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Intercalation of n-alkylamines into α-tin(IV) bis(hydrogenphosphate)

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The intercalation reaction of n-alkylamines from methyl- to hexadecylamine into α-tin(IV) bis(hydrogenphosphate) has been investigated. The reaction was conducted by mixing the phosphate and solutions of the amines dissolved in water or benzene. The amine/phosphate molar ratios in the reaction mixtures were 0.43, 0.85, 1.71 and 3.41. The nitrogen/phosphorus atomic ratio in the intercalation compound was not changed by the amine/phosphate molar ratio. The interlayer distances of the intercalates obtained in the reaction mixtures with molar ratios of 3.41 and 1.71 increased with an increase in the number of carbon atoms in the alkyl chain of the amine. The slope of the straight line obtained in plot of interlayer distance versus number of carbon atoms in the alkyl chain of the amine indicates that the amine molecules form a double layer in the interlayer space of the phosphate and are inclined at an approximate angle of 67.7° to the phosphate layer. The interlayer distances of the intercalates of butyl- to nonylamines obtained at the molar ratio of 0.85 are smaller than those of the corresponding compounds from the molar ratios of 3.41 and 1.71, while those of decyl- to hexadecylamine intercalates lie on the previously discussed line. This behaviour is interpreted by assuming kink formation in the short alkyl chains between the phosphate layers.

1. Introduction

Tetravalent metal bis(hydrogenphosphates) with the general formula M(IV) $(HPO_4)_2 \cdot nH_2O$ (where M(IV) = Ti, Zr and Sn) are known to have two-dimensional layered structures. The layered phosphates possess intercalation properties and are of interest because of their potential applications as ion-exchangers, sorbents, solid ionic conductors and heterogeneous catalysts [1–3].

Since materials of the type $M(IV)(HPO_4)_2 \cdot nH_2O$ are Brönsted acids, organic bases can intercalate into the interlayer spaces. A considerable amount of work has been performed on the intercalation reactions of amines into layered phosphates such as α-zirconium(IV) bis(hydrogenphosphate) [α-ZrP] and α-titanium(IV) bi(hydrogenphosphate) [α-Tip] [4–7]. The title compound, α-tin(IV) bis(hydrogenphosphate) [α-SnP], is known to have a similar structure to that of α-ZrP [8–11] and the intercalation reactions of aromatic amines and of alkydiamines have been reported in the literature [12–15]. For the intercalation of n-alkylamines, Rodriguez-Castellon *et al.* [16] have reported the reaction of amines of $n_c = 4$–7, where n_c stands for the number of carbon atoms in the alkyl chain, and Michel and Weiss [17] for $n_c = 8$.

The present authors have previously reported on the intercalation of n-alkylamines into α-SnP over a wide range of n_c and have briefly discussed the arrangement and orientation of the alkyl chains in the interlayer space [18]. In the previous work the reaction was carried out only at the amine/α-SnP molar ratio of 1.71 (an erroneous figure of 0.43 was reported as the molar ratio in the previous paper [18], and thus 0.43 should be read as 1.71) and thus the amines of $n_c = 7$, 9, 11, 13 and 15 remain to be investigated.

The present paper describes the intercalation reaction of the homologous series of n-alkylamines of $n_c = 1$–16 into α-SnP, and discusses the conformational behaviour of the guest molecules in the α-SnP interlayer space.

2. Experimental procedure

2.1 Chemicals

Unless otherwise stated, guaranteed-grade reagents were used without further purification.

2.2 Preparation of α-tin(IV) (bis(hydrogenphosphate)

The α-tin(IV) bis(hydrogenphosphate) [α-SnP] was prepared according to the method of Fuller [9]. The number of moles of hydrated water depends on the atmospheric humidity [9, 10]. The chemical analyses

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TABLE I The combination of the weight of α-SnP and the concentration and volume of n-alkylamine solution

α-SnP (g)	Amine solution (water or benzene) Concentration (mol dm^{-3})	Volume (cm^3)	Amine/α-SnP molar ratio
0.1	0.1	10	3.41
0.2	0.1	10	1.71
0.2	0.05	10	0.85
0.2	0.025	10	0.43

of the product air-dried at room temperature gave an empirical formula of $Sn(HPO_4)_2 \cdot 1.7H_2O$ [10].

2.3 Intercalation of n-alkylamines

The intercalation reaction was performed by mixing at 25 °C for 2 days 0.1 or 0.2 g of α-SnP in 10 cm^3 of either water or benzene to produce solutions with concentrations of 0.025–0.1 mol dm^{-3}. The water-insoluble amines (n_c = 6–16) were dissolved in benzene. The weight of α-SnP and also the concentration of amine solution used in each reaction are listed in Table I, where the molar ratio of amine/α-SnP (r) in the reaction mixture is also shown.

2.4 Analyses

The phosphorus concentration was determined colorimetrically with a JASCO HPLC-Flow injection analysis system by the method of standard addition [19]. The nitrogen concentration was determined by the Kjeldahl method.

X-Ray diffraction patterns were recorded on a Rigaku Denki Geigerflux X-ray diffractometer, RAD-IA, using nickel-filtered Cu K_α radiation.

3. Results and discussion

Fig. 1 shows the atomic ratios of nitrogen/phosphorus (N/P) in the intercalation compounds, which were obtained by the reactions under various r values, as a function of n_c. Within each r, N/P does not depend on n_c which demonstrates that there is no steric effect of the alkyl chains on the intercalation processes. The N/P values of 0.90 corresponds to the point where almost all the P–OH groups of α-SnP are bonded to amine molecules.

In agreement with the results of Rodriguez-Castellon *et al.* [16], reflections corresponding to the (002) and higher harmonics (004), (006) were observed on the X-ray diffraction patterns of most of the intercalation compounds obtained in the present work. Unless otherwise stated, the interlayer distances (d) were calculated from the average of these first three-order reflections of the 002 plane [19].

When r = 3.41, the solutions of methyl- and ethylamine dissolved α-SnP, so that intercalation compounds were not obtained. The X-ray diffraction pattern of the propylamine/α-SnP intercalate showed only the (002) reflection from which a d value was

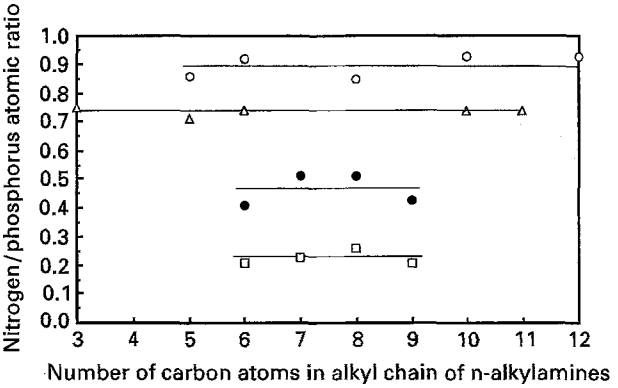

Figure 1 Nitrogen/phosphorus atomic ratio in the n-alkylamine/α-SnP intercalates as a function of the number of carbon atoms in the alkyl chain of amines. (○) r = 3.41, (△) r = 1.71, (●) r = 0.85, (□) r = 0.43, r refers to amine/α-SnP molar ratio (see text).

calculated. In the case of the butylamine/α-SnP intercalate the (002) and (004) diffraction peaks were observed, and in this case d was calculated from the average of the (002) and (004) reflections.

When r = 1.71 the diffraction patterns of the methyl- and ethylamine/α-SnP intercalation compounds contained only the (002) reflection from which a d value was calculated. The diffraction pattern of the propylamine/α-SnP intercalate contained both the (002) and (004) reflections and in this case d was calculated from the average of the two reflections.

For methyl- to propylamines the intercalates obtained from mixtures at which r = 0.85 were amorphous. Since the diffraction patterns for products obtained from mixtures at which r = 0.43 contained no clear diffraction peaks other than those from the host lattice, the reaction is thought to occur with the phosphate groups on the outer surfaces and edges of the α-SnP cyrstals.

The d values of the intercalates obtained from mixtures at r = 3.41 and 1.71 are plotted against n_c in Fig. 2. In each case d increases linearly with an increase in n_c. The dependence of d on n_c is expressed by Equation 1 for r = 3.41 and Equation 2 for r = 1.71.

$$d(\text{nm}) = 1.089 + 0.235n_c \quad (1)$$

$$d(\text{nm}) = 1.064 + 0.235n_c \quad (2)$$

Equations 1 and 2 have the same slope ($\Delta d/\Delta n_c$) of 0.235 nm. Following the calculation procedure of Rodriguez-Castellon *et al.* [16] and assuming a trans–trans alkyl-chain conformation, the slope indicates that the amines form a double layer of molecules inclined approximately at an angle $\theta = \sin^{-1}(0.235/0.254) = 67.7°$ with respect to the α-SnP layer. This value of θ is slightly larger than the previously reported value of 65° [18].

Fig. 2 shows that the d value of decyl- to hexadecylamine intercalates, obtained from mixtures with r = 0.85, are very close to those of intercalates obtained from the mixtures with r = 3.41. For butyl- to nonylamine, on the other hand, the d values of the intercalates obtained from the mixtures with r = 0.85

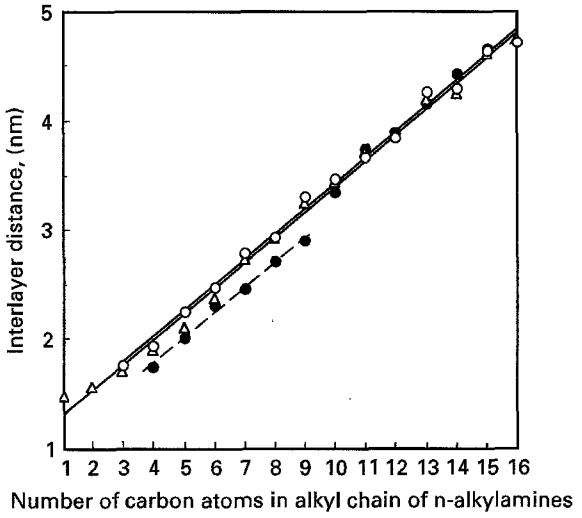

Figure 2 Interlayer distance of n-alkylamine/α-SnP intercalation compounds as a function of the number of carbon atoms in the alkyl chain of amines. (○) $r = 3.41$, (△) $r = 1.71$, (●) $r = 0.85$.

are less than those of the intercalates obtained from the mixtures with $r = 3.41$ by, on average, 0.259 nm.

Lagaly has demonstrated that in n-alkanol complexes of n-alkylammonium derivative of layer silicates, where n-alkyl chains were oriented perpendicular to the silicate layers, the formation of kinks in the alkyl chains shortened the interlayer distance by 0.127 nm or multiples thereof [20]. If the amines in the butyl- to nonylamine intercalates, obtained from the mixtures with $r = 0.85$, form a double layer of molecules and their alkyl chains are inclined at an angle of 67.7° the formation of one kink would reduce the interlayer distance by 0.235 nm ($= 0.127 \times 2 \times \sin 67.7°$). Although 0.259 nm is somewhat larger than 0.235 nm, it seems likely that the formation of one kink per alkyl chain in butyl- to nonylamine intercalates occurs.

For the intercalates obtained from the mixtures with $r = 3.41$ and 1.71, it appears that the high packing density of the alkyl chain in the interlayer space makes kink formation unlikely. Lagaly has also reported that the temperature at which the kink formation can occur rises with an increase in the chain length [20]. In the intercalates of amines where n_c is higher than 10, a trans–trans conformation can be assumed at room temperature.

4. Conclusion

The intercalation reaction of n-alkylamines from methyl- to hexadecylamine into α-tin(IV) bis(hydrogenphosphate [α-SnP] was carried out by mixing α-SnP and the amine solutions with the variation of amine/α-SnP molar ratios (r).

Within each r, the nitrogen/phosphorus atomic ratio of the intercalation compound does not depend on the number of carbon atoms in the alkyl chain, which demonstrates that there is no steric effect of the alkyl chains on the intercalation process.

When $r = 3.41$ and 1.71, assuming a trans-trans alkyl-chain formation, the amine molecules form a double layer in the interlayer space of α-SnP and are inclined at an approximate angle of 67.7° to the phosphate layer. The interlayer distances of the intercalates of butyl- to nonylamines obtained at r of 0.85 are smaller than those of the corresponding compounds at r of 3.41 and 1.71, which is interpreted by assuming kink formation in the short alkyl chains between the phosphate layers.

Acknowledgements

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