



Intercalation of 1-Alkanol Binary Mixtures into the Layered Structure of Vanadyl Phosphate

KLÁRA MELÁNOVÁ, LUDVÍK BENEŠ and VÍTEŽSLAV ZIMA

Joint Laboratory of Solid State Chemistry of the Academy of Sciences of the Czech Republic and University of Pardubice, Studentská 84, 532 10 Pardubice, Czech Republic

JAROSLAVA KALOUSOVÁ and JIŘÍ VOTINSKÝ

Department of General and Inorganic Chemistry, University of Pardubice, Čs. Legií 565, 532 10 Pardubice, Czech Republic

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Abstract. Mixed intercalates $\text{VOPO}_4 \cdot \text{C}_2\text{H}_5\text{OH} \cdot \text{C}_4\text{H}_9\text{OH}$, $\text{VOPO}_4 \cdot \text{C}_3\text{H}_7\text{OH} \cdot \text{C}_5\text{H}_{11}\text{OH}$, $\text{VOPO}_4 \cdot \text{C}_3\text{H}_7\text{OH} \cdot \text{C}_6\text{H}_{13}\text{OH}$ and $\text{VOPO}_4 \cdot \text{C}_4\text{H}_9\text{OH} \cdot \text{C}_6\text{H}_{13}\text{OH}$ have been prepared by reaction of polycrystalline vanadyl phosphate dihydrate with liquid mixtures of the 1-alkanols in a microwave field. The same mixed layer-type complexes were also obtained as intermediary products of exchange reactions consisting in substitution of one alkanol bound in the solid intercalate by another alkanol introduced in the form of vapour. The composition of products has been determined, and the basal spacing of all the mixed layer-type complexes prepared has been found by diffraction. A structural principle is suggested which governs the depositing of two kinds of 1-alkanol molecules (differing in the lengths of their aliphatic chains) while acting as guests in the layered structure of vanadyl phosphate.

Key words: intercalation, 1-alkanols, vanadyl phosphate, mixed layer-type complexes, x-ray powder diffraction.

1. Introduction

In a recently published article [1] we have shown that the reaction of vanadyl phosphate with 1-alkanols produces layer-type complexes of the formula $\text{VOPO}_4 \cdot 2\text{C}_n\text{H}_{2n+1}\text{OH}$ ($n = 2$ to 18) which can be considered as intercalates. The structure of these complexes retains the planar layers of $(\text{VOPO}_4)_\infty$ present in the original host. The intercalated alcohol is arranged in bimolecular layers between the host layers. The OH groups of one half of the guest alcohol molecules are bound to the $(\text{VOPO}_4)_\infty$ layers by means of donor-acceptor $\text{O}_{\text{alc}} \rightarrow \text{V}_{\text{host}}$ bonds. The other half of the alcohol molecule is anchored to the host by a system of hydrogen bonds $(\text{O}-\text{H})_{\text{alc}} \cdots \text{O}_{\text{host}}$. The aliphatic chains of alcohols probably are in *all-trans* conformation, the chain axes being perpendicular to the $(\text{VOPO}_4)_\infty$ layers. The structure suggested for the complexes is depicted schematically in Figure 1.

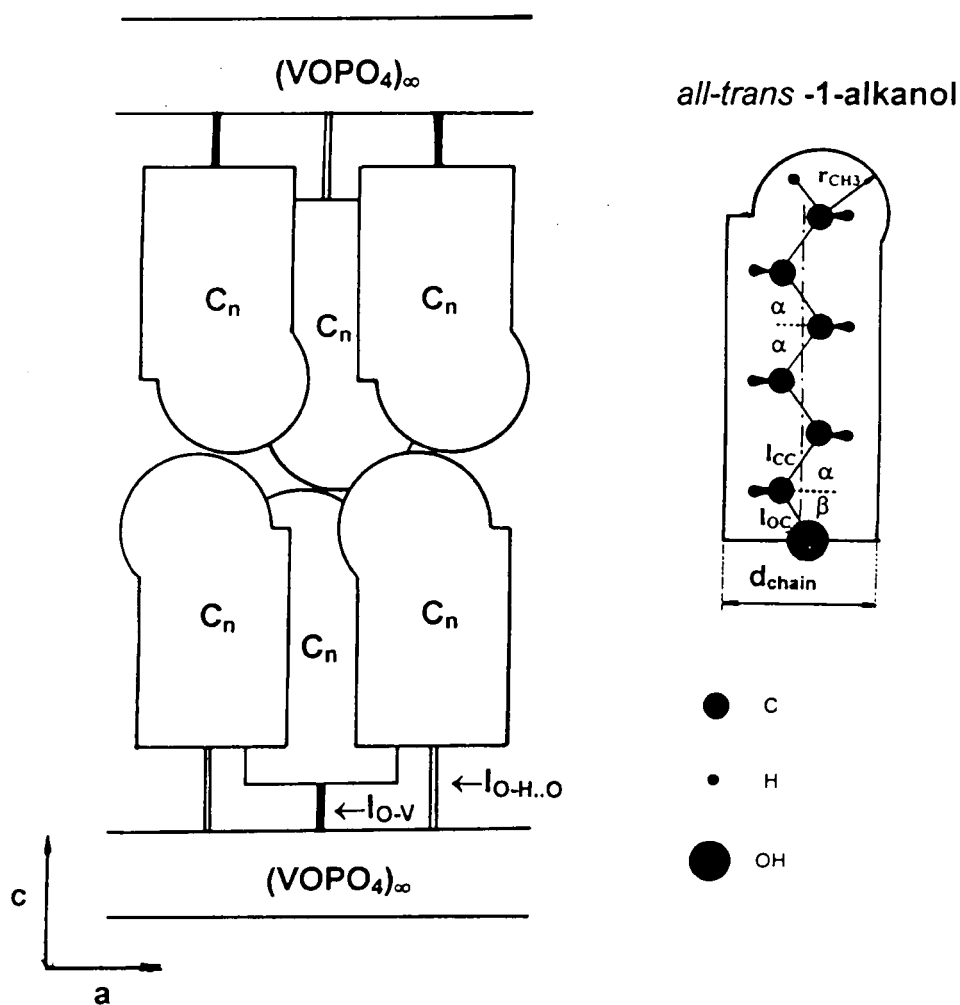
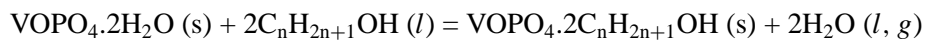


Figure 1. The principles of location of 1-alkanol molecules in the interlayer space of the $VOPO_4$ host [1].

The preparation of an extensive group of complexes involving the first eighteen members of the homologous series of 1-alkanols was successful owing to the application of a new preparation procedure. This consisted in carrying out a heterogeneous exchange reaction between solid vanadyl phosphate dihydrate and liquid alcohol $C_nH_{2n+1}OH$ without solvent:



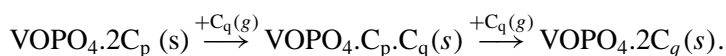
The reaction was realized in a microwave field and was relatively fast, its equilibrium being shifted completely to the right. Usually the product obtained formed a single phase and was easily submitted to diffraction analysis [1].

In this context we were also interested in the problem of potential co-intercalation reactions in the systems of the given type. Hence we were trying to find an answer to the following question: What will happen if the host is simultaneously offered molecules of two 1-alkanols differing in their chain lengths?

From earlier papers it is known that mixed layer-type complexes can be formed in such a case. For instance, polycrystalline VOSO_4 suspended in a liquid mixture of two 1-alkanols is transformed very rapidly into a crystalline phase composed of $\text{VOSO}_4 \cdot \text{C}_p\text{H}_{2p+1}\text{OH} \cdot \text{C}_q\text{H}_{2q+1}\text{OH}$ ($p < q$; $p, q = 2$ to 8). The two alcohols are present in the intercalate at the molar ratio of 1 : 1 [2].

Similarly, vanadyl phosphate in contact with a liquid mixture of ethanol and 1-butanol forms a microcrystalline phase of $\text{VOPO}_4 \cdot \text{C}_2\text{H}_5\text{OH} \cdot \text{C}_4\text{H}_9\text{OH}$ [3]. On the other hand, in systems containing methanol as one of the guests, the complexes formed can be of varying composition, e.g. $\text{VOPO}_4 \cdot (\text{CH}_3\text{OH})_{2-x} \cdot (\text{C}_2\text{H}_5\text{OH})_x$ ($x = 1.6$ to 2.0) or $\text{VOPO}_4 \cdot (\text{CH}_3\text{OH})_{2-x} \cdot (\text{C}_3\text{H}_7\text{OH})_x$ ($x = 1.8$ to 2.0) [3].

We have made use of the new preparation procedure to undertake attempts at a systematic search for formation of mixed intercalates in systems formed by vanadyl phosphate dihydrate and a pair of 1-alkanols. (In the following text, the 1-alkanols $\text{C}_p\text{H}_{2p+1}\text{OH}$ with shorter chain and $\text{C}_q\text{H}_{2q+1}\text{OH}$ with longer chain will be denoted as C_p and C_q , respectively.) The co-intercalations of the following pairs of 1-alkanols have been studied: (a) *ethanol + butanol*, (b) *propanol + pentanol*, (c) *propanol + hexanol*, (d) *butanol + hexanol*. Additionally, in the systems containing the alcohols mentioned we tried to obtain the mixed intercalates as intermediates in exchange reactions in the sense of the following scheme:



The results of our experiments are presented in this paper.

2. Experimental

2.1. PREPARATIONS

Vanadyl phosphate dihydrate was obtained by long-term boiling of a V_2O_5 suspension in aqueous phosphoric acid [4].

The samples of layered complexes with 1-alkanols were prepared by suspending microcrystalline $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ (0.25 g; grain size 0.01–0.08 mm) in dry liquid alcohol or alcohol mixture (10 g), and subsequent short exposure (0.5–2 min) to a microwave field. The reaction mixture was placed in a 15 mL glass flask equipped with a reflux condenser and put into the waveguide of the microwave generator with stirring. After cooling, the solid product formed was filtered off. The samples for X-ray diffraction analysis were left wetted with a small residue of the alcohols. The samples for thermogravimetric and gas chromatographic analyses were washed with pentane and dried in a stream of nitrogen.

Before using for preparation of the complexes, all the 1-alkanols were dried and distilled under dry nitrogen. The composition of the starting alcohol mixtures is expressed by the mol fraction y of the alcohol, C_q , with the longer chain.

2.2. MICROWAVE APPARATUS

The microwave apparatus used for preparing the complexes was specially constructed by RADAN Ltd., Pardubice, Czech Republic. It operates at a frequency of 2450 ± 30 MHz with a total generator output of 800 W, out of which 30–50 W is absorbed by the reaction mixture. The metal waveguide with a square cavity (5.2×5.2 cm) is equipped with an opening of 2 cm diameter which serves to locate the reaction vessel.

2.3. ANALYSES

The TGAs of the intercalates were performed with a Derivatograph MOM (Hungary), the measurements being carried out in the temperature interval of 25–700 °C in a N_2 atmosphere at a heating rate of 5 °C min^{-1} . The weight of the samples was 100 mg.

The molar ratio of the intercalated alcohols in the layered complexes was determined by means of gas chromatography. Before the analysis, the solid samples were washed with pentane, dried and filtered in a dry inert atmosphere, and then a known amount was hydrolyzed. The obtained extract was analyzed with the help of a Fractovap GV apparatus (Carlo Erba, Italy) with a flame ionization detector. The reproducibility of the measurements was $\pm 10\%$ related to the content of alcohols.

2.4. DIFFRACTION MEASUREMENTS

The powder data of the intercalates with a minor surplus of the guest alcohol mixtures were obtained with an X-ray diffractometer (HZG 4, Germany) using $CuK\alpha_1$ radiation ($\lambda = 1.5405 \text{ \AA}$) with discrimination of the $CuK\beta$ by a Ni-filter. The $CuK\alpha_2$ intensities were removed from the original data. Silicon ($a = 5.43055 \text{ \AA}$) was used as the internal standard. The diffraction angles were measured from 1.5° to 50° (2θ). The samples were kept under protection foil during the measurements and the signal of this foil in the diffractograms was compensated. The obtained data were refined by a least-squares program minimizing $(2\theta_{\text{exp}} - 2\theta_{\text{calc}})^2$.

The recording of diffractograms of the solid phase during the exchange of alcohols was done in the following way: the sample of original intercalate with one alcohol was placed on the surface of a thermostated (25 °C) corundum target plate under dry nitrogen, whereupon the stream ($\text{ca } 0.5 \text{ l min}^{-1}$) of nitrogen saturated with vapours of the other alcohol was introduced to the sample. The reaction taking place in the solid phase was monitored by recording diffractograms (from 3 to 25°

2 θ) after every 8 minutes. In the experimental arrangement given, the reaction was usually complete within 1 to 2 hours depending on the alcohols used.

3. Results and Discussion

3.1. FORMATION OF SOLID PHASES IN THE SYSTEMS OF VANADYL PHOSPHATE AND LIQUID BINARY ALCOHOL MIXTURE

All the prepared intercalates are polycrystalline powders, which release intercalated alcohol and uptake water very easily when kept in air. It was only possible to determine the total content of alcohols in the intercalate by TG analysis. The ratio of both alcohols in the intercalate was therefore determined by GC.

The curves in Figure 2 illustrate the observed dependence of the basal spacing of the solid products formed by intercalation reaction upon the composition y of the liquid alcohol mixture used (C_p and C_q , $p < q$). The composition of the reaction liquid entering (intercalating) the solid phase cannot change very much during the reaction because the alcohol mixture is used in a large excess as compared with vanadyl phosphate.

The curves exhibit a characteristic course with three sections denoted here as R, S, T (see inset in Figure 2). The sections R include the compositions of the solid phase with a low proportion of alcohol C_q (zero in the limit case). The regions T correspond to the opposite situation. The S type regions correspond to a reaction liquid with both alcohols at comparable amounts and the solid phase with the molar ratio of the two alcohols close to 1 : 1.

In the R regions, the basal spacing of the reaction product changes only very slightly, being practically identical with that of the $\text{VOPO}_4 \cdot 2C_p$ intercalate. The gas chromatographic analysis indicates the predominance (up to 98%) of the C_p alcohol in these solid phases in all the cases, the amount of C_p present in the dry sample corresponding with the above mentioned formula. The solid phases present in the S regions of all four systems exhibit the basal spacing values very close to a simple arithmetic mean of the basal spacing values of the two limit intercalates $\text{VOPO}_4 \cdot 2C_p$ and $\text{VOPO}_4 \cdot 2C_q$ (see Tables I and II). As already stated the content of the two alcohols in the solid phases corresponds well to the formula $\text{VOPO}_4 \cdot C_p \cdot C_q$.

In all the systems studied the samples of solid phases obtained from the T regions contain a surplus of alcohol C_q as compared with C_p . The composition of the solid phase corresponds best to the formula $\text{VOPO}_4 \cdot (C_p)_x \cdot (C_q)_{2-x}$ where x approaches zero in the samples whose basal spacing approaches the value of $\text{VOPO}_4 \cdot 2C_q$.

The graphs in Figure 2 show that the transitions between the R, S and T regions are characterized by sharp changes in the basal spacing values of the solid phases. Figure 3 gives, as an example, five diffractograms of solid phases prepared in the system of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O} + 1\text{-propanol} + 1\text{-pentanol}$. The diffractograms obtained from the reaction liquid with pentanol content $y = 0.33$ and 0.78 , i.e. from the points of both jump changes in basal spacing, show distinctly broadened and few

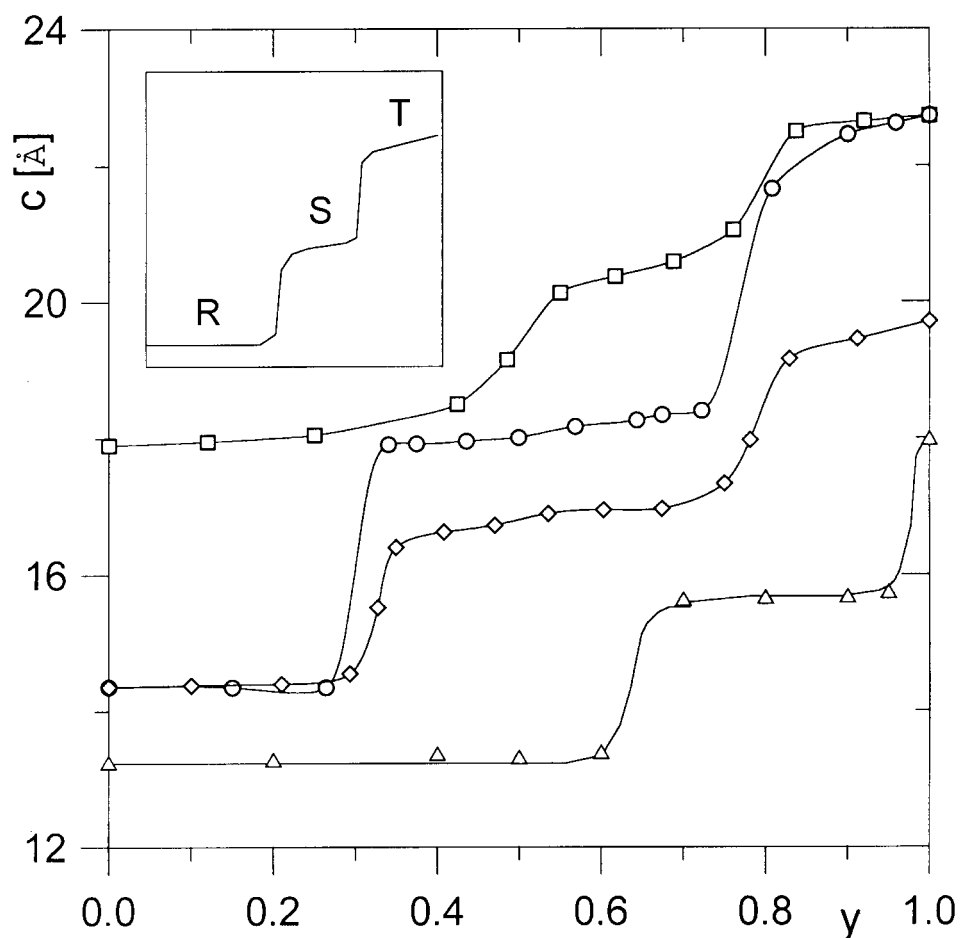


Figure 2. Dependence of the basal spacing c of the prepared solid phases on the composition y of the starting liquid 1-alkanol mixtures in the systems: (Δ) $\text{VOPO}_4 \cdot 2\text{H}_2\text{O} + \text{C}_2 + \text{C}_4$, (\diamond) $\text{VOPO}_4 \cdot 2\text{H}_2\text{O} + \text{C}_3 + \text{C}_5$, (\circ) $\text{VOPO}_4 \cdot 2\text{H}_2\text{O} + \text{C}_3 + \text{C}_6$, (\square) $\text{VOPO}_4 \cdot 2\text{H}_2\text{O} + \text{C}_4 + \text{C}_6$. Three typical regions R, S, and T are observed in the dependence of basal spacing on the composition of the starting alcohol mixture as given in the inset. In the region R, the content of the alcohol with the longer chain is $x = 0-0.05$, in S $x = 1.0 \pm 0.1$, and in T $x = 1.7-2.0$.

intense lines. The diffractograms do not show the least evidence of the presence of more than one solid phase. The same situation is observed also in the remaining three systems studied.

The basic interpretation of all the experimental results is simple:

If the short-chain alcohol predominates in the liquid mixture of alcohols, the reaction product is relatively pure intercalate of the formula $\text{VOPO}_4 \cdot 2\text{C}_p$, the trend to incorporation of the long-chain alcohol (as its proportion is increased) being very small at the beginning.

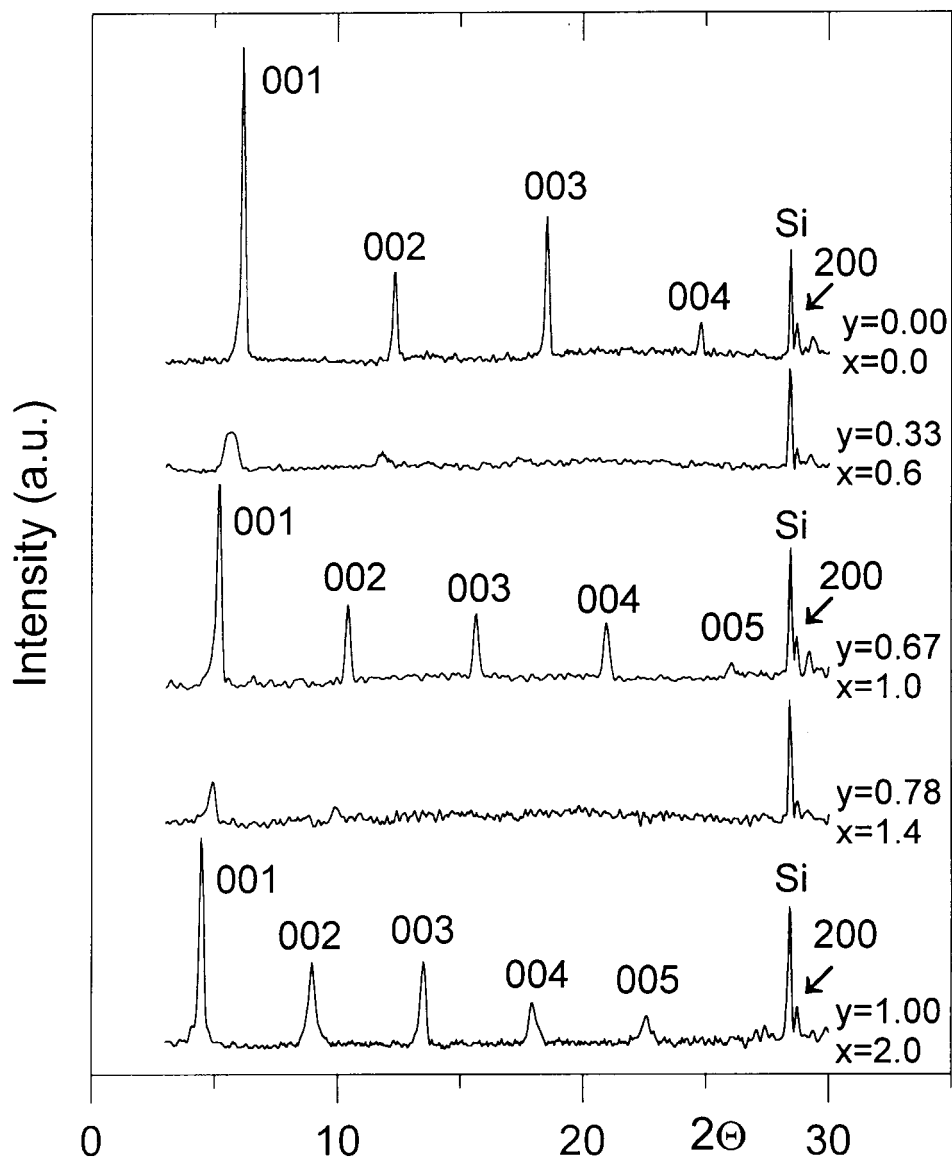


Figure 3. Diffractograms of solid phases prepared in the system $\text{VOPO}_4 \cdot 2\text{H}_2\text{O} + \text{C}_3 + \text{C}_5$, y is the mole fraction of 1-pentanol in the starting mixture of the alcohols and x is content of 1-pentanol in the intercalate.

Table I. Basal spacing d_{exp} of layered complexes of vanadyl phosphate with 1-alkanols

Composition	d_{exp} (Å)
VOPO ₄ .2C ₂	13.17
VOPO ₄ .2C ₃	14.30
VOPO ₄ .2C ₄	17.90
VOPO ₄ .2C ₅	19.71
VOPO ₄ .2C ₆	22.73

Table II. Basal spacing d_{exp} of mixed intercalates of vanadyl phosphate with pairs of 1-alkanols (column one) and the arithmetic mean d_{calc} of basal spacing values corresponding to the intercalates with a single 1-alkanol (column two)

Composition	d_{exp} (Å)	d_{calc} (Å)
VOPO ₄ .C ₂ .C ₄	15.69	15.53
VOPO ₄ .C ₃ .C ₅	16.96	17.03
VOPO ₄ .C ₃ .C ₆	18.37	18.55
VOPO ₄ .C ₄ .C ₆	20.33	20.32

In contrast, the VOPO₄.2C_q intercalates accept the short-chain alcohol C_p into their structure very readily even at its low concentration in the reaction mixture. This process is always connected with a distinct drop in basal spacing of the solid phase formed.

The composition of mixed intercalates VOPO₄.C_p.C_q is determined by the structure of the bilayer of alcohol molecules inserted between the host layers (Figure 1). This structure makes it possible to combine the molecules of both alcohols in such a way that the bilayer thickness is determined by one short-chain molecule and one long-chain one. The resulting arrangement is presented in Figure 4.

The presumed structure of the bilayer of alcohol molecules also explains the fact that the long-chain alcohol is not easily incorporated into the bilayer formed by short-chain molecules at the beginning. The steric requirements of long chains cannot be satisfied because this would inevitably mean inserting pillars into the intercalate structure, but the small rigid carbon chains do not make strong enough pillars. On the other hand, the incorporation of short-chain molecules into the bilayer of long-chain alcohol is possible since the molecules of the C_q alcohol

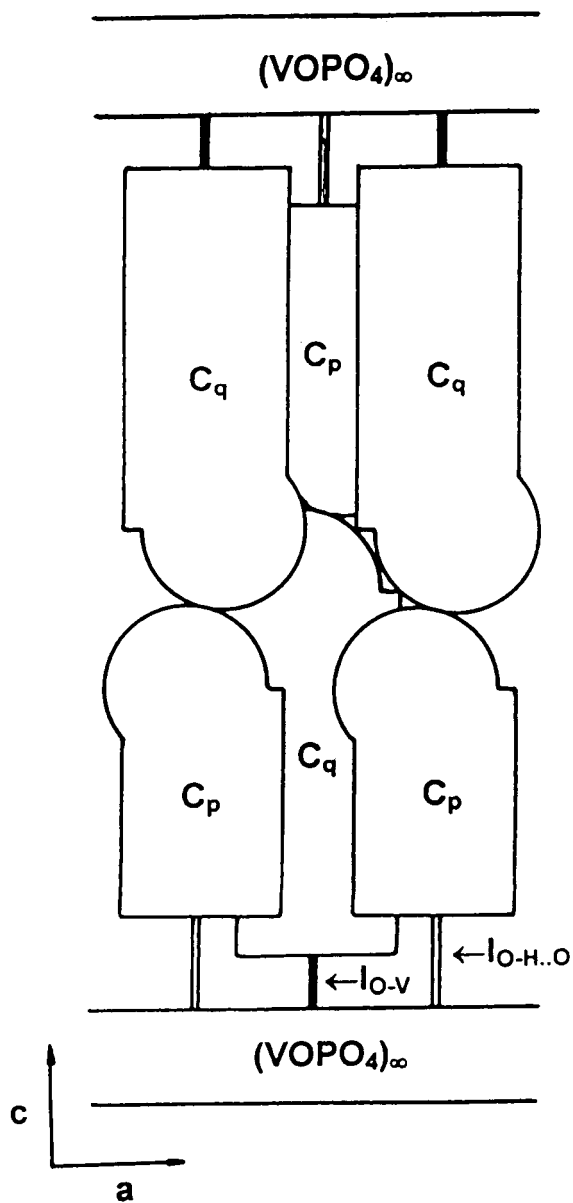


Figure 4. Probable arrangement of the two different types of 1-alkanol molecules in the mixed layered complexes $VOPO_4 \cdot C_p \cdot C_q$ ($p < q$).

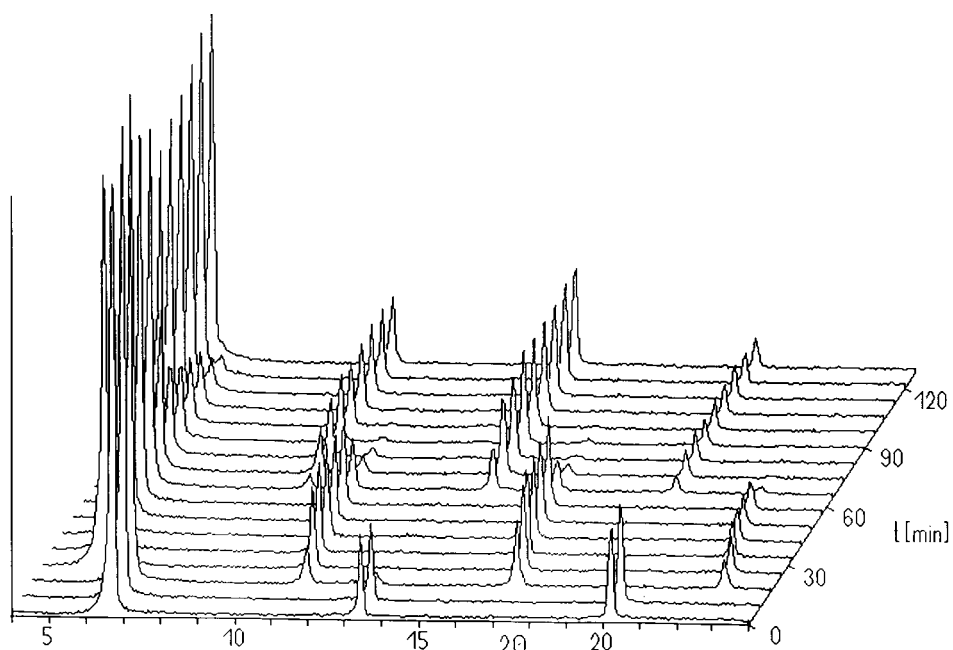


Figure 5. Time changes of the diffractogram of the solid phase during the reintercalation reaction $\text{VOPO}_4 \cdot 2\text{C}_2 \rightarrow \text{VOPO}_4 \cdot \text{C}_2 \cdot \text{C}_4 \rightarrow \text{VOPO}_4 \cdot 2\text{C}_4$.

respond by forming the *kink*-configurations of their chains thus decreasing the basal spacing of the intercalate [5].

The samples of solid phases obtained at the R/S or S/T boundaries are characterized by a “hidden” two-phase nature. The $\text{VOPO}_4 \cdot 2\text{C}_p$ intercalate is just being transformed into the mixed complex $\text{VOPO}_4 \cdot \text{C}_p \cdot \text{C}_q$ or the mixed complex $\text{VOPO}_4 \cdot \text{C}_p \cdot \text{C}_q$ is being changed into $\text{VOPO}_4 \cdot 2\text{C}_q$. The structure of these samples shows irregular alternation of the guest layers containing a single alcohol and those containing both alcohols. The diffractogram shows the diffraction lines due to a single phase, but the diffractions exhibit large halfwidth values and also somewhat varying positions. When adopting volatile alcohols, this phenomenon cannot be measured quantitatively. It can only be stated to be probably present and to be in accordance with the theoretical prediction by Hendricks and Teller which has been experimentally verified many times [6].

3.2. REINTERCALATION OF ALCOHOLS

The aim of these experiments was to find out whether it would be possible to detect formation of mixed intercalates in the process of slow substitution of one intercalated alcohol by molecules of another one entering the solid complex from the gas phase in the systems (a)–(d). Therefore the exchange was carried out by

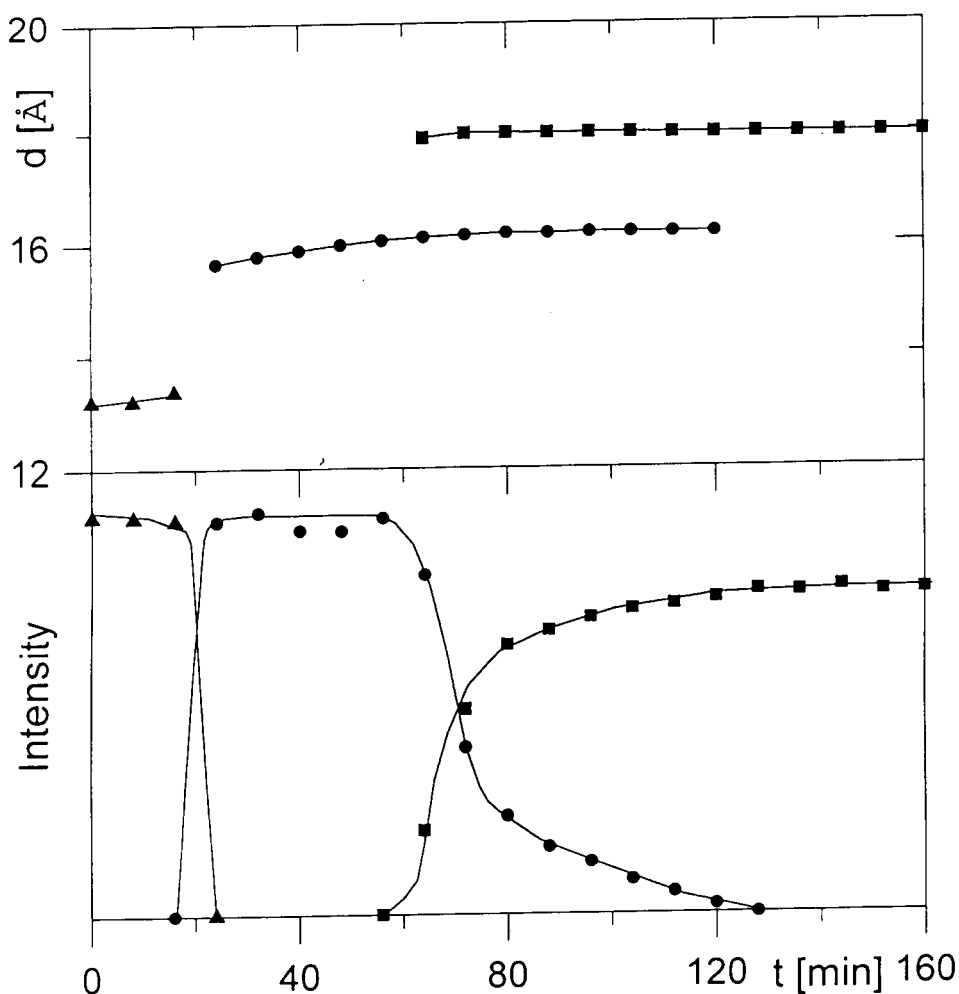


Figure 6. Time changes in the intensity of the diffraction line (001) and the basal spacing d in the solid phase and solid reaction product during the reintercalation reaction $\text{VOPO}_4 \cdot 2\text{C}_2(\blacktriangle) \rightarrow \text{VOPO}_4 \cdot \text{C}_2 \cdot \text{C}_4(\bullet) \rightarrow \text{VOPO}_4 \cdot 2\text{C}_4(\blacksquare)$.

heterogeneous reactions between the solid intercalate of one alcohol and vapour of the other in the way described in the Experimental.

The series of diffractograms recorded during the contact of the solid intercalate containing ethanol, $\text{VOPO}_4 \cdot 2\text{C}_2\text{H}_5\text{OH}$, with 1-butanol vapour at 25°C is presented in the time sequence in Figure 5. The time dependence of the intensities of the (001) line and that of the inter-layer distance calculated from its position are presented in Figure 6. It can be seen that after ca 20 min from the beginning of the reaction, the mixed intercalate $\text{VOPO}_4 \cdot \text{C}_2\text{H}_5\text{OH} \cdot \text{C}_4\text{H}_9\text{OH}$ appears whose basal spacing is practically identical with that of the mixed intercalate prepared by reaction of vanadyl phosphate dihydrate with the liquid mixture of both alcohols. The last traces of

mixed intercalate disappear from the system after more than 120 min of reaction. The final product of the reintercalation reaction is the intercalate with 1-butanol, $\text{VOPO}_4 \cdot 2\text{C}_4\text{H}_9\text{OH}$, whose presence in the reacting solid sample is revealed by diffraction measurements after about 1 hour from the start of reaction.

The whole procedure can also be reversed, i.e. it can start from the solid intercalate containing 1-butanol and transform it into the intercalate of ethanol. In this case, the reaction goes very rapidly, nevertheless, the transient formation of the mixed intercalate can be detected here, too. The results obtained from the same procedure in the remaining three systems were similar.

Acknowledgments

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