Intercalation of 1,2-Alkanediols into α-Zirconium Hydrogenphosphate

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Abstract

Intercalation compounds of α-Zr(HPO$_4$)$_2 \cdot$ H$_2$O with 1,2-alkanediols (from C3 to C16) have been prepared by replacing 1-propanol in α-Zr(HPO$_4$)$_2 \cdot$ 2C$_3$H$_7$OH with the desired 1,2-alkanediols by a treatment in a microwave field. It was found that the intercalates contain 1.5 molecules of diol per formula unit. The diol molecules are placed between the host layers in a bimolecular way with their aliphatic chains tilted at an angle of 51°. The diol molecules are anchored in the interlayer space by H-bonds. A mixed intercalate, containing 1,2-butanediol and 1,2-decanediol in a roughly equimolar ratio, is formed when the α-Zr(HPO$_4$)$_2 \cdot$ 2C$_3$H$_7$OH intercalate, suspended in a mixture of 1,2-butanediol and 1,2-decanediol, is exposed to microwave radiation. No new phase containing both types of the guest molecules was observed when the 1-propanol intercalate, suspended in a mixture of 1-propanol and 1,2-octanediol, is exposed to microwave radiation.

Introduction

α-Zr(HPO$_4$)$_2 \cdot$ H$_2$O, (hereafter α-ZrP) is a layered compound, generated by the packing of two-dimensional macromolecular units that are weakly interacting each other. Due to the presence of ionogenic P–OH groups on the surface of the layers, and to the easy accessibility of the interlayer region, this compound is able to act as a host for cationic or molecular polar guest species.

Host–guest chemistry of α-ZrP has been summarized in several reviews [1–3] and chapters of books [4–6]. A growing interest has recently been paid to the intercalation of guest species having special functionalities in the field of photochemistry [7], molecular and chiral recognition [8] and bio-catalysis [9–11]. While much work has been published about alkylamine intercalation [6], very few investigation has been accounted for alkanol intercalation compounds. Costantino [12] prepared some intercalation compounds with alcohols and glycols by contacting sodium salt forms of α-ZrP with the guest species acidified with strong mineral acids. Tomita and co-workers [13] observed the formation of alcohol intercalation compounds when α-ZrP micro-crystals were boiled in pure liquid alkanols.

A series of 1-alkanols and 1,ω-alkanediols with chain lengths ranging from 2 to 18, and 2 to 10 carbon atoms, respectively, was intercalated into α-Zr(HPO$_4$)$_2 \cdot$ H$_2$O by exposing it, intimately dispersed with the guest species, to microwave radiation [14]. Thermogravimetric analysis showed that the intercalation compounds contained as a maximum 2 mol of alkanol or 1 mol of alkanediol per one mol of zirconium phosphate. The correlation between the interlayer distance of the samples, determined at room temperature, and the number of carbon atoms in the alkyl chain indicates that the alkanol molecules are arranged as an ordered bimolecular film in the interlayer region of the host. Differential scanning calorimetry analysis and X-ray powder diffraction patterns of representative samples taken at different temperatures showed a phase transition in which the bimolecular film undergoes a change from an all-*trans* conformation to a conformation in which the O–C$_1$–C$_2$–C$_3$ torsion angle changes from 180 to 136°. The temperature at which this phase transition occurs was found to increase with the increasing number of the carbon atoms in the alkyl chain. Similar effects were observed with the 1,ω-alkanediol intercalates.

In order to find whether the existence of this phenomenon is hindered when another OH group is placed on the C$_2$ atom and to investigate the way these guest molecules are anchored in the interlayer space of Zr(HPO$_4$)$_2$, we prepared intercalates of α-ZrP with a homologous set of 1,2-diols.

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Experimental

Well-crystallized α-ZrP, of formula α-$Zr(HPO_4)_2 \cdot H_2O$, was obtained according to the method proposed by Alberti and Torracca [15]. A clear solution was prepared by dissolving 10.1 g of $ZrOCl_2 \cdot 8H_2O$, 8 ml of hydrofluoric acid (40% w/w) and 92 ml H_3PO_4 (85% w/w) in 160 ml of water. The solution was heated at 80 °C for 4 days, maintaining a constant volume by continuously adding water. α-ZrP precipitate was washed with deionized water and dried in air.

Zirconium phosphate intercalates with 1,2-alkanediols were prepared by a displacement reaction. The intercalation compound of zirconium phosphate and 1-propanol was prepared at first [14]. The finely ground α-ZrP (0.3 g), mixed with the propanol (7 ml), was exposed to microwave radiation for 10 min, filtered off, and the solid, mixed with a new dose of 1-propanol, was again exposed to microwave radiation for another 10 min. Then 1-propanol in the intercalate was replaced with desired 1,2-alkanediol (7.5 g) by a treatment in the microwave field for 10 min. After cooling, the solid product formed was filtered off and washed with acetone or toluene.

Compositions of the intercalates prepared were calculated from thermogravimetry (Stanton Redcroft STA-801, heating rate 5 °C/min, Pt crucible, Pt–Pt/Rh thermocouples, air flow) and elemental analysis. The weight of the gray rest obtained by heating to 1200 °C was corrected for the carbon remained in the sample, which was determined by elemental analysis. The difference between the original weight of the sample and the corrected weight of the sample after heating is a weight of the organic substance, hydration water, and condensation water. From the corrected weight of the heated sample, the amount of zirconium pyrophosphate was calculated which also corresponds to the amount of condensation water. The amount of hydration water corresponds to the weight loss observed to about 200 °C. The amount of the organic substance is calculated as a difference between the total weight loss and the amount of water. From the amount of organic substance one can calculate content of C and H in the sample and compare it with the results from elemental analysis.

X-ray powder diffraction (XRPD) patterns of the intercalates, wetted with a small amount of the guest, were obtained with an X-ray diffractometer (D8 Advance, Bruker AXS, Germany) using CuKα radiation and graphite secondary monochromator. The CuKα2 intensities were removed from the original data. Silicon ($a = 5.43055$ Å) was used as internal standard. Diffraction angles were measured from $2\theta = 1.5°$ to $2\theta = 65°$.

Infrared measurements in the range from 400 to 4000 cm^{-1} were made with a fully computerized Bruker IFS 55 EQUINOX FTIR Spectrometer with a DLATGS detector (256 scans per spectrum at 4 cm^{-1} resolution). Measurements of intercalates were performed *ex situ* in the transmission mode in KBr pellets. The spectrum of the corresponding liquid 1,2-hexanediol was measured by an ATR technique on a ZnSe crystal. The spectra were corrected for the content of H_2O and CO_2 in the optical path.

FT Raman spectra were collected using a Bruker IFS 55 EQUINOX FTIR Spectrometer equipped with a FT Raman module FRA 106/S with a diode-pumped, temperature-stabilized Nd YAG laser, and InGaAs detektor (128 interferograms were co-added per spectrum in the range from 4000 to (−1000) cm^{-1} at 4 cm^{-1} resolution).

Results and discussion

Preparation and characterization of materials

Intercalation of 1,2-alkanediols into α-ZrP was unsuccessful. Intercalation compounds of 1,2-diols were prepared by using the 1-propanol intercalate as a precursor, contacting it with the desired liquid or melted guest under microwave radiation. All intercalates are white crystalline powders stable in air. Figure 1 shows the XRPD patterns of some of the intercalation compounds obtained. They have a good degree of crystallinity and the (00*l*) lines are very evident up to the fifth order. As shown in Figure 2, the dependence of the basal spacing on the number of carbon atoms in the aliphatic chains of the 1,2-alkanediols is linear with a slope of 2.00 (except the 1,2-propanediol intercalate). Assuming that the alkyl chains of the diol molecules are in an all-*trans* configuration, the slope indicates a bilayer arrangement of the guest molecules. The diol molecules are tilted at an angle of 51° to the host layers.

The compositions of the intercalates obtained are reported in Table 1. The experimental diol/host molar
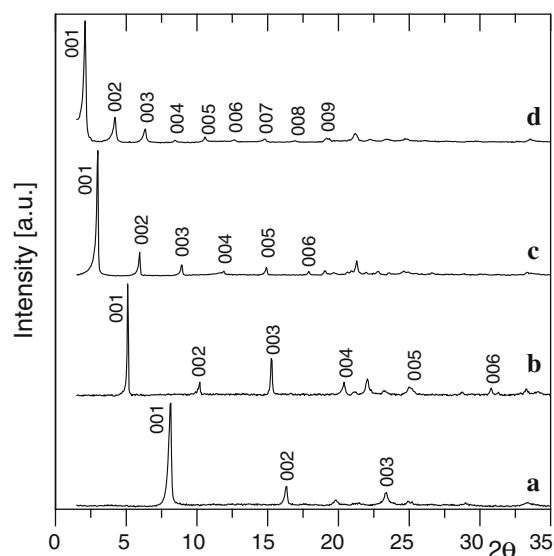

Figure 1. XRPD patterns of α-$Zr(HPO_4)_2$ intercalated with (a) 1,2-propanediol, (b) 1,2-butanediol, (c) 1,2-decanediol, and (d) 1,2-hexadecanediol.
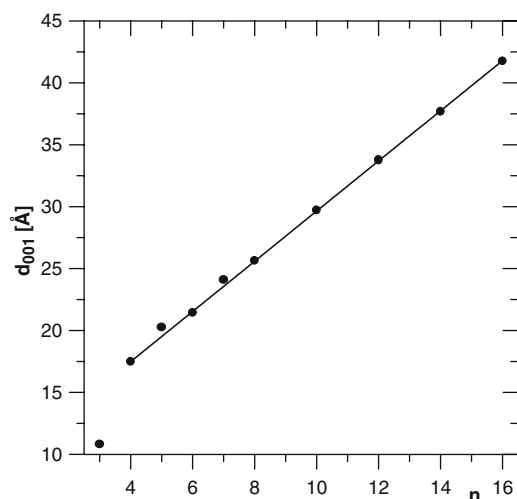
Figure 2. Dependence of basal spacing, *d*, on the number of carbon atoms, n_C, in the aliphatic chain of the intercalated 1,2-diols.

ratio is close to 1.5 with exception of 1,2-propanediol where this ratio is 1. It is in agreement with formerly observed fact that the intercalate with the shortest member of the homologous series differs in composition as well as in the guest arrangement. For example, methanol intercalated $VOPO_4$ and $VOSO_4$ contain 1.33 molecules of methanol per formula unit whereas intercalates of longer alcohols contain two alcohol molecules per formula unit [16]. Similar phenomenon was observed in the case of 2-alkanol intercalated $VOPO_4$ and $NbOPO_4$ where 2-propanol and 2-butanol intercalates have different compositions [17]. Molecular mechanics simulation of vanadyl phosphate intercalated with ethanol, 1-propanol, and 1-butanol showed that the angle, at which the alcohol molecules are tilted to the plane of the host sheets increases with increasing number of carbon atoms [18].

As follows from the TG measurement (Figure 3), the diols are released in one step. The decomposition temperature increases with increasing chain length. The decomposition is endothermic process. In the case of the long diols intercalates, the observed exothermic effect is probably due to the combustion of the released diol molecules. Condensation water is released at 450–550 °C. There are sharp endothermic effects on the

DTA curves of all intercalates which occur at the temperatures from 95 °C (for the 1,2-butanediol intercalate) to 145 °C (for the 1,2-hexadecanediol intercalate). No weight loss accompanies these effects. This phenomenon could be caused by a change of the arrangement of the guest molecules in the interlayer space similarly as in the case of 1-alkanols [14]. Small endothermic effects observable at about 230 °C at the DTA curves of the intercalates with the short diols are probably due to the phase transition of anhydrous α-ZrP [19, 20].

Vibrational spectroscopic study

The analysis of the host structure $Zr(HPO_4)_2 \cdot H_2O$ and the intercalate $Zr(HPO_4)_2$ with various diols has been made by the infrared and Raman spectroscopy. Figure 4 shows the comparison of the infrared spectra for the host compound $Zr(HPO_4)_2 \cdot H_2O$ and for the intercalate $Zr(HPO_4)_2$ with 1,2-hexanediol together with the spectrum of the pure guest. Figure 5 shows the corresponding Raman spectra. The spectra of the host structure $Zr(HPO_4)_2 \cdot H_2O$ and the spectra of the intercalate preserve the same character. This indicates that the host layers are not changed in the intercalate.

The vibrational spectra of the host structure $Zr(HPO_4)_2 \cdot H_2O$ and its intercalate with ethanol $Zr(HPO_4)_2 \cdot 2C_2H_5OH$ have been studied by ATR FTIR and Raman spectroscopy [21]. Combination of IR and Raman spectroscopy with the molecular mechanic simulations have been used for detailed analysis of the bands of the vibration spectra and their interpretation. The IR absorption between 1300–900 cm^{-1} of $Zr(HPO_4)_2 \cdot H_2O$ can be attributed to the vibration of the orthophosphate group. The bands in the infrared spectrum of the host at about 1072, 1043 and 1035 cm^{-1} can be assigned to $v_1(PO_4)$ symmetric stretching vibration (see Figure 4). These bands correspond to the two peaks at 1078 and 1053 cm^{-1} observed in the Raman spectrum (see Figure 5). The fundamental mode $v_1(PO_4)$ in the free ion (τ_d symmetry) is theoretically not degenerated and should be IR inactive. An asymmetry of the HPO_4^{2-} ion, however, makes these vibrations IR active. According to Hezel and Ross the site symmetry allows more vibration modes [22].

Table 1. Basal spacings and composition of the intercalates prepared

n_C	d (Å)	Composition	C % found/calc.	H % found/calc.	Total weight loss % found/calc.
3	10.82	$Zr(HPO_4)_2 \cdot 0.95C_3H_8O_2$	9.59/9.63	2.81/2.72	25.88/26.04
4	17.49	$Zr(HPO_4)_2 \cdot 1.55C_4H_{10}O_2$	17.66/17.61	4.18/4.17	37.46/37.29
5	20.26	$Zr(HPO_4)_2 \cdot 1.32C_5H_{12}O_2$	18.95/18.85	4.14/4.28	35.57/36.96
6	21.44	$Zr(HPO_4)_2 \cdot 1.56C_6H_{14}O_2$	24.04/24.05	5.23/5.14	43.47/43.28
7	24.09	$Zr(HPO_4)_2 \cdot 1.61C_7H_{16}O_2$	27.31/27.29	5.59/5.64	46.02/46.54
8	25.64	$Zr(HPO_4)_2 \cdot 1.44C_8H_{18}O_2$	27.97/28.02	5.75/5.70	45.95/46.30
10	29.70	$Zr(HPO_4)_2 \cdot 1.39C_{10}H_{22}O_2$	31.67/31.77	6.19/6.25	49.07/49.54
12	33.76	$Zr(HPO_4)_2 \cdot 1.48C_{12}H_{26}O_2$	36.58/36.61	7.12/7.00	53.98/54.49
14	37.70	$Zr(HPO_4)_2 \cdot 1.58C_{14}H_{30}O_2$	41.10/41.05	7.56/7.69	58.47/59.03
16	41.75	$Zr(HPO_4)_2 \cdot 1.40C_{16}H_{34}O_2$	41.53/41.72	7.54/7.75	57.88/58.79

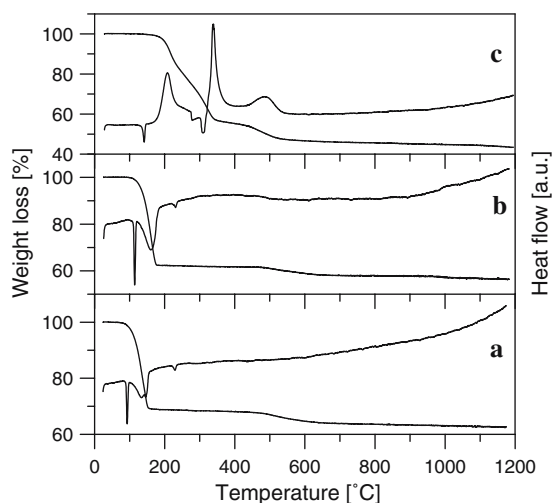*Figure 3*. TG curves of α-Zr(HPO$_4$)$_2$ intercalated with (a) 1,2-butanediol, (b) 1,2-hexanediol, and (c) 1,2-hexadecanediol.

The v_3(PO$_4$) asymmetric stretching vibration appears as shoulders at about 1171 and 1117 cm^{-1} in the infrared spectrum of the host. This is in a good agreement
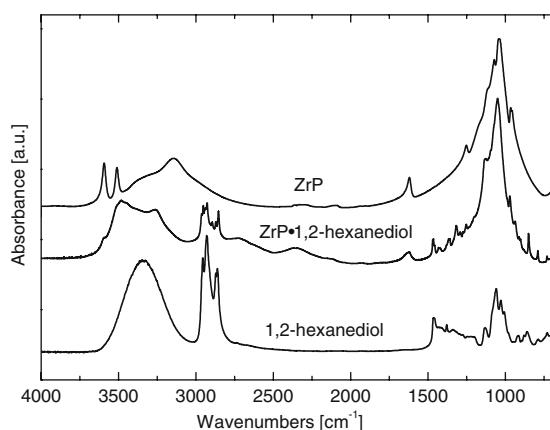

Figure 4. The FTIR spectrum of the host structure Zr(HPO$_4$)$_2 \cdot$ H$_2$O, of the intercalate Zr(HPO$_4$)$_2$ with 1,2-hexanediol in KBr pellets and the FTIR ATR spectrum of pure liquid 1,2-hexanediol.

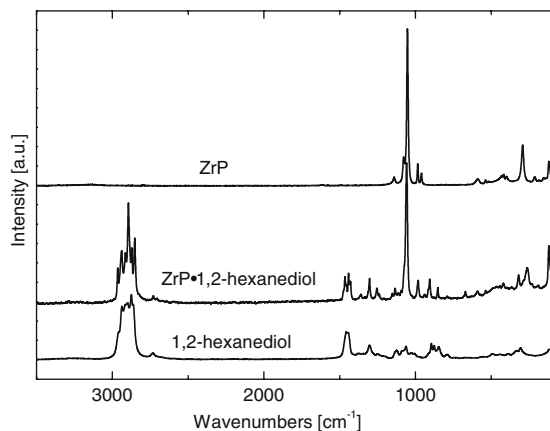*Figure 5*. The Raman spectrum of the host structure Zr(HPO$_4$)$_2 \cdot$ H$_2$O, of the intercalate Zr(HPO$_4$)$_2$ with 1,2-hexanediol and of pure 1,2-hexanediol.

with the 1141 cm^{-1} Raman frequency in the spectrum in Figure 5. The v_1 and v_3 frequencies of the HPO$_4^{2-}$ ion are also influenced by the hydrogen bonding that exists between the doubly charged negative phosphate ion and the partially positively charged hydrogen atom of the water molecules which hydrates it [23]. The band at 1252 cm^{-1} in the infrared spectrum of the host is due to the δ(P–O–H) in-plane deformation mode. This mode is inactive in the Raman spectrum. The doublet, observed in the infrared spectrum at 966 and 957 cm^{-1} and corresponding to the δ(P–O–H) out-of-plane deformation mode, is the result of two different hydrogen bonding schemes for the OH-groups [21].

The presence of the water molecules in the host compound Zr(HPO$_4$)$_2 \cdot$ H$_2$O is manifested in the infrared spectrum by the band of the deformation mode at about 1620 cm^{-1}. In the region of the stretching vibrations of the water molecule we observed a broad band at about 3145 cm^{-1} with a shoulder at about 3355 cm^{-1}. Two sharp peaks observed at 3510 cm^{-1} and 3593 cm^{-1} are usually attributed to the intercalated water [24]. As we observed these peaks also in anhydrous Zr(HPO$_4$)$_2$, we supposed that they can be attributed to the (P–)O–H stretching modes corresponding to the two non-equivalent O–H groups.

Comparing the infrared spectra for the host structure and the intercalate with 1,2-hexanediol in Figure 4, one can see the same character of the vibration bands for both cases. The observable changes can be explained by the differences in the hydrogen bonding scheme for water and the 1,2-hexanediol molecules. The v_1(PO$_4$) vibration is observable in the both spectra of the host structure and the intercalate at the same frequency region, however the profile of this band is slightly modified in the spectrum of the intercalate. The doublet δ(P–O–H) corresponding to the out-of-plane deformation mode is observable in both infrared spectra and its position is shifted from 957 and 966 cm^{-1} in the host structure to 936 and 972 cm^{-1} in the intercalate. As it has been mentioned by Pimentel [25], the frequency of the out-of-plane torsion modes increased as a result of the hydrogen bond formation. This means that the position of one of the bands of the δ(P–O–H) doublet is slightly shifted to the higher frequency for the intercalate structure, as a result of stronger hydrogen bonding of one 1,2-hexanediol molecule in comparison with the water molecule. The second peak of the doublet is shifted to lower frequency, which may correspond to weaker hydrogen bonding of the second 1,2-hexanediol molecule in comparison with the water molecule.

In the region of the stretching vibrations of the OH group we observe three overlapping broad bands with the maxima at about 3480, 3350 and 3261 cm^{-1} in the spectrum of the intercalate. The broad bands correspond most probably to the hydrogen bonded OH group of 1,2-hexanediol molecules. The band at 3350 cm^{-1} corresponds to the O–H stretching vibration in the spectrum of liquid 1,2-hexanediol with intermolecular hydrogen bonds. It suggests that the

intermolecular hydrogen bonds between two adjacent 1,2-hexanediol molecules occur also in the intercalate. There are several sharp peaks observed on the described broad bands situated at 3593, 3508, 3483 and 3261 cm^{-1}. They are attributed to the (P–)O–H stretching modes corresponding to the non-equivalent O–H groups of the host. The first two sharp peaks are situated at the same positions compared to the spectrum of the host structure $Zr(HPO_4)_2 \cdot H_2O$, the other two are shifted to the lower frequency due to stronger hydrogen bonding of the guest molecules.

The infrared spectrum of the intercalate at ambient temperature exhibits pronounced peaks which correspond to the 1,2-hexanediol vibrations [26] (see Figure 4). The strong band at about 1060 cm^{-1} observed in the spectrum of pure liquid 1,2-hexanediol corresponds most probably to the C–O stretching vibration. This band together with the band of the C–C stretching vibration observed at 1131 cm^{-1} in the spectrum of pure 1,2-hexanediol is overlapped by the band of the orthophosphate group of the host in the spectrum of the intercalate. The relatively strong doublet observed at about 1466 cm^{-1} in the spectrum of 1,2-hexanediol corresponds most probably to the CH_2 bending vibration. The band at 1379 cm^{-1} in the spectrum of 1,2-hexanediol results most probably from the interaction between the O–H in-plane bending and C–H wagging vibrations. In the spectrum of the intercalate we observe two doublets at 1465 and 1432 cm^{-1}, which may correspond to two non-equivalent positions of the 1,2-hexanediol molecules. This idea is strongly supported in the Raman spectrum, where the doublet observed at about 1457 cm^{-1} in the spectrum of pure 1,2-hexanediol is split into two doublets at 1465 and 1442 cm^{-1} in the spectrum of the intercalate (see Figure 5). The alkyl chains are reasonably assumed to be in an all-*trans* conformation in the intercalate [14]. The splitting of the absorption bands in the region 1500–700 cm^{-1} is observed for fully extended alkyl chain in the crystalline state. This corresponds to the interaction between the CH_2 wagging and C–C skeletal vibrations [27]. We observe the splitting of the bands of the CH stretching vibrations when going from pure 1,2-hexanediol to the intercalate (see Figure 4). This splitting is also observed in the region of the CH stretching vibrations in the Raman spectra. Very similar features are observed in the infrared and Raman spectra of 1,2-dodecanediol and its intercalate.

Suggestion of the arrangement of the guest molecules in the interlayer space

The X-ray diffraction structure analysis is usually difficult in the case of the intercalates. Their diffractograms are often affected by many phenomena like disorder in the arrangement of the guest molecules in the interlayer space and disorder in the stacking of the layers. As a result of this disorder, it is almost impossible to prepare a single crystal suitable for the diffraction analysis. The powder diffraction patterns are in addition influenced by a strong preferred orientation. Therefore the arrangement of the guest molecules in the interlayer space is usually suggested on the basis of the steric demands of the guest molecules, host layer thickness, and the experimentally found basal spacing and composition of the intercalate. The proposed arrangement of the 1,2-hexanediol molecules in the interlayer space is given in Figure 6. The guest molecules form a bimolecular film and are tilted at an angle 51° to the host layers. Bilayer arrangement indicates that the 1,2-alkanediol molecules are placed in a way somewhat similar to that found for the 1-alkanol intercalates, i. e., with functional hydrophilic OH groups close to the $Zr(HPO_4)_2$ layers and with alkyl group extending to the interlayer space. The intercalates contain 1.5 molecules of the diol per formula unit, $Zr(HPO_4)_2$. The host/guest molar ratio (2/3) suggests that the arrangement of the diol molecules in the interlayer space is more complicated in comparison with 1,ω-alkanediols and 1-alkanols. In the structure of $Zr(HPO_4)_2$, there are OH groups pendant above and below the host layer. These groups are considered to be active sites, that is the sites where the guest molecules are anchored by their active groups. It means that there are two active sites per formula unit of $Zr(HPO_4)_2$. The 1,2-diol intercalates, with general formula $Zr(HPO_4)_2 \cdot 1.5$ diol, can be therefore considered as compounds containing three molecules of the guest per four active sites. 1,2-Alkanediols can be coordinated to the active sites either by the first, or terminal, (O1) oxygen or by the second (O2) oxygen of the hydroxy groups. We can assume that two of the intercalated guest molecules are bonded by its O1, each of them to one active site. The space between these two guest molecules is filled by their free (O2)H groups which mutually interacts by H-bonds. Such arrangement generates a space between these diols molecules so that another molecule of the diol can be bonded by both of its OH groups to the active sites of the $Zr(HPO_4)_2$ layers. The steric hindrance caused by the neighboring diol molecules forces this third molecule of the diol to arrange slightly upright, with O2 further away from the active site than O1. The total arrangement is then composed of three guest molecules per four active sites (or two formula units) of the host layer.

Co-intercalation of two different guests

As already described, the microwave-assisted intercalation of 1,2-alkanediols requires the presence of small amounts of 1-propanol. Therefore, it was of interest to investigate the nature of the materials formed when the 1-propanol intercalate, suspended in mixtures of 1-propanol and 1,2-octanediol, is exposed to microwave radiation. No new phase containing both types of the guest molecules was observed, only the intercalates of either 1-propanol or 1,2-octanediol were formed.

A mixed intercalate is formed when the 1-propanol intercalate, suspended in the mixtures of 1,2-butanediol and 1,2-decanediol, is exposed to microwave radiation.
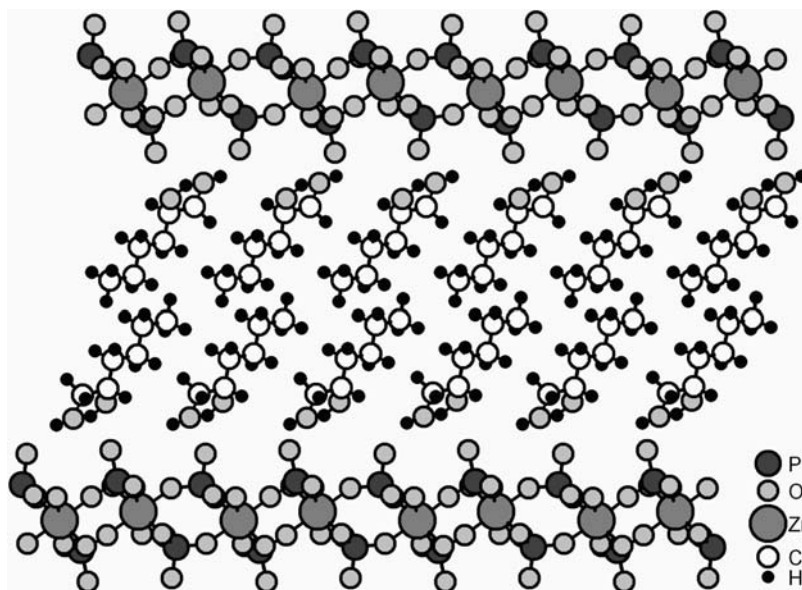
Figure 6. Proposed arrangement of the 1,2-hexanediol molecules in the interlayer space of zirconium hydrogenphosphate.

The diffractograms of some intercalates prepared in this way are given in Figure 7. Figure 8 reports the interlayer distance of the obtained intercalation compounds as a function of the molar fraction y of 1,2-dekanediol in the starting guests mixtures. The discontinuous change of the interlayer distance indicates that the system is polyphasic. As expected, the 1,2-butanediol intercalate, with an interlayer distance of 17.49 Å, is obtained when y is zero. This phase continues up to y about 0.2, without appreciable solubilization of the 1,2-decanediol molecules in the interlayer region. At $0.2 \leq y \leq 0.45$, 1,2-decanediol partly displaces 1,2-butanediol from the interlayer and an intercalation compound, containing 1,2-butanediol and 1,2-decanediol in a roughly equimolar ratio, is formed. Both phases, the 1,2-butanediol intercalate and the mixed intercalate, are present in the narrow range of y around 0.24. It is interesting to note that the observed interlayer distance of the mixed intercalate, 23.64 Å, is very near to that calculated when assuming the formation of a phase with an ideal diol ratio 1:1. The molecules of both diols combine in the interlayer region in such a way that the thickness of the bilayer is determined by the sum of the lengths of one molecule of 1,2-butanediol and one molecule of 1,2-decanediol. A similar arrangement was observed in $VOSO_4$ [28], $VOPO_4$ [29], and α-ZrP [14] mixed alkanol intercalates. In the 0.45–0.6 compositional range, the solid product formed is amorphous. At y higher than 0.6, pure 1,2-decanediol intercalate with basal spacing 29.70 Å is formed.
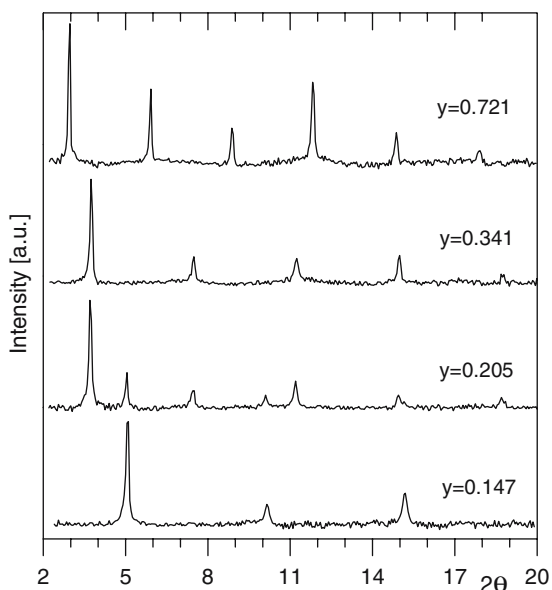

Figure 7. XRPD patterns of the intercalates prepared by reacting of the 1-propanol intercalate with mixtures of 1,2-butanediol and 1,2-decanediol with various 1,2-decanediol content y.
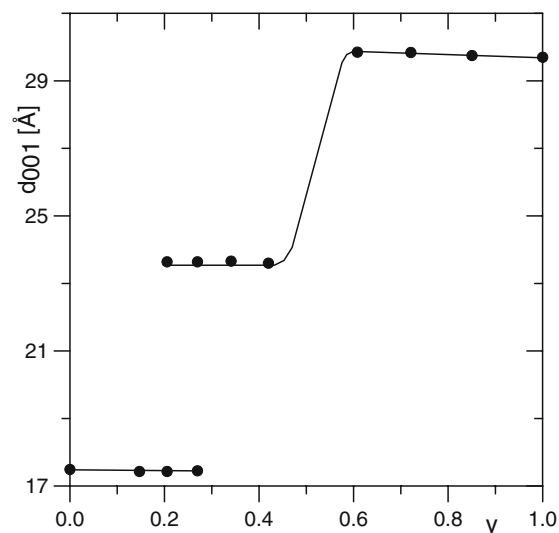

Figure 8. Dependence of the basal spacing, d, of the prepared solid phases on the composition, y, of the starting mixture 1,2-butanediol–1,2-decanediol.

As can be seen from these experiments, there are two requirements for the formation of mixed intercalates (i) the molecules of both guest should be of the same type and (ii) the pure intercalates of both guest should have the same host/guest ratio.

Acknowledgements

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