

Inclusion Behaviour of Benzoic Acid towards Intercalates of α - and γ -Zirconium Hydrogen Phosphates with 2-Aminopropylamino-Substituted β -Cyclodextrin

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Abstract. The inclusion behaviour of benzoic acid towards intercalates of α - and γ -zirconium hydrogen phosphates with mono[6-(2-aminopropylamino)-6-deoxy]- β -cyclodextrin (CDpn) has been studied at 25°C. Both intercalates take up benzoic acid to form a complex, with an accompanying partial release of CDpn. It is concluded that the remaining CDpn molecules in the α -complex are rearranged as a bilayer with their cavity axes perpendicular to the phosphate layers. Those in the γ -complex act as a molecular prop to maintain the initial structure in which the CDpn molecules are arranged as a bilayer with their cavity axes parallel to the phosphate layers. The benzoic acid molecules are embedded inside and outside the CDpn cavity. The pore volume between the CDpn molecules amounts to approximately 0.07 and 0.29 cm³ per gram of the α - and γ -complexes, respectively.

Key words. Zirconium phosphates, cyclodextrin, intercalates, benzoic acid, inclusion compound.

1. Introduction

New classes of microporous materials have been obtained by the pillaring of layered compounds such as smectite clays with polynuclear hydroxy metal cations or bulky organic molecules [1]. We have attempted to obtain a similar but novel family of inclusion compounds by the intercalation of host molecules such as cyclodextrins in layered parent hosts [2–5]. So far, several intercalates of layered montmorillonites and zirconium hydrogen phosphate have been prepared with α -, β -, and γ -cyclodextrins and their derivatives containing methoxyl, 2-aminoethylamino (en) or 8-amino-3,6-diazoctylamino (trien) substituents. However, few studies have been reported on the inclusion properties of these intercalates.

There are two fundamental forms of layered zirconium hydrogen phosphate: α -zirconium phosphate (α -ZrP), $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, with an interlayer spacing of 7.6 Å and γ -zirconium phosphate (γ -ZrP), $\text{Zr}(\text{HPO}_4)_2 \cdot 2 \text{H}_2\text{O}$, with an interlayer spacing of 12.3 Å [6]. Both phases act not only as cation exchangers but also as intercalating agents for polar substances. Recently [7], we have prepared intercalates of the α - and γ -zirconium phosphates with mono-(6- β -aminopropylamino-6-deoxy)- β -cyclodextrin (CDpn), in which the CDpn molecules are arranged as a bilayer with their cavity axes parallel to the phosphate layers. Benzoic acid is one compound which can be included by β -cyclodextrin [8, 9], but cannot be taken up by the zirconium phosphates alone.

An attempt was thus made to investigate the inclusion behaviour of the CDpn intercalates of α - and γ -zirconium hydrogen phosphates towards benzoic acid.

2. Experimental

The two host samples of α - and γ -ZrP intercalates with CDpn used were selected from those obtained in the preceding work [7]. The compositions and the interlayer spacings of these two samples were α -Zr(HPO₄)₂(CDpn)_{0.38}·5.4 H₂O (38.5 Å) and γ -Zr(HPO₄)₂(CDpn)_{0.31}·3.0H₂O (42.6 Å), respectively. Benzoic acid was reagent grade and used without further purification.

The intercalate sample was soaked in an aqueous solution containing various amounts of benzoic acid at 25°C for 5 days, centrifuged, washed with water and lipophilized. The uptakes of benzoic acid were obtained as differences between the initial and final concentrations determined by the colorimetric method using the absorbance at 233 nm. The amounts of CDpn released into solution were also determined by the ninhydrin colorimetric analysis of the supernatants. X-ray diffraction patterns were taken using FeK_α rays with tetradecanol as external standard.

3. Results

The uptake of benzoic acid (BA) (y), in moles, per formula weight of α - or γ -ZrP for the resulting solids is plotted against the amount of benzoic acid added per gram of the anhydrous form of the starting α -ZrP-CDpn or γ -ZrP-CDpn intercalate in Figure 1. The benzoic acid uptake for the α - or γ -intercalate increases

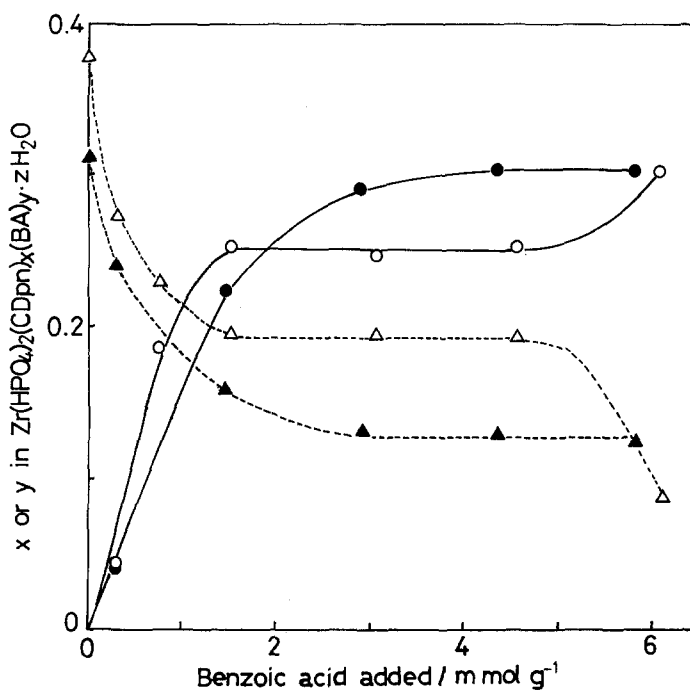


Fig. 1. Plots of the benzoic acid (BA) (y , circles) and CDpn (x , triangles) contents against benzoic acid added for the α - (open) and γ - (closed) ZrP-CDpn-BA complexes, Zr(HPO₄)₂(CDpn) _{x} (BA) _{y} · z H₂O.

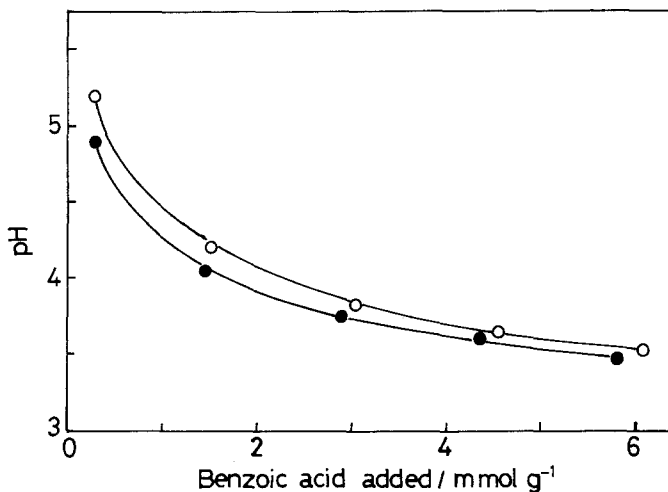


Fig. 2. Potentiometric titration curve with benzoic acid for the α -(\circ) and γ -(\bullet) ZrP-CDpn intercalates.

remarkably with an increase of the addition level of benzoic acid to reach constant values of $y \sim 0.25$ and $y \sim 0.3$ at levels of 1.5 and 4 mmol g⁻¹, respectively, and only the former uptake increases again at levels of more than 4.6 mmol g⁻¹. The benzoic acid uptakes for the α - and γ -intercalates were simultaneously accompanied by the release of CDpn amounting to 50 and 58 mole % of its initial content, respectively, as shown in Figure 1. The pH of the equilibrated solution decreased uniformly with increasing level of benzoic acid added, as shown in Figure 2.

The interlayer spacings of the resulting complexes were determined from the 001 reflections in the X-ray diffraction patterns. The results are summarized in Figure 3, where the thickness of the intercalated layer, Δ , on the right ordinate was obtained by subtracting the thickness of each inorganic layer, 7.4 Å for α -ZrP or 9.4 Å for γ -ZrP, from the observed spacings. With increasing amounts of benzoic acid, the Δ value for the γ -ZrP-CDpn-BA complex decreases gradually from the initial value of 33.2 Å down to 28.3 Å at levels of greater than 3 mmol g⁻¹, while that for the α -ZrP-CDpn-BA complex decreases much more significantly from 31.3 Å down to 16.9 Å at levels greater than 1.5 mmol g⁻¹. Table I lists the

Table I. Interlayer spacing and composition of complexes formed by the addition of benzoic acid (BA) to the CDpn intercalates of α - and γ -zirconium phosphates.

Complex	Benzoic acid added/mmole g ⁻¹ ^a	Interlayer spacing/Å	Δ /Å	Composition ^b			
				x	y	z	y/x
α -complex	4.57	24.3	16.9	0.191	0.252	2.1	1.32
γ -complex	5.82	37.7	28.3	0.124	0.301	2.1	2.43

^aAmount per gram of the anhydrous form of the starting CDpn intercalates.

^bThe composition of complex is represented by $Zr(HPO_4)_2(CDpn)_x(BA)_y \cdot z H_2O$.

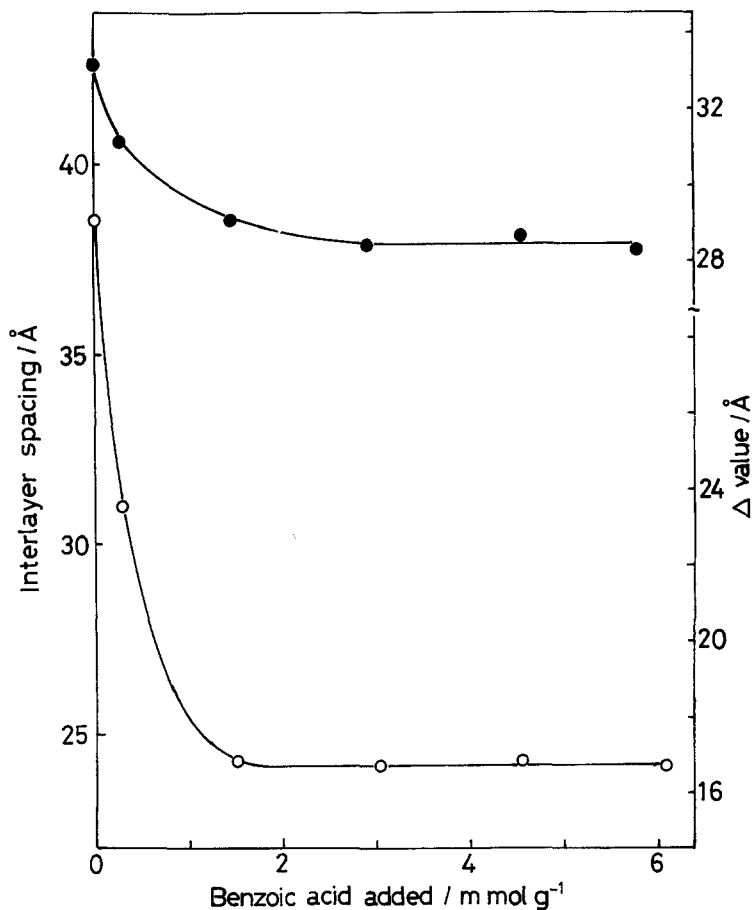


Fig. 3. Interlayer spacing or Δ value (see text) as a function of benzoic acid added for the α - (○) and γ - (●) ZrP-CDpn-BA complexes.

characterization of the α - and γ -ZrP-CDpn-BA complexes formed at an addition levels of 4.57 and 5.82 mmol g⁻¹, respectively.

4. Discussion

4.1. MECHANISM OF BENZOIC ACID UPTAKE AND CDpn RELEASE

The uptake of benzoic acid by the α - and γ -ZrP-CDpn intercalates is fully or almost fully completed at pH > 4. In this pH range the molecules of benzoic acid, with a pK_a of 4.2, would exist predominantly in the neutral form. β -CD includes benzoic acid in aqueous solution [8], which is driven by the cooperative action of those types of intermolecular interaction such as hydrophobic interaction, van der Waals interaction, and hydrogen bonding [9]. The molar ratios of benzoic acid to CDpn, y/x , for the resulting α - and γ -complexes are 1.3 and 2.3, respectively. Thus,

the primary uptake of benzoic acid by the α - and γ -intercalates would be ascribed to the formation of a 1:1 complex of CDpn with benzoic acid in the interlayer space, due to the same effect as in solution. The remaining (secondary) uptake, on the other hand, is probably due to the hydrogen bonding of benzoic acid molecules through their carboxyl group to the alcoholic or 2-amino groups of the CDpn molecules, resulting in the placement of benzoic acid molecules in the intermolecular free space within the CDpn layer. The partial release of CDpn from the intercalated solid would be mainly induced by the high stability of a CDpn-BA complex in aqueous solution.

4.2. MOLECULAR ARRANGEMENT IN THE RESULTING COMPLEXES

4.2.1. α -ZrP-CDpn-BA Complex

In the starting α -intercalate, with a Δ value of 31.1 Å, the CDpn molecules, each 15.4 Å in the van der Waals diameter and 8.0 Å in the thickness of the torus, are arranged in the parallel-bilayered form, i.e. as bilayers with their cavity axes parallel to the phosphate layers [7]. On the other hand, the Δ value of 16.9 Å observed for the resulting α -ZrP-CDpn-BA complex is roughly similar to the value of 15.4 Å for the molecular diameter of CDpn or fairly close to twice the value of 8.0 Å for the thickness of the torus. It is therefore reasonable to assume that the remaining CDpn molecules are arranged either in the parallel-monolayered form or in the perpendicular-bilayered one in which they are disposed with their cavity axes perpendicular to the phosphate layers and with their 2-aminopropylamino groups alternately pointing upward and downward. The observed x value of 0.191 for the resulting complex is also less than the maximum values of 0.20 and 0.24 for these two forms, expected from previous calculations [3]. However, based on previous considerations [7], it is inconceivable that the parallel-monolayered form is more advantageous for the total effect of the van der Waals and/or hydrophobic interaction between the intercalated CDpn molecules and the hydrophilic interaction between the surface of the phosphate layers and the opening face of the CDpn molecules than the other. In fact, α - or γ -ZrP forms a parallel-bilayered phase with CDpn or CDen without any formation of intermediate monolayered phases [3, 7]. In contrast, the perpendicular-bilayered form is similar to that observed in the intercalates of Ca-, Zn-, and Cu-montmorillonites with 8-amino-3,6-diazooctylamino-substituted β -cyclodextrin [5]. It is thus concluded that the remaining CDpn molecules in the α -ZrP-CDpn-BA complex would be rearranged from the parallel-bilayered form to the perpendicular-bilayered one.

Using the method described previously [5], if we assume that the perpendicular-bilayered CDpn molecules, each 15.4 Å in diameter, are hexagonally packed at a distance of $(15.4 + \xi)$ Å (center to center) in every upper or lower layer, the CDpn content in the α -ZrP-CDpn-BA complex, x_{rem} , is expressed as $x_{\text{rem}} = 2A_{\text{POH}} / \{(\sqrt{3}/2)(15.4 + \xi)^2\}$, where A_{POH} is the effective area per POH site. Substituting 0.191 for x_{rem} and 24.3 Å² for A_{POH} [7] in the above expression yields a ξ value of 1.8 Å. This result suggests that the remaining CDpn molecules are loosely packed to form pores in the interlayer space. The volume of the pores and other related quantities are estimated as follows.

The volume of the intercalated layer per formula weight of the resulting complex, V_{inter} , which is given by $V_{\text{inter}} = A_{\text{POH}} \times \Delta \times N_A$ (N_A = the Avogadro number), can be divided into those occupied by CDpn, benzoic acid and water molecules independently, V_{CDpn} , V_{BA} and V_w , and the remaining volume assignable to the pore (unoccupied) volume outside the CDpn cavity, V_p . The last four quantities can be evaluated by $V_{\text{CDpn}} = x_{\text{rem}} \times V_{\text{CDpn}} \times N_A$, $V_{\text{BA}} = y_{\text{inter}} \times V_{\text{BA}} \times N_A$, $V_w = z_{\text{inter}} \times V_w \times N_A$ and $V_p = V_{\text{inter}} - V_{\text{CDpn}} - V_{\text{BA}} - V_w$. Here y_{inter} and z_{inter} are the amounts of benzoic acid and water molecules located outside the CDpn cavity and V_{CDpn} , V_{BA} , and V_w the molecular volumes of CDpn, benzoic acid and water, respectively. Based on the above suggestions for the mechanism of benzoic acid uptake, it is reasonable to assume that y_{inter} and the amount of benzoic acid molecules penetrated into the CDpn cavity, y_{intra} , are equal to $y - x_{\text{rem}}$ and x_{rem} , respectively. The water molecules in the α -complex are likely to exist both inside and outside the CDpn cavity, but no data is available for estimating their amounts separately. We assume, therefore, for simplicity that $z_{\text{inter}} = z$, i.e. that all the observed amount of water, as small as 14 \AA^3 in molecular volume [10], is located outside the CDpn cavity. This approximation will lead to the underestimation of the V_p value. The values of V_{CDpn} and V_{BA} were calculated as $\pi \times (15.4/2)^2 \times 8.0 + 91.5$ or 1.58×10^3 and $\pi(7.3/2)^2 \times 3.4 + 28.5$ or $1.71 \times 10^2 \text{ \AA}^3$ respectively. Here the first term in each equation corresponds to the van der Waals volume of the torus or that of the benzene ring, which were evaluated using values of 15.4 and 8.0 or 7.3 and 3.4 \AA for their molecular diameter and thickness. The second terms corresponding to the van der Waals volume of the side chain group of each molecule were determined using the volume increments of the atomic groups such as CH_2 and NH , calculated by Slonimski *et al.* [11]. The uptake parameters thus obtained are summarized in Table II. A tentative model is shown for the probable arrangement of the CDpn and BA molecules in the α -ZrP-CDpn-BA complex in Figure 4(a), where water molecules are omitted.

4.2.2. γ -ZrP-CDpn-BA Complex

The interlayer thickness of the γ -ZrP-CDpn-BA complex is decreased by 4.7 \AA , relative to that of the starting host intercalate, but the Δ value of 28.3 \AA for the

Table II. Parameters for the full uptakes of benzoic acid (BA) by the CDpn intercalates of α - and γ -zirconium phosphates.

Complex	Amount of benzoic acid ^a			Interlayer volume/cm ³ mol ⁻¹ ^b				
	Intra	Inter	Total	Occupant				Total
	y_{intra}	y_{inter}	y	CDpn	BA	Water	pore ^c	
α -complex	0.19	0.06	0.25	181	6.3	17.7	41.5(0.071)	247
γ -complex	0.12	0.18	0.30	117	18.1	27.8	136(0.288)	300

^aAmount per formula weight of host phosphate.

^bVolume per formula weight of host phosphate.

^cValues in parentheses are expressed in cm³ per gram of complex.

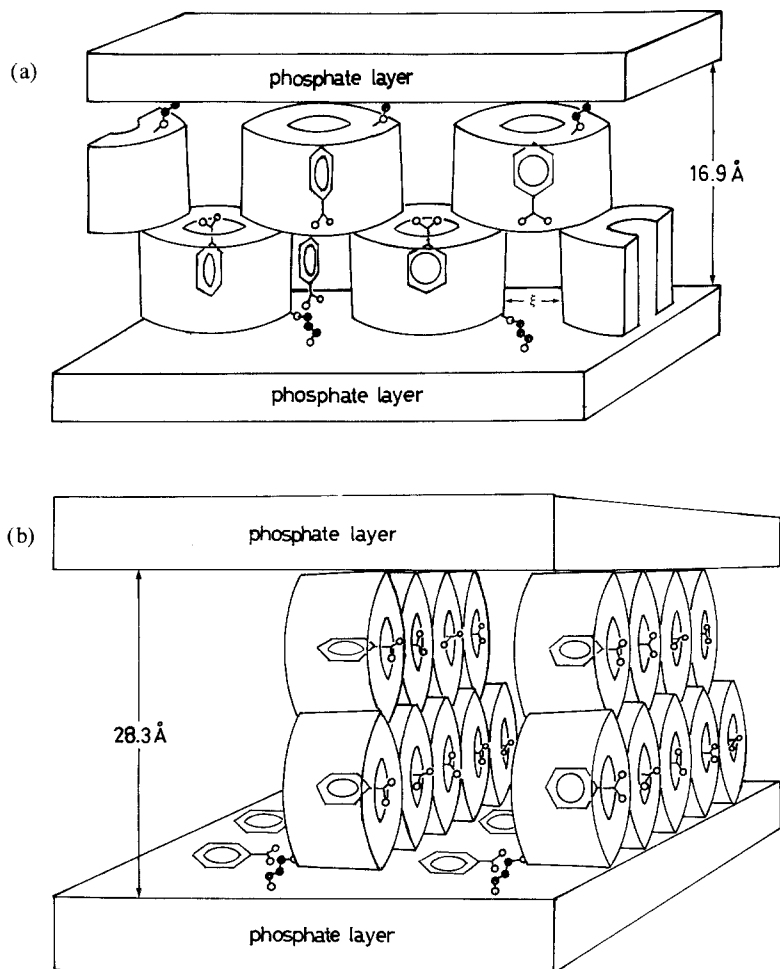


Fig. 4. Tentative models of the arrangement of CDpn and benzoic acid molecules between phosphate layers of (a) α - and (b) γ -ZrP-CDpn-BA complexes. Water molecules are omitted.

resulting complex is in good agreement with the minimum value of 28.7 Å for the bilayer of CDpn molecules with their parallel arrangement. This means that the remaining CDpn molecules act as molecular props to keep the initial parallel-bilayered form in the benzoic acid uptake process. The calculation of uptake parameters was made as above and the results are listed in Table II, where the A_{POH} value of 17.6 Å² for γ -ZrP [7] was used. Figure 4(b) shows a tentative model for the molecular arrangement in the γ -ZrP-CDpn-BA complex.

4.2.3. Comparison between the α - and γ -ZrP-CDpn-BA Complexes

Both complexes have two types of including spaces, one the CDpn cavity including benzoic acid molecules and the other the intermolecular pore outside the cavity. The intermolecular unoccupied pore volume of the γ -complex is about 3.3 times

larger than that of the α -complex and is comparable to that of zeolites, e.g., $0.32 \text{ cm}^3\text{g}^{-1}$ for zeolite CaA [12].

In the preceding paper [7], we pointed out a general rule that the packing manner of aminated cyclodextrin molecules in the interlayer space of α - and γ -ZrP is determined primarily by the intermolecular hydrophobic and/or van der Waals interaction, leading to the parallel bilayered form. The γ -ZrP-CDpn-BA complex follows this rule, but not the α -complex. This means that the parallel-bilayered form of the α -complex is more easily destabilized by the formation of vacancies or pores in the intercalated layer and is converted into the perpendicular-bilayered form in which the pore volume is largely reduced. The exceptional behaviour of the α -ZrP-CDpn-BA complex would stem from essentially the same reason as one of the previous observations that α -ZrP is totally converted into the parallel-bilayered intercalate with CDpn at a much higher level of CDpn added than γ -ZrP [7]. These striking contrasts between the α and γ forms are due to the difference between the geometrical arrangements of POH sites, available for the bonding of CDpn molecules, in both forms [7]: in γ -ZrP the POH sites belonging to any adjacent layers are face to face with each other, while those in the other are staggered, with a less compact arrangement at the interlayer surface. Definite explanations, however, must await further work.

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