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β-Cyclodextrin Complexes of Different Type with Inorganic Compounds

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Cyclodextrins are often used as enzyme models because the rates of several hydrolytic reactions are increased by cyclodextrins or by their substituted derivatives, and the mechanism may be similar to that of the effect of enzymes [1].

It is well known that the cycloamyloses, and among them the cycloheptaamylose (β-cyclodextrin, β-CD), form inclusion complexes with several compounds. The guest molecules studied are mainly organic compounds, relatively less data being known about the complexes of inorganic salts [2].

There are also several acid–base indicators which form complexes [3] and their properties are influenced to such an extent by β-CD that the formation constants of β-CD–dye complexes can be easily measured spectrophotometrically, and possibilities are open for the study of other equilibria through competing reactions.

It has been noticed that one of the most used indicator dyes, phenolphthalein, forms (at pH = 10.5, supported by 4 $\times 10^{-3}$ M Na_2CO_3) a very stable complex with β-CD.

During our measurements, the concentration of phenolphthalein was 3 $\times 10^{-5}$ M; its solutions were always prepared freshly; the concentration of cycloheptaamylose varied from 0 to 3 $\times 10^{-4}$ M. The absorbances were measured at 550 nm with a Spectromom 361 spectrophotometer in 1 cm cells and at 25 ± 2 °C. As the concentrations of the species were nearly the same, numerical methods based on the generally known relations of coordination chemistry were used instead of the simple Hildebrand–Benesi method, giving the possibility for controlling the formation of 1:2 or mixed complexes [4].

The stability constant of the phenolphthalein–β-CD complex has been found to be relatively high (2.16 $\times 10^4$) but its formation is influenced in competing reactions by several compounds, both organic and inorganic. Based on this fact, we have started to investigate the interaction between cycloamylose and inorganic salts. Assuming that only β-CD–anion complexes are formed [2], the stability constants shown in Table I could be calculated from data measured in 0.1 M solutions.

TABLE I.

Anion	β	β
	as sodium salt	as potassium salt
ClO_4^-	9.0	10.9[a]
SCN^-	–	5.7
NO_3^-	0.2	0.7
Cl^-	~0	~0
Br^-	–	1.1
SO_4^{2-} [b]	<0	–

[a] As lithium salt. [b] For sulfate 0.05 M.

Although the sequence of the formation constants fits into those measured by Rohrbach *et al.* [2], the actual values differ considerably. Moreover, there are definite differences between the values measured with the same anions (and under the same circumstances) but in presence of different cations. But the biggest inconsistency is that the apparent (calculated) equilibrium concentration of β-CD increases in presence of sulfate ions which could be interpreted as a formal but meaningless negative constant (with the chlorides, a similar effect can be observed but it is in 0.1 M solutions on the limit of experimental errors).

To clear all of these inconsistencies, the interactions have been investigated at different concentrations of the salts (but of course the concentration was constant in every series of measurements). The data were evaluated as the apparent formation constants of β-CD–phenolphthalein complex in different supporting electrolytes, and one part of the results are shown in Fig. 1. It proves that the phenomena are much more complicated than assumed by Rohrbach *et al.* [2], whose measurements were performed only with one concentration of the electrolytes.

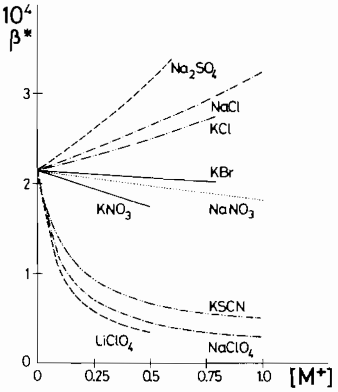

Fig. 1. The change of apparent stability constants in different electrolytes (25 °C).

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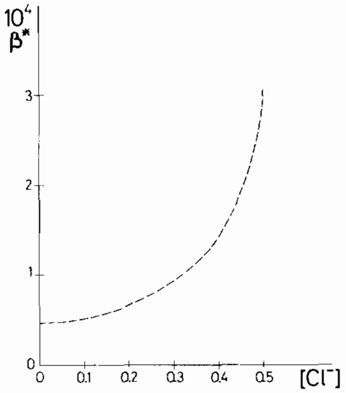

Fig. 2. The influence of $ClO_4^- \rightarrow Cl^-$ substitution ($[Na^+]$ = 0.5 *M*).

The conclusion that cations take also part in the interactions is proved by these results like the fact that the apparent formation constant of β-CD–dye complex is significantly increased by sulfate and chloride ions. This phenomenon can only be explained by formation of mixed ligand complexes.

This conclusion is supported by the results of measurements where the cation (anion) concentration was kept constant and the concentration of anions (cations) was continuously changed. The effect on the apparent stability constant of β-CD–phenolphthalein complex in solutions at constant 0.5 *M* sodium but changing ClO_4^-–Cl^- concentrations is represented in Fig. 2 as a function of chloride concentration.

As can be seen in Fig. 2, there is no simple competing reaction, and what is more, the existence of a β-CD–anion–cation mixed complex can be also supposed.

Summarizing the results, the following interactions can be concluded in the reaction of cycloamylose and inorganic compounds (made even more complicated by the presence of an organic compound):

i) The anions have the main (but not single) effect. The formation constant of their β-CD complexes can be signed as β_{CD,X^-}.

ii) β-CD forms complexes with cations, among them with alkali ions (β_{CD,M^+}).

iii) The phenolphthalein (and supposedly several other organic compounds) forms in addition to the simple β-CD complex ($\beta_{CD,I}$) also mixed complexes, first of all with anions (β_{CD,I,X^-}) but the existence of mixed cation complexes (β_{CD,I,M^+}) cannot be excluded.

iv) The formation of β-CD–cation–anion mixed complexes is also very probable (β_{CD,X^-,M^+}).

Based on the known mathematical background of coordination chemistry [4] but leaving out the details, the following connection can be drawn between the apparent stability constant of β-CD–dye complex and the mentioned constants:

$$\beta^* = \frac{\beta_{CD,I} + \beta_{CD,I,X^-}[X^-] + \beta_{CD,I,M^+}[M^+]}{1 + \beta_{CD,X^-}[X^-] + \beta_{CD,M^+}[M^+] + \beta_{CD,X^-,M^+}[X^-][M^+]}$$

As the equation is rather complicated, a lot of highly precise data are needed for computing the different constants but our preliminary calculations prove that all of the phenomena observed so far can be explained by it [5].

It can be seen that the most stable mixed complexes are formed with chloride and sulfate ions. In the case of the relatively small chloride ion, the chloride ion and the guest molecule can be assumed to find room together in the cage of cycloheptaamylose. But the totally different behaviour of sulfate and perchlorate ions which have nearly similar size and structure, shows that not only host–guest inclusion (or inner-sphere) complexes can be formed with β-cyclodextrin but also normal or outer-sphere complexes, where the β-CD reacts as a simple polyhydric compound.

The alcoholic hydroxy groups of β-CD as strong proton donors seem to play the main role in these complexes and mainly the hydrogen bridged character of the outer-sphere CD-complexes can be supposed.

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5 It means that only 1:1 and 1:1:1 species can be detected but there is no reason to exclude other stoichiometries in other systems or in more concentrated solutions.