Intercalation of 2-Aminoethylamino-substituted β-Cyclodextrin by γ-Zirconium Phosphate

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The uptake of [6-(2-aminoethylamino)-6-deoxy]-β-cyclodextrin (cden) by γ-zirconium phosphate $Zr(HPO_4)_2\cdot 2H_2O$ has been studied at 25 °C. The intercalation behaviour of cden for the γ phosphate is in marked contrast to that observed previously with α-zirconium phosphate $Zr(HPO_4)_2\cdot H_2O$. The γ phosphate forms initially an intercalated phase in which the cden molecules are arranged as a bilayer of thickness 31.3 Å with cavity axes parallel to the phosphate layers. With further increase in the amount of cden added, the thickness of the intercalant layer rapidly decreases to 24.7 Å, with an accompanying appreciable decrease in the cden content.

Cyclodextrins, cyclic oligosaccharides of D-glucopyranose, can act as highly functional molecular materials because they contain a cylindrical cavity capable of including a variety of molecules.[1] We have made an attempt to obtain a novel family of microporous materials by the pillaring of layered compounds such as zirconium hydrogenphosphate with the channel-like cyclodextrin molecules.[2-4] Zirconium phosphate with a layer structure can be obtained in two fundamental forms: α-zirconium phosphate (α-ZrP), $Zr(HPO_4)_2\cdot H_2O$, with an interlayer spacing of 7.6 Å and γ-zirconium phosphate (γ-ZrP), $Zr(HPO_4)_2\cdot 2H_2O$, with an interlayer spacing of 12.3 Å.[5] Both phases act not only as cation exchangers but also as intercalating agents for polar substances.[6] Recently, we reported a striking contrast between these two phosphates as host matrices for [6-(2-aminopropylamino)-6-deoxy]-β-cyclodextrin (cdpn).[3]

In a previous paper[2] we showed that α-ZrP forms an intercalated compound with [6-(2-aminoethylamino)-6-deoxy]-β-cyclodextrin (cden) in which the cden molecules are arranged as a bilayer with their cavity axes parallel to the phosphate layers. An attempt was thus made to study the intercalation behaviour of γ-ZrP towards cden. The cden and cdpn used in this and the preceding studies are derivatives of β-cyclodextrin, in which 2-aminopropylamino (propylenediamine) and 2-aminoethylamino (ethylenediamine) groups are substituted, respectively, in place of a primary alcoholic hydroxyl group on the narrow side of the truncated cone-shaped cyclodextrin molecule.

Experimental

The γ-ZrP sample used was the same as that used in the previous work.[3] The cden derivative was prepared in a manner similar to that previously reported.[2] The zirconium phosphate sample was soaked in an aqueous solution containing various amounts of cden at 25 °C for 10 d, centrifuged, fully washed with water, and air-dried at 40 °C. The cden and water contents in the resulting solids were determined by thermogravimetric analysis. X-Ray diffraction measurement was made using Fe-Kα radiation and tetradecanol was used as an external standard.

Results

The cden uptakes in moles, x, per mol of γ-ZrP for the resulting solids are plotted against the amount of cden added in Fig. 1. The uptake of cden by γ-ZrP increases up to a maximum value of $x = 0.256$, followed by an appreciable decrease down to $x \approx 0.189$ at a level of $q = 1.62$. Here q represents the amount in mol of cden added per mol of ZrP. This is in contrast to the uptake behaviour of α-ZrP where x increases to a constant value, as shown by the open circles in Fig. 1. The titration curve for cden and γ-ZrP was in close agreement with that observed with cdpn.

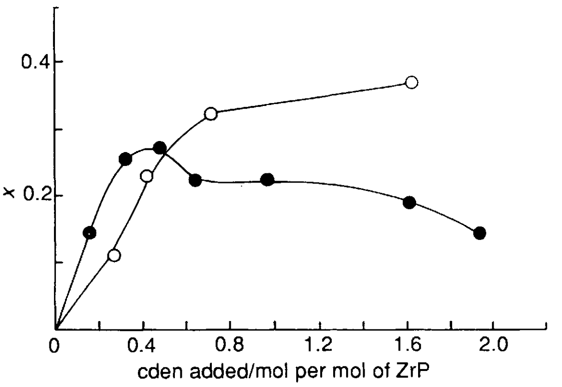

Fig. 1 Uptake of cden by α- (○) and γ-zirconium phosphate (●) as a function of the amount of cden added at 25 °C. The data referring to the α form are taken from ref. 4

Fig. 2 shows the X-ray diffraction patterns of the resulting solids as a function of the amount of cden added. As a result of the addition of cden, the peak at $2\theta = 9.03°$ ($d = 12.3$ Å) attributable to the 002 reflection of the host phase decreased considerably in intensity, while a new diffraction peak appeared near $2\theta = 2.82°$ ($d = 39.3$ Å) along with its three or four higher-order counterparts, indicating that the uptakes of cden by γ-ZrP can be attributed to its 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, 9.4 Å for γ-ZrP, from the observed spacings, as previously.[3] These results are summarized in Fig. 3, along with those observed previously for the α-ZrP-cden system. The resulting solids obtained using the reaction time of 10 d would be equilibrated because the Δ values of selected samples were little affected by reaction with cden for 4 d longer. Based on the above X-ray observations, the intercalation behaviour of γ-ZrP towards cden is characterized as follows.

In contrast to α-ZrP,[4] γ-ZrP is totally converted into an cden intercalate with a Δ value of 31.3 Å, $Zr(HPO_4)_2(cden)_{0.256}\cdot$

$4.2H_2O$, at an addition level of as low as $q = 0.32$. This indicates that the γ-phosphate is more available for intercalating cden molecules than is the α-phosphate, as observed in the γ-ZrP–cdpn system. At higher addition levels the Δ value of the intercalated phase rapidly decreases to 24.7 Å with an accompanying decrease in the cden content, yielding a phase of $Zr(HPO_4)_2(cden)_{0.143}\cdot 1.6H_2O$. It is noted that the 001 diffraction peak for the intercalated phase of γ-ZrP tends to become broad at the intermediate stage, while its sharpness is restored in the final stage. Therefore, the crystal having Δ = 24.7 Å is likely to be highly ordered. For convenience, the intercalated phases of α- and γ-ZrP with cdpn will hereafter be termed α and γ intercalates, respectively.

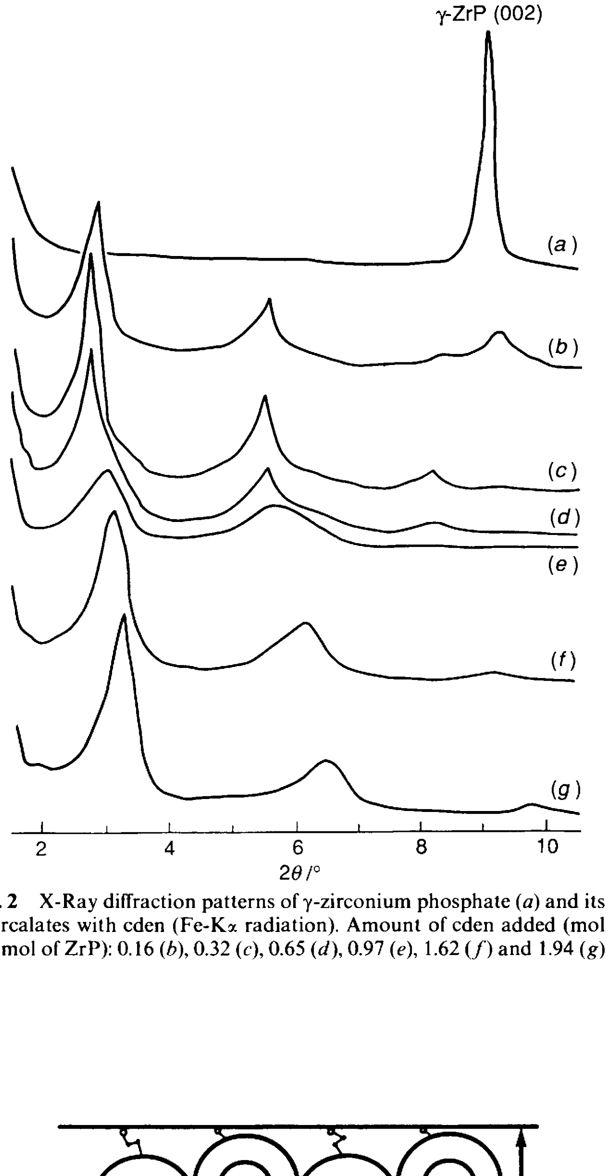

Fig. 2 X-Ray diffraction patterns of γ-zirconium phosphate (*a*) and its intercalates with cden (Fe-Kα radiation). Amount of cden added (mol per mol of ZrP): 0.16 (*b*), 0.32 (*c*), 0.65 (*d*), 0.97 (*e*), 1.62 (*f*) and 1.94 (*g*)

Discussion

For the γ intercalate phases with Δ = 31.3 and 24.7 Å it is reasonable to assume that cden molecules, each 15.4 Å in diameter and 8.0 Å in torus thickness, are intercalated as a bilayer with their cavity axes parallel or perpendicular to the phosphate layers. Referring to previous calculations for the γ intercalate with cdpn,[3] the minimum Δ and maximum x values expected for a parallel arrangement of cden molecules are 28.7 Å and 0.289, respectively, which are consistent with the 31.3 Å and 0.256 observed for the phase with Δ = 31.3 Å. The increase of 0.8–2.1 Å in the Δ value of the γ relative to that of the α intercalate could be ascribed to the layer expansion due to the unfolding of the aminoethylamino chains and that due to a puckered

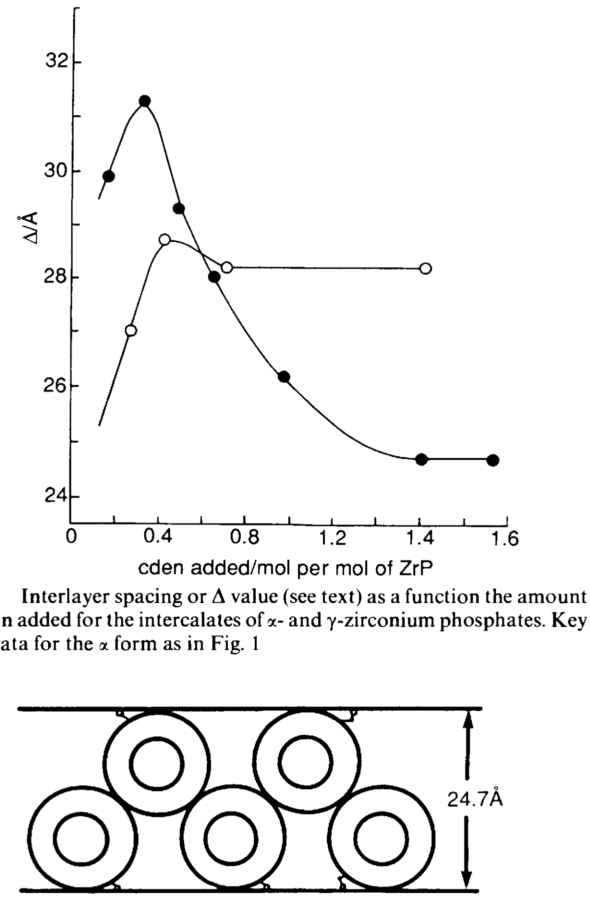

Fig. 3 Interlayer spacing or Δ value (see text) as a function the amount of cden added for the intercalates of α- and γ-zirconium phosphates. Key and data for the α form as in Fig. 1

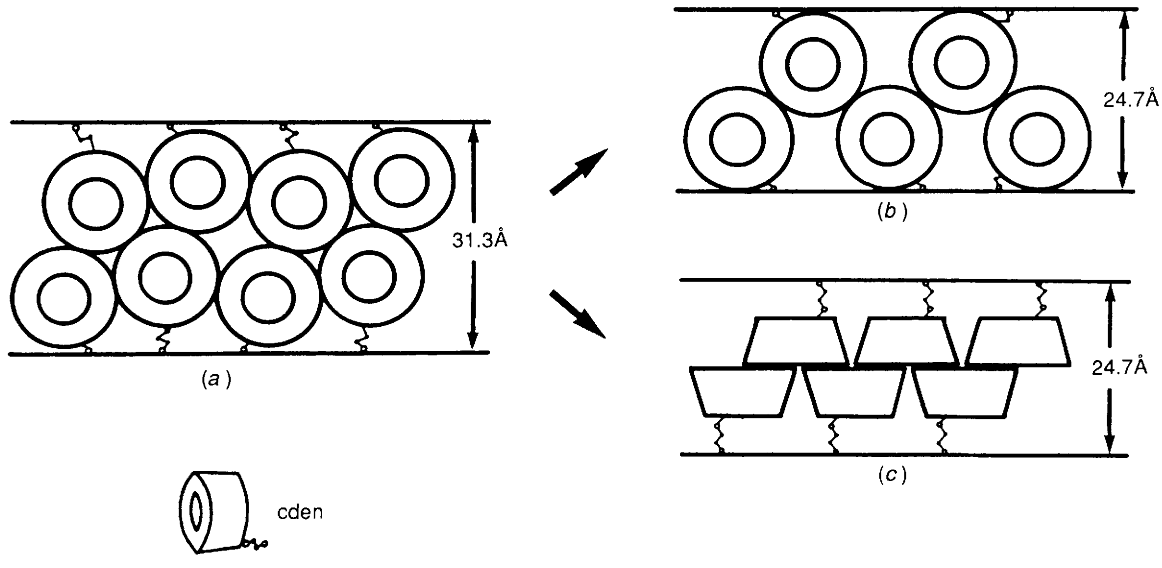

Fig. 4 Possible models for the molecular arrangement of the cden layer in the initial (*a*) and the converted (*b* and *c*) intercalates of γ-zirconium phosphate

arrangement of the bilayered molecules, as illustrated in Fig. 4 (*a*). A similar model was suggested for the cdpn intercalate of γ-ZrP.[3]

Fig. 4 (*b*) and (*c*) illustrate two possible models for the conversion of the phases with $\Delta = 31.3$ and 24.7 Å. Assuming that cden molecules in their parallel orientation form a loosely packed bilayer, 24.7 Å in thickness, the effective area per molecule is $2\,[15.4^2 - (24.7 - 15.4)^2] \times 8$ or 196 Å^2. As the effective area per POH site in γ-ZrP is 17.6 Å^2[7,8] the maximum value of x can be evaluated as $2 \times 17.6/196$ or 0.180, which is consistent with the observed value, 0.143. On the other hand, if we assume that cden molecules in their perpendicular orientation are hexagonally close-packed as a bilayer, the maximum values of Δ and x can be estimated, respectively, as 24.4 Å and as $2 \times (17.6/205)$ or 0.172. These values are also in close agreement with those observed for the phase with $\Delta = 24.7$ Å. However, such a perpendicular bilayered structure in the α- or γ-ZrP–cyclodextrin system has been observed only for a α-ZrP–cdpn intercalate with benzoic acid.[4] Moreover, the Δ value for the 24.7 Å phase is much larger than the 16.9 Å observed for the α-ZrP–cdpn–benzoic acid complex. Thus, the cden molecules in the phase having $\Delta = 24.7$ Å are more likely to be arranged as a loosely packed bilayer in their parallel orientation.

In previous work [3] it was shown that the Δ value and the cdpn content of the intercalate of γ-ZrP decrease appreciably at high levels of cdpn, but the essential arrangement of the cdpn layer remains unchanged. This was ascribed to the relaxation of the structural distortion of the cdpn layer concerned with the geometrical arrangement of POH sites in the host crystal. In the γ intercalate with cden, on the other hand, the structural distortion of the intercalant layer with the parallel arrangement would be enhanced by reduced flexibility of the aminoethylamino chain bonded to the POH sites. These combined effects would be responsible for the structurally drastic conversion from the closely packed parallel bilayered to the loosely packed parallel bilayered arrangement in which the structural distortion due to both constraints is relaxed.

References

1 W. Saenger, *Angew. Chem.*, 1980, **19**, 344.
2 T. Kijima and Y. Matsui, *Nature (London)*, 1986, **322**, 533.
3 T. Kijima, *J. Chem. Soc., Dalton Trans.*, 1990, 425.
4 T. Kijima, *J. Incl. Phenom. Mol. Recogn. Chem.*, 1990, **9**, 171.
5 A. Clearfield, G. H. Nancollas and R. Blessing, *Ion Exchange and Solvent Extraction*, eds. J. A. Marinsky and Y. Marcus, Marcel Dekker, New York, 1973, vol. 5, ch. 1.
6 G. Alberti and U. Constantino, *Intercalation Chemistry*, eds. M. S. Whittingham and A. J. Jacobson, Academic Press, New York, 1985, ch. 5.
7 U. Constantino, *J. Inorg. Nucl. Chem.*, 1981, **43**, 1859.
8 G. Alberti, *Inorganic Ion Exchange Materials*, ed. A. Clearfield, CRC Press, Boca Raton, FL, 1982, ch. 2.

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