostratic arrangement of the layers is formed in the crystals of the intercalates. This is in agreement with an absence of the  $hkl$  diffractions in the diffractograms of these intercalates.

## Conclusions

Based on the experimental values of the basal spacing and stoichiometry of the intercalates of vanadyl and niobyl phosphates with a 2-alkanol homologous series, a bimolecular arrangement of the guest molecules in the interlayer space was proposed. The axis of the *all-trans* carbon chain is tilted to the host layers at an angle of 25.6°. The chains are roughly directed along the diagonal of the host tetragonal lattice. Besides the donor-acceptor bond of the alcohol oxygen atom to the vanadium or niobium atom, H-bonds between the hydroxy hydrogen of the alcohol and oxygens of the host layer are present. The large vanadium-oxygen distance ( $l_{V-OR} = 2.87 \text{ \AA}$ ) obtained from the model proposed explains the low thermal and humidity stabilities of these intercalates. The 2-alcohol chains can be oriented in eight directions in the interlayer space with the interlayer distance unchanged. The consequent shift of the layers forms a turbostratic structure. Three other discussed ways of packing of the 2-alkanol molecules with a 'pseudomonomolecular' arrangement and with an inclination of the chain at 60° were rejected as highly improbable. The given model of the intercalate layer explains why the intercalations of 3-heptanol, 3-octanol, and 4-octanol were not successful. These alcohol molecules cannot be coordinated to every atom of vanadium (niobium) of the host layer due to steric reasons.

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