Intercalation of Alkanols and Glycols into Zirconium(IV) Hydrogenphosphate Monohydrate

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Alkanols and glycols have been intercalculated in the layered structure of $Zr(HPO_4)_2 \cdot H_2O$ by regenerating salt forms of the exchanger with the protonated alkanols or glycols. The increase in the interlayer spacing of the obtained compounds with the length of the guest molecule suggests that n-alkanols are intercalated as a bimolecular film of extended molecules while glycols form a unimolecular film. Owing to the weak forces holding the molecules within the layers of zirconium phosphate and their high interlayer spacing, the intercalated compounds have been used successfully to intercalate other polar organic molecules. The use of zirconium phosphate–alkanol compounds as ion exchangers in aqueous and non-aqueous media is also reported and discussed.

POLAR organic molecules (such as alkanols, glycols, amines, *etc.*) can be intercalated in the layered structure of clay minerals and an extensive literature on reactions of clays with organic compounds is available.[1] Crystalline zirconium(IV) hydrogenphosphate, $Zr(HPO_4)_2 \cdot H_2O$, has a layered structure [2] (interlayer distance 0.76 nm) similar to that of clay minerals.[3] In the last ten years the ion-exchange properties of this compound have been investigated [4-6] but very few papers deal with the interaction with polar organic molecules. In 1965 Michel and Weiss [7] were able to intercalate n-alkylamines into $Zr(HPO_4)_2 \cdot H_2O$, but only recently has there been a renewed interest in the intercalation of organic molecules in this material [8,9] because of its chemical and thermal stability and its ion-exchange properties. Until now, intercalation compounds of $Zr(HPO_4)_2 \cdot H_2O$ have been obtained with organic molecules possessing a strong basic character and they are stable to thermal treatment and to washing.

In this paper are reported the preparation of intercalation compounds of zirconium hydrogenphosphate with alkanols and glycols and some structural considerations. The use of zirconium hydrogenphosphate–alkanol compounds as starting materials to intercalate other polar organic molecules or as ion exchangers in aqueous and non-aqueous media is also discussed.

EXPERIMENTAL

Chemicals.—C. Erba R.P.E. reagents were used, except for $ZrCl_2O \cdot 8H_2O$ which was a Merck ' pro analysis ' product and glycols which were supplied by Fluka. Microcrystals of $Zr(HPO_4)_2 \cdot H_2O$ were prepared according to the direct-precipitation method in the presence of hydrofluoric acid.[10] The monosodium form was obtained by titrating $Zr(HPO_4)_2 \cdot H_2O$ (suspended in 0.5 N NaCl) with 0.2 N Na[OH] until half conversion and stored in a vacuum desiccator over saturated NaCl solution (relative humidity *ca.* 75%).

Analyses.—Sodium ion was determined by flame photometry using a Perkin-Elmer A.A.S. 305 instrument. The uptake of amines, as a function of time, was followed by means of a Mettler automatic titrimeter operating in a pH-stat mode. The *X*-ray powder patterns (of the wet and dried samples) were obtained with nickel-filtered Cu-K_α radiation, using a General Electric diffractometer. The sensitivity of the *X*-ray goniometer was within ±0.01°. Interlayer spacing of the compounds was calculated from the average of the first three-order reflections of the 002 plane and the error can be evaluated as ±0.01 nm.

RESULTS AND DISCUSSION

Preparation, Structure, and Stability of Alkanol and Glycol Intercalation Compounds.—Preliminary attempts to intercalate alkanols in $Zr(HPO_4)_2 \cdot H_2O$ by contacting the exchanger with the pure solvents, for several days, failed. It is likely that in ionic forms of crystalline zirconium phosphate having a large interlayer distance, such as $ZrNaH(PO_4)_2 \cdot 5H_2O$ (interlayer distance 1.18 nm), $ZrLiH(PO_4)_2 \cdot 4H_2O$ (1.01 nm), or $Zr(HPO_4)_2 \cdot (6 \pm 1)H_2O$ (1.04 nm), the diffusion of alkanol molecules would be greatly facilitated. On the other hand, $ZrNaH(PO_4)_2 \cdot 5H_2O$ contacted with pure methanol or ethanol loses its hydration water and the interlayer distance collapses to 0.76 nm, the value corresponding to the monohydrate form. It was found that alkanols and glycols can be intercalated between the layers of zirconium phosphate by regenerating, at room temperature, $ZrNaH(PO_4)_2 \cdot 5H_2O$ with 0.1 mol dm^{-3} $HClO_4$ solution. In fact, reaction (1) (R = n-alkyl chain)

$$ZrNaH(PO_4)_2 \cdot 5H_2O + ROH_2^+ + (x-1)ROH \longrightarrow Zr(HPO_4)_2 \cdot xROH + Na^+ + 5H_2O \quad (1)$$

leads to forms of crystalline zirconium hydrogenphosphate in which the protons are solvated by the solvent used. *X*-Ray diffractograms were taken of wet samples of zirconium hydrogenphosphate swollen with several n-alkanols and glycols. The samples maintained their crystallinity and sharp reflections corresponding to the 002 plane were observed. Generally, harmonics up to the fourth order (004, 006, 008) were evident, their intensity being lower than that of the first reflection. Reflections due to other lattice planes were weak or absent. Figure 1 shows the basal spacings of the n-alkanol or glycol complexes as a function of the number of carbon atoms in the n-alkyl chain. The basal spacings increase linearly and the best-fit curves were computed by the method of least squares. Correlation coefficients of 0.998 7 and 0.968 6 were obtained for n-alkanols and glycols respectively. Values of the gradient, $\Delta d/\Delta n = 0.207$ for alkanols and 0.110 for glycols, were calculated by regression analysis. Since the increment of the alkyl-chain length for each additional carbon atom is generally estimated as 0.127 nm, it is likely that glycols are intercalated as a unimolecular layer, while n-alkanols seem to form a double layer of extended molecules inclined at an angle $\alpha = \sin^{-1}(0.207/0.254) = 54.5°$ with respect to the sheet.

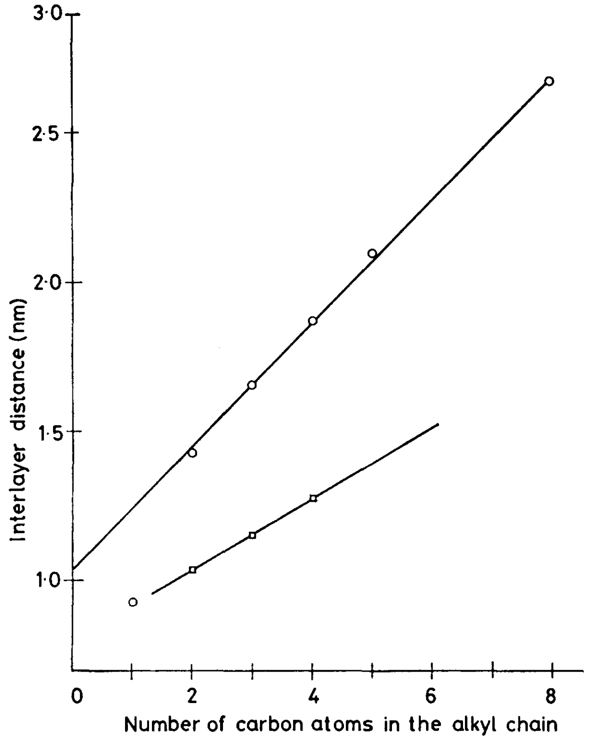

FIGURE 1 Interlayer distances of n-alkanol (○) and glycol (□) intercalate compounds of zirconium phosphate as a function of the number of carbon atoms in the alkyl chain

Figure 2 shows an idealized representation of a possible arrangement of a double layer of n-pentanol molecules between the sheets of zirconium phosphate. The distance between the oxygens of the $\geqslant$P–OH groups in the same plane is 0.53 nm and the sheets are shifted relative to each other by two thirds of this value [2]; bond lengths and bond angles were taken from ref. 11, while C and H van der Waals radii are 0.17 and 0.12 nm respectively. A symmetrical hydrogen bond is assumed to be formed between the oxygen of the phosphate group and that of the alcohol group. This bonding is very similar to that of the oxygen of the water molecule in $Zr(HPO_4)_2{\cdot}H_2O$ as recently determined by Albertsson *et al.*[12] It is noted that the experimental value of the interlayer distance (2.09 nm) is obtained with an inclination of the pentanol molecules of 54.5° with respect to the sheet, and that each $\geqslant$P–OH group is engaged in a hydrogen bond with one alkanol molecule to form compounds containing 2 mol of intercalated molecule per mol of exchanger.

The interlayer distance of the intercalated methanol compound, whose value has not been used in computing the best curve, does not fit the curve for n-alkanols (see Figure 1). Only 1 mol of solvent per mol of exchanger seems to be intercalated, probably because of the spherical shape of the molecule. The determination of the amount of methanol taken up is very difficult, owing to the instability of the intercalation compound which loses the guest molecule when exposed to air. Experimental evidence for the presence of only 1 mol of methanol between the sheets of the exchanger can be derived by comparing the interlayer distance of the intercalated methanol compound (0.93 nm) with that for intercalation compounds of $Zr(HPO_4)_2{\cdot}H_2O$ with methylamine. Methylamine, which is about the same size as MeOH, forms two very stable intercalation compounds: the first contains 1 mol of amine per mol of exchanger and has an interlayer spacing of 0.95 nm; the second, with a 2 : 1 mol ratio, has an interlayer spacing of 1.15 nm, very near to the value estimated for a zirconium phosphate complex containing 2 mol of MeOH per mol (see Figure 1). Attempts were made to intercalate branched alkanols between the layers of $Zr(HPO_4)_2{\cdot}H_2O$ using a procedure identical to that used for n-alkanols and glycols. Propan-2-ol gives a complex with an interlayer spacing of 1.56 nm, while 2-methylpropan-1-ol and 3-methylbutan-1-ol were not taken up and the anhydrous hydrogen form of the exchanger was obtained.

The intercalation compounds containing alkanols lose the guest molecules on drying at room temperature and the interlayer distance generally collapses to 0.76 nm. Attempts were made to follow the desorption process by *X*-ray diffraction, but only in the case of the ethanol compound was a new diffraction maximum detected corresponding to $d = 1.02$ nm (attributable to an intercalation compound containing 1 mol of ethanol per mol of exchanger). The stability of the intercalated glycol compounds examined is much higher than those of the alkanol compounds. In fact, it was possible to quickly wash the glycol complexes with acetone, dry them over silica gel, and obtain the weight-loss curves (see Figure 3) by heating the samples in an oven at various temperatures. The total weight loss at 800 °C corresponds fairly well to the loss of 1 mol of intercalated glycol plus 1 mol of water (due to the condensation of phosphate groups to pyrophosphate) per mol of exchanger. The guest molecules are completely lost

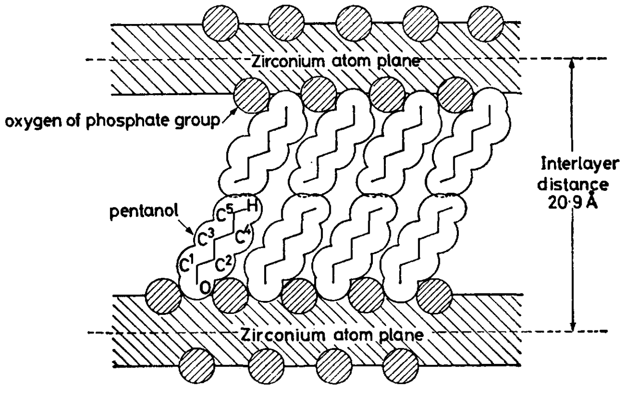

FIGURE 2 Iidealized model of a possible arrangement of pentanol molecules between the sheets of zirconium phosphate

between 210 and 250 °C. For example, ethylene glycol is completely lost at 210 °C and during the desorption process the interlayer distance of the intercalated compound changes from 1.06 to 0.74 nm discontinuously and solid phases with interlayer distances of 1.02 and 0.92 nm, coexistent with $Zr(HPO_4)_2$, were also found. This behaviour can be explained by assuming that the intercalation process occurs by a stepwise mechanism involving phase transitions and the coexistence in a single crystallite of different interlayer distances. A similar mechanism has been recently proposed by Alberti[6] for ion-exchange and hydration processes on layered exchangers, such as zirconium phosphate.

Exchange of Intercalated Alkanol Molecules with Other Polar Molecules.—Taking into account the weak forces holding the alkanols between the layer of $Zr(HPO_4)_2$ and the large interlayer distances, allowing free diffusion of charged and neutral species in the lattice, zirconium phosphate–alkanol compounds can be considered as very good starting materials for the intercalation of other polar molecules. The alkanols are easily replaced by other polar molecules at room temperature by simply contacting the intercalation compounds with the corresponding pure liquid or with a solution containing the species to be intercalated. The Table gives the basal spacings of several intercalation compounds of $Zr(HPO_4)_2$ obtained by contacting the corresponding methanol or ethanol compounds with pure liquids. The following comments can be made.

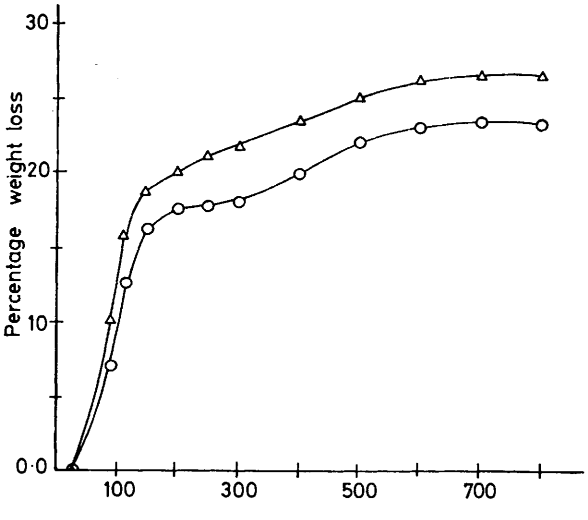

FIGURE 3 Percentage weight loss at different temperatures of compounds of ethylene glycol (○) and propyleneglycol (△) with zirconium phosphate

(*a*) The zirconium phosphate–methanol compound dispersed in water gives rise to a polyhydrated hydrogen phase with an interlayer spacing of 1.04 nm. This phase (designed θ-ZP by Clearfield *et al.*[4]) can be also obtained by regenerating, under appropriate conditions, salt forms of zirconium phosphate, such as $ZrNaH(PO_4)_2\cdot 5H_2O$, using dilute HCl solutions.[13] The θ phase can be prepared in a pure form only when the zirconium phosphate has a good but not high degree of crystallinity.

Interlayer distances for some intercalation compounds of $Zr(HPO_4)_2$ obtained by contacting its methanol or ethanol intercalates with pure liquids at room temperature

Methanol compound

Intercalated molecule	Interlayer distance (nm)
Water	1.04
Dimethylformamide	1.12
Acetonitrile	1.13
Urea [a]	0.94
Aniline [b]	1.8
Heptylamine [b]	2.7
Decylamine [b]	3.2

Ethanol compound

Intercalated molecule	Interlayer distance (nm)
Propan-2-one	0.99
Pentane-2,4-dione	1.35
Octan-1-ol	2.67
Propan-2-ol	1.56
2-Methylpropan-1-ol	1.75
3-Methylbutan-1-ol	1.92
Benzyl alcohol	2.10

[a] 1 mol dm^{-3} solution in water. [b] 0.1 mol dm^{-3} solution in methanol.

The salt $ZrNaH(PO_4)_2\cdot 5H_2O$, obtained from highly crystalline zirconium phosphate, such as that prepared by the direct-precipitation method in the presence of hydrofluoric acid, always gives, after regeneration, a mixture of the monohydrate and θ phase.[13] In the present work, although zirconium hydrogenphosphate prepared by the direct-precipitation method was employed, the pure θ phase was obtained. The method of washing the zirconium phosphate–methanol compound with water can therefore be considered as a good procedure for preparing $Zr(HPO_4)_2\cdot 6H_2O$ which readily undergoes exchange with cations having a large ionic radius[13] such as Cs^+ or Ba^{2+} or which are highly hydrated such as Mg^{2+} or Cr^{3+}.

(*b*) Isoalkanols and long-chain n-alkanols are easily intercalated by contacting the pure liquids with the zirconium phosphate–ethanol compound (interlayer distance 1.42 nm), while they are not able to replace methanol in the corresponding complex (*d* 0.93 nm). This behaviour can be explained by taking into account the fact that, as discussed by Alberti,[14] when the basal spacing of zirconium phosphate is >1.0 nm the distance between two fixed charges in two adjacent layers is higher than that of two fixed charges in the same plane; the interactions between the layers are therefore strongly weakened and the diffusion of the polar molecules is facilitated. Furthermore, with the present procedure, intercalation compounds containing polar molecules such as MeCN, MeCOEt, Me_2NCHO, *etc.*, are easily obtained at room temperature, while Beherendt *et al.*[9] claimed to have obtained similar compounds by contacting zirconium phosphate ' for several days at 60—80 °C '.

(*c*) Amines can be intercalated within the layers of

$Zr(HPO_4)_2 \cdot H_2O$ by allowing the exchanger to react with the pure liquids.[7] We found that amines are also taken up by zirconium phosphate from dilute aqueous solutions, but the process (presumably the protonation of amines by the hydrogens of the exchanger) is very slow. Figure 4 shows the kinetics of uptake of ethylenediamine on zirconium phosphate (*b*) and on the zirconium phosphate–methanol compound (*a*) dispersed in water. These curves were obtained with an automatic titrimeter filled with 0.1 mol dm^{-3} ethylenediamine and operating in the pH-stat mode (pH 8). It can be seen that saturation of the exchanger is reached in a few minutes in the case of the zirconium phosphate–methanol compound, while several hours are necessary to saturate $Zr(HPO_4)_2 \cdot H_2O$. It is noted that while n-alkylamines form compounds containing 2 mol of guest molecules per mol of exchanger, in the case of ethlyenediamine the complete saturation corresponds to the uptake of 1 mol of the amine per mol of zirconium phosphate.

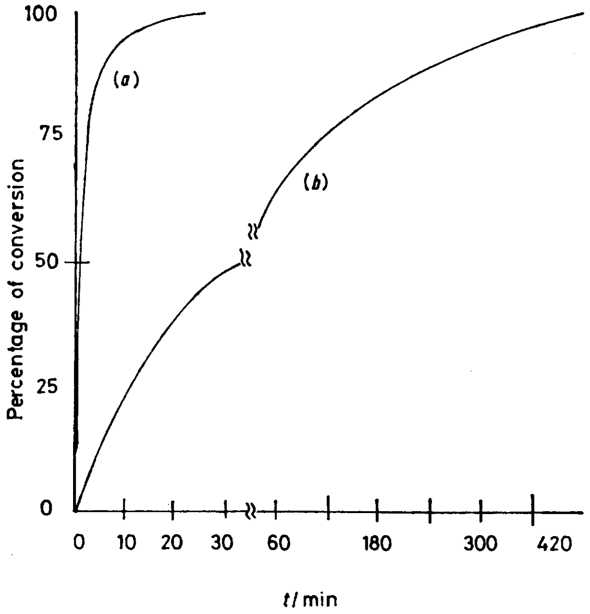

FIGURE 4 Uptake of ethylenediamine on zirconium phosphate (*b*) and on the zirconium phosphate–methanol compound (*a*) as a function of time at 25 ± 1 °C

Conclusions.—The purpose of the present work was mainly to show how, with a simple procedure, it is possible to intercalate in layered inorganic ion exchangers belonging to the class of insoluble acid salts of quadrivalent metals, such as $Zr(HPO_4)_2 \cdot H_2O$, polar organic molecules having a very low basicity. Further work is necessary to draw definite conclusions about the mechanism of intercalation and the position of the intercalated molecules in the structure. It can be pointed out that the intercalated alkanol compounds obtained are very attractive materials since they can be used as starting materials to intercalate other polar organic molecules, the zirconium phosphate–ethanol compound can be used to prepare the θ phase, and they undergo exchange of the guest molecules with molecules of the solvent in which they are dispersed. In this manner, it is possible to obtain zirconium phosphates, solvated by the chosen solvent, which generally have a high interlayer spacing. These materials may be used to perform ion-exchange processes in non-aqueous media and zirconium phosphate can be easily loaded with organic cations or basic molecules, such as aromatic amines insoluble in water. Furthermore, these compounds may find applications in many other fields such as those of separations, synthesis, and heterogeneous catalysis. Zirconium phosphate and its ionic forms have already been used as catalysts,[15,16] and the possibility of intercalating active substrates makes this layered exchanger a suitable support for catalytic processes. Finally, the transport phenomena occurring in the interlayer region will be greatly modified by the presence of different guest molecules and this will be of interest in the field of ionic conductors and ion-exchange membranes.

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REFERENCES

[1] B. K. G. Theng, ' The Chemistry of Clay-Organic Reactions,' Adam Hilger, London, 1974.

[2] A. Clearfield and G. D. Smith, *Inorg. Chem.*, 1969, **8**, 431.

[3] D. Leigh and A. Dyer, *J. Inorg. Nuclear Chem.*, 1972, **34**, 569.

[4] A. Clearfield, G. H. Nancollas, and R. H. Blessing, in ' Ion Exchange and Solvent Extraction,' vol. 5, eds. J. A. Marinsky and Y. Marcus, Marcel Dekker, New York, 1973, ch. 1.

[5] G. Alberti and U. Costantino, *J. Chromatog.*, 1974, **102**, 5.

[6] G. Alberti, *Accounts Chem. Res.*, 1978, **11**, 163.

[7] E. Michel and A. Weiss, *Z. Naturforsch.*, 1965, **B20**, 1507.

[8] S. Yamanaka and M. Koizumi, *Clay and Clay Min.*, 1975, **43**, 477.

[9] D. Beherendt, K. Beneke, and C. Lagaly, *Angew. Chem. Internat. Edn.*, 1976, **15**, 544.

[10] G. Alberti, S. Allulli, U. Costantino, and M. A. Massucci, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1779.

[11] ' Tables of Interatomic Distances,' *Special Publ.*, The Chemical Society, London, 1958, no 11.

[12] J. Albertsson, A. Oskarsson, R. Teligen, and J. O. Thomas, *J. Phys. Chem.*, 1977, **81**, 1574.

[13] G. Alberti, U. Costantino, and J. S. Gill, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1173.

[14] G. Alberti in ' Study Week on Biological and Artificial Membranes on Desalination of water,' ed. R. Passino, Pontificia Academia Scientiarum, Città del Vaticano, 1976, p. 629.

[15] T. Kalman, M. Dudukovic, and A. Clearfield, *Adv. Chem. Ser.*, 1974, **113**, 654.

[16] Y. Onone, Y. Mizutani, S. Akiyama, Y. Izumi, and Y. Watanabe, *Chem. Tech.*, 1977, 36.