Intercalation of 2-Aminopropylamino-substituted β-Cyclodextrin by α-and γ-Zirconium Phosphates

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The uptake of 6-(2-aminopropylamino)-6-deoxy-β-cyclodextrin (cdpn) by α-and γ-zirconium phosphates has been studied at 25 °C. The intercalation behaviour of the α-phosphate and the cdpn arrangement in the resulting intercalate are essentially the same as those observed previously with 6-(2-aminoethylamino)-6-deoxy-β-cyclodextrin (cden). On the other hand, the γ-phosphate forms a similar but slightly distorted bilayer of cdpn molecules with their cavity axes parallel to the phosphate layers. The interlayer spacing and the cdpn content in the intercalate vary abnormally with the amount of cdpn added. The cdpn or cden arrangement in α- or γ-zirconium phosphate is in marked contrast to that in copper-montmorillonite, which is explained in terms of the physicochemical characteristics of the individual inorganic interlayers and cyclodextrin molecules.

Cyclodextrins are cyclic oligosaccharides of D-glucopyranose and contain a cylindrical cavity capable of including a variety of molecules.[1] Zirconium phosphate with a layer structure is represented by two fundamental forms: α-ZrP, $Zr(HPO_4)_2{\cdot}H_2O$, with an interlayer spacing of 7.6 Å and γ-ZrP, $Zr(HPO_4)_2{\cdot}2H_2O$, with an interlayer spacing of 12.3 Å.[2] Both phases act not only as cation exchangers but also as intercalating agents for polar substances.[3] Previously, a striking contrast was revealed between these two phosphates as host matrices for pyridine,[4] histamine (1*H*-imidazole-4-ethanimine),[5] and basic amino acids.[6,7]

In a recent paper[8] it was shown that α-ZrP forms an intercalated compound with 6-(2-aminoethylamino)-6-deoxy-β-cyclodextrin (cden). The present paper is concerned with the intercalation behaviour of α- and γ-ZrP towards 6-(2-aminopropylamino)-6-deoxy-β-cyclodextrin (cdpn). Cdpn and cden are derivatives in which propylenediamine and ethylenediamine groups replace a primary alcohol hydroxyl group on the narrow side of the truncated cone-shaped β-cyclodextrin molecule.

Experimental

The α- and γ-ZrP samples used were the same as those used in previous work.[4–8] The cdpn was prepared from β-cd and propylenediamine in a manner similar to that used for cden.[8] The zirconium phosphate sample was soaked in an aqueous solution containing various amounts of cdpn at 25 °C for 10 d, centrifuged, fully washed with water, and air-dried at 40 °C. The cdpn and water content in the resulting solids were determined by thermogravimetric analysis. *X*-Ray diffraction measurements were made using Fe-K_α radiation and tetradecanol as an external standard.

Results

The cdpn uptakes in moles, x, per formula weight of α- and γ-ZrP for the resulting solids are plotted against the amount of cdpn added in Figure 1. The uptake of cdpn for α-ZrP increases with an increase in the addition of cdpn to reach a constant value of $x \approx 0.40$ at levels of greater than 2 mmol g^{-1}. For γ-ZrP, the cdpn uptake becomes a maximum of $x = 0.31$ at levels of 2—3 mmol g^{-1} and decreases slightly with further addition of cdpn. Figure 2 shows the variation of the pH of the equilibrated solution in the uptake process.

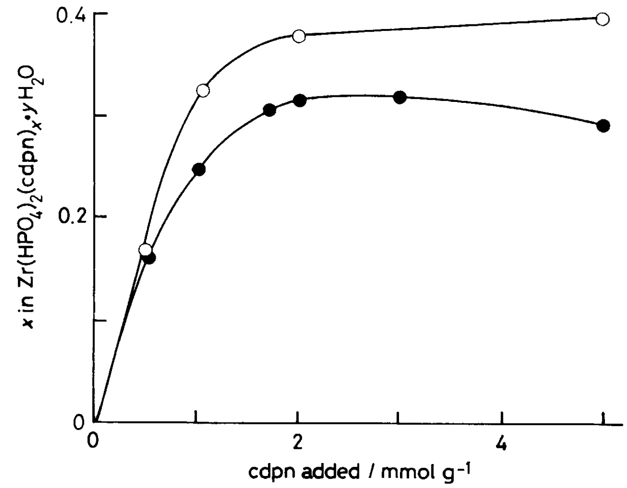

Figure 1. Uptake of cdpn by α- (○) and γ-zirconium phosphates (●) as a function of cdpn added at 25 °C

Figures 3 and 4 show the *X*-ray diffraction patterns of the resulting solids in the α-ZrP–cdpn and γ-ZrP–cdpn systems, respectively. With increasing addition of cdpn, the peak at $2\theta = 14.6$ ($d = 7.6$) or 9.03° ($d = 12.3$ Å) attributable to the 002 reflection of the host phase in each system decreased considerably in intensity, while a new diffraction peak appeared near $2\theta = 3.03$ ($d = 36.6$) or 2.87° ($d = 40.0$ Å) along with its three or four higher-order counterparts and increased in intensity, indicating that the uptakes of cdpn by α- and γ-ZrP can be attributed to their conversion into an intercalated phase. The interlayer spacings of the resulting intercalates were determined from the 002 and/or 001 reflection in the *X*-ray diffraction patterns and the thickness of the intercalate portion, Δ, was obtained by subtracting the thickness of the inorganic layer, 7.4 Å for α-ZrP or 9.4 Å for γ-ZrP,[5–7] from the observed spacings. These results are summarized in Figure 5. Based on the above *X*-ray observations, the intercalation behaviour of α-and γ-ZrP towards cdpn is characterized as follows.

The intercalation of cdpn by α-ZrP proceeds in two steps, in agreement with the titration data. At addition levels of less than 1 mmol g^{-1} a cdpn intercalate with a Δ value of 29.2—29.4 Å forms and coexists with its host phase. With further addition of cdpn the intercalated phase increases in interlayer spacing

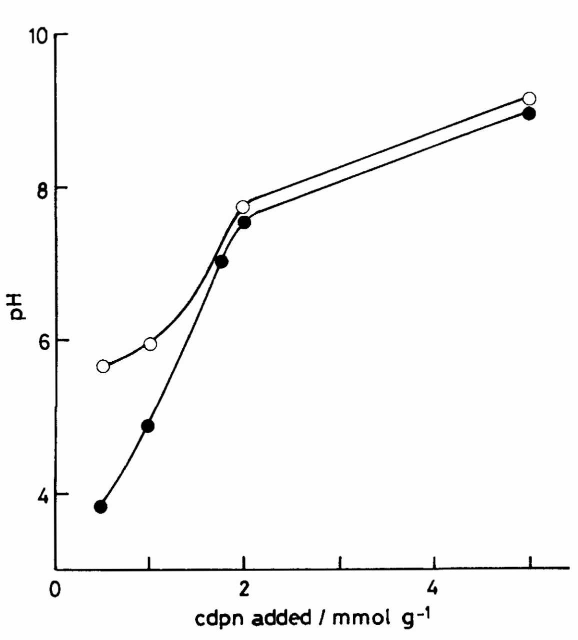

Figure 2. Potentiometric titration curves with cdpn for α- and γ-zirconium phosphates at 25 °C. Key as in Figure 1

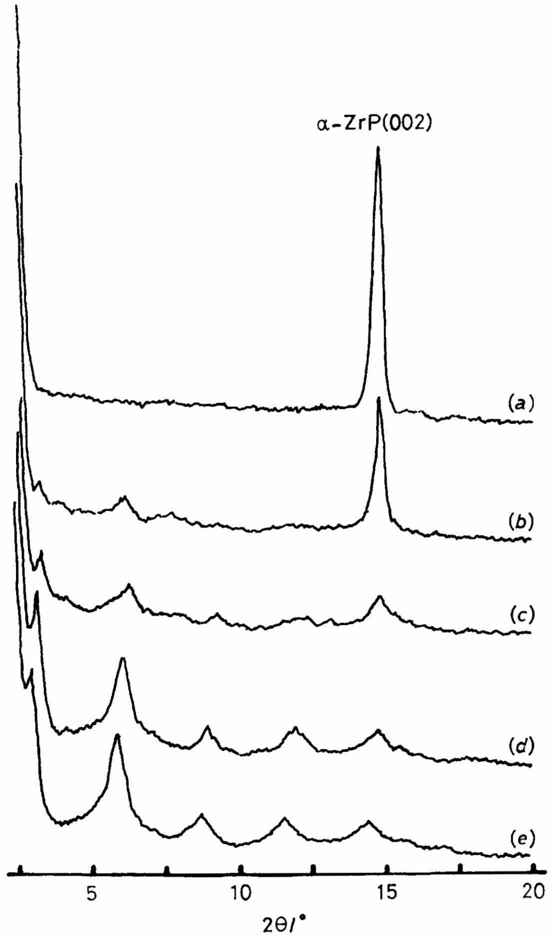

Figure 3. *X*-Ray diffraction patterns of α-zirconium phosphate (*a*) and its intercalates with cdpn (Fe-K_α radiation). Addition of cdpn (mmol g^{-1}): 0.5 (*b*), 1.0 (*c*), 2.0 (*d*), and 5.0 (*e*)

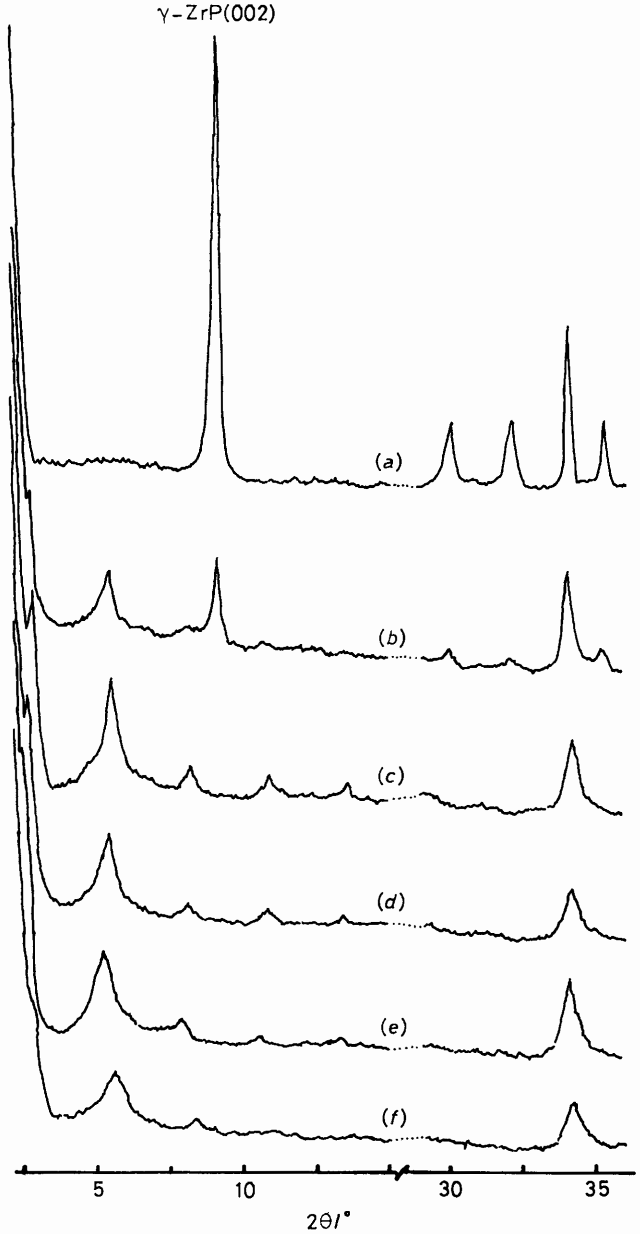

Figure 4. *X*-Ray diffraction patterns of γ-zirconium phosphate (*a*) and its intercalates with cdpn (Fe-K_α radiation). Addition of cdpn (mmol g^{-1}): 0.5 (*b*), 1.0 (*c*), 1.75 (*d*), 2.0 (*e*), and 5.0 (*f*)

until at a level of 5 mmol g^{-1} the α-ZrP is almost totally converted into a cdpn intercalate with a Δ value of 31.3 Å, $Zr(HPO_4)_2(cdpn)_{0.40}\cdot 5.6H_2O$. A similar observation was made for the α-ZrP–cden system.[8] On the other hand, the intercalation behaviour of cdpn for γ-ZrP is different in some respects. First, γ-ZrP is totally converted into an intercalated phase at additions as low as 1 mmol g^{-1}, indicating that the γ-phosphate is more available for intercalating cdpn molecules than is the α form. Secondly, the intercalation process consists of three steps. At the initial addition levels of less than 1.75 mmol g^{-1} the interlayer thickness of the intercalated phase moderately increases with an accompanying increase in the cdpn content. At intermediate levels of 1.75—2 mmol g^{-1} the Δ value rapidly increases to 33.1 Å along with a slight increase in the cdpn content, yielding a phase of $Zr(HPO_4)_2(cdpn)_{0.31}\cdot 3.0H_2O$. At higher addition levels the Δ value decreases considerably, while the cdpn content of the solid phase remains constant until it

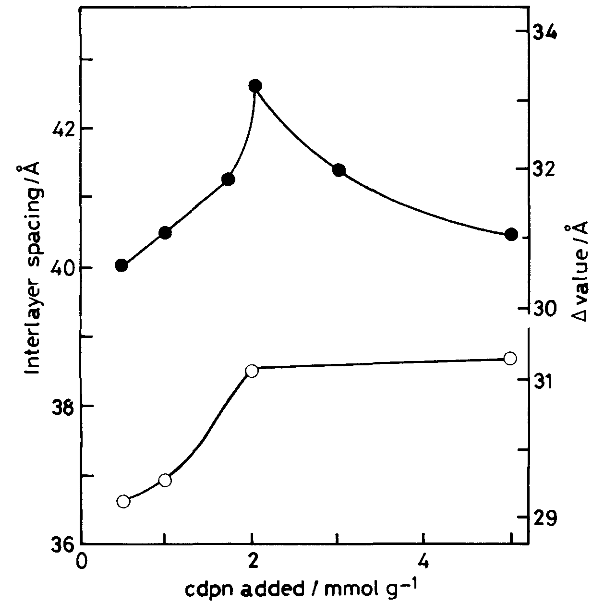

Figure 5. Interlayer spacing or Δ value (see text) as a function of cdpn added for the cdpn intercalates of α- and γ-zirconium phosphates. Key as in Figure 1

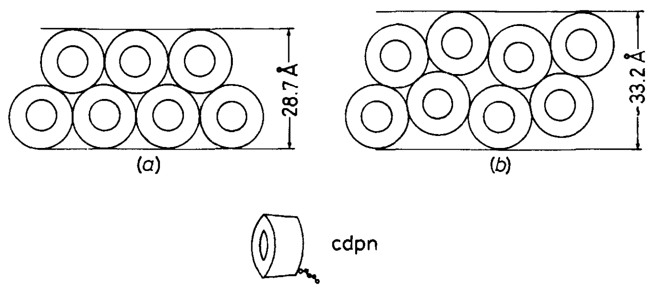

Figure 6. Possible models for the molecular arrangement of the cdpn layer projected onto a plane perpendicular to the phosphate layer of (*a*) α- and (*b*) γ-zirconium phosphate

Table. Interlayer spacing and composition of cdpn intercalates of α- and γ-zirconium phosphates

Host phase	cdpn added/ mmol g^{-1}	Interlayer spacing/Å	Δ/Å	Composition *
α-ZrP	1.0	36.9	29.5	0.32
	5.0	38.7	31.3	0.40
γ-ZrP	1.0	40.5	31.1	0.25
	1.75	41.2	31.8	0.30
	2.0	42.6	33.2	0.31
	5.0	40.5	31.1	0.29

* In mol of cdpn per formula weight of host phosphate, or x value in $Zr(HPO_4)_2(cdpn)_x \cdot yH_2O$.

decreases slightly at additions greater than 3 mmol g^{-1}. At the intermediate and the final stages the 001 diffraction peak for the intercalated phase of γ-ZrP tended to decrease in intensity, indicating that the intercalate becomes slightly disordered. The *X*-ray diffraction pattern for the γ-ZrP–cdpn system also showed that the diffraction peak at 3.3 Å has significant intensity throughout the intercalation process. The Table lists the intercalation parameters for some selected samples. For convenience, the intercalated phases of α- and γ-ZrP with cdpn will hereafter be termed α and γ intercalates, respectively.

Discussion

The thickness of the intercalated layer for the α intercalate with cdpn, 29.5—31.3 Å, is close to that of 28.2 Å observed for the analogue with cden.[8] We can assume, therefore, that the molecular arrangement of the intercalant layer in the former intercalate is substantially the same as that in the latter, as illustrated in Figure 6(*a*). From previous calculations,[8] the minimum Δ and maximum x values for the cdpn intercalate with the arrangement (*a*) are also expected to be 28.7 Å and 0.394, respectively. These expectations are in fairly close agreement with the observations. The difference of 0.8—2.7 Å between the observed and calculated values of Δ for the cdpn intercalate could be ascribed to the layer expansion concerned with the aminoethylamino chains through which the cdpn molecules are anchored to the phosphate layers. In the arrangement (*a*) the upper intercalated layer of cdpn molecules is shifted by half the molecular diameter to the lateral direction, relative to the layer below, and both layers are in a close contact with each other. This would enhance the intermolecular van der Waals and/or hydrophobic interaction, leading to stabilization of the bilayer structure. As discussed for the cden intercalate,[8] the arrangement (*a*) for the cdpn intercalate of α-ZrP is also in geometrical conformity with that of POH sites at the interlayer surface of the host crystal and is most available for the anchoring of cdpn molecules. This suggests that the arrangement (*a*) would also contribute to the minimization of the interfacial energy between the intercalated layer and the phosphate layer of the host crystal.

The intercalated layer of the γ intercalate with cdpn ranges in thickness from 31.1 to 33.2 Å and hence corresponds to a bilayer of cdpn molecules with the parallel orientation. If we assume that the cdpn bilayer for the γ intercalate is in the same arrangement as that for the α intercalate and the effective area per POH site is taken as 17.6 Å^2,[9,10] the minimum Δ and maximum x values for the former can be evaluated in the same manner as previously,[8] being 28.7 Å and 0.289, respectively. These values are less than those observed, suggesting that the cdpn molecules are packed in such a manner that adjacent molecules are shifted diagonally up or down, relative to those in the arrangement (*a*), to form a puckered bilayer, as shown in Figure 6(*b*). This arrangement gives $x \approx 0.3$ and $\Delta \approx 33.2$ Å which are in close agreement with observations. In γ-ZrP the POH groups belonging to any two adjacent layers are face to face with each other in the interlayer space.[9] It is obvious for the γ intercalate that the arrangement (*a*) is more advantageous for the intermolecular interaction within the intercalated layer than is (*b*), but the former may be less favourable for the molecular anchoring, *i.e.* for the host–guest interfacial energy, than the latter. Thus, the cdpn molecules would be intercalated as a distorted bilayer with the arrangement (*b*) in the interlayer space of γ-ZrP. It is conceivable that the adjustment of the two opposite effects may lead to the occurrence of structural disorder. The abnormal λ-like variation of the Δ value for the γ intercalate may be explained by assuming that the chemical potential of cdpn in the solid is increased by the high addition of cdpn, but it is compensated by the development of structural disorder to such an extent that the interlayer thickness and cdpn content cannot be kept at their maximum values.

As mentioned above, α- or γ-ZrP intercalates cdpn or cden molecules with their cavity axes parallel to the host layers to form a bilayered phase without any formation of intermediate monolayered phases. In contrast, it was observed that copper-montmorillonite intercalates cden in two steps, initially as a monolayer and successively as a bilayer, both with their cavity axes perpendicular to the host layers.[11] The opening and outer side faces of cdpn and cden molecules are hydrophilic and hydrophobic, respectively, and the interlayer surface of α- and γ-ZrP is much less hydrophilic than that of copper-montmorillonite. It is thus reasonable to assume that the packing of intercalated cdpn or cden molecules in copper-montmorillonite is determined mainly by the hydrophilic attraction, *i.e.* van der Waals interaction and/or hydrogen bonding, between the opening face of the intercalated molecules and the surface of the silicate layers, while that in α- or γ-ZrP is determined predominantly by the hydrophobic and/or van der Waals interaction between the intercalated molecules which is enhanced by the bilayering of the intercalant molecules with the parallel orientation.

Further work on the inclusion properties of the resulting α and γ intercalates is now in progress.

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Received 5*th May* 1989; *Paper* 9/01904I