

THERMAL STABILITY OF PRODUCTS PREPARED BY THE COMBINATION OF CYCLODEXTRINS AND ZEOLITES

P. Mondík, Anna Sopková and P. Králik

Department of Inorganic Chemistry, Šafarik's University, Moyzesova 11, 041 54 Košice, Slovakia

(Received January 25, 1994; in revised form April 15, 1994)

Abstract

Derivatographic and calorimetric measurements were used to study the thermal properties of combined inclusion compounds of zeolite-cyclodextrin type and of zeolite-cyclodextrin-pharmaceutical type. There were differences in the characteristic decomposition temperature intervals and in the modes of cyclodextrin and pharmaceutical liberation from the products. Calorimetric measurements revealed that the process in the newly-formed complex host is connected with a glass transition.

The products are intended for use in veterinary medicine.

Keywords: inclusion compounds, cyclodextrins, zeolites

Introduction

Inclusion compounds of tetracyano complexes and more recently zeolites and cyclodextrins (CDs) are the three types mainly studied in our laboratories [1]. The former two represent layered intercalates with more or less intersected layers, while the third has a channel-like structure formed by spirals that is available for the guest component [2-5]. Through a combination of two of these three types of inclusion compounds, a further increase of the voids in the host can be achieved. Thus, a greater possibility for enclosing the guest occurs. The area of the original host component becomes enriched through the interaction between the various guest components present or through their interactions with the host lattice.

Results on products prepared in our Department by the sorption of different compounds in natural zeolites were reported earlier [1]. Products involving combinations of zeolite with tetracyano complex [2], CDs [3], fragrances [6], nutrient ions and iodine [7] have been prepared. In the present paper, combinations of natural and synthetic zeolites with CDs are discussed. In our products,

the CDs contain water molecules or pharmaceuticals such as salicylic acid and iodine as the guest. Such products to which pharmaceuticals have been added are the current subject of our research work, with the aim of their utilization in veterinary medicine. The thermal stability of these combined inclusion compounds is discussed here.

Experimental

Materials

Natural zeolitic material of clinoptilolite type (CT) from the East Slovakian deposit at Nižny Hrabovec was used (grain size <0.1 mm). In our work, it was treated with Cu(II) ions before synthesis, 1 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Lachema, Brno) being used. The synthetic zeolite of NaY type was a product of VURUP, Bratislava.

The following CDs were used: α -cyclodextrin (α CD), and the ethylenediamine derivative of β -cyclodextrin (β CDen) prepared according to [8]. α CD and β CD were products of Chinoïn, Budapest.

Salicylic acid and iodine were products of Lachema, Brno.

Methods

The products of zeolites (CTCu, NaY) with incorporated CDs were prepared similarly as in [3], but using a 0.1 M aqueous solution of the CD.

The final products of zeolite-CD-pharmaceutical combinations were prepared by contact of the zeolite-CD compound with ethylalcohol (96%) and salicylic acid or iodine (1 g of each pharmaceutical to 10 g of alcoholic solution) for 10 days. Products were centrifuged, washed with pure ethanol and air-dried.

Instrumentation

A Specord M80 IR spectrophotometer (Carl Zeiss, Jena) was used in the range $4000\text{--}200\text{ cm}^{-1}$ with KBr discs.

For DTA and TG analyses, a derivatograph (MOM 102, Budapest: TG 100 mg, DTA 1/5, DTG 1/5, heating rate $9\text{ deg}\cdot\text{min}^{-1}$) was used. For DTA definition by the DSC method, a DSC-7 Perkin-Elmer instrument was used.

Diffractographic measurements were performed with Micrometa 2 instrumentation (Chirana, Brno), using monochromatic $\text{CuK}\alpha$ radiation, 30 kV/20 mA.

The ^1H NMR measurements were performed by the impulse method with a hydrogen nucleus resonance frequency of 30 MHz. The times of spin magnetization relaxation T_1 were measured in the temperature interval 133–298 K.

The ESCA spectra were collected by a LHX1 Leibold spectrometer using unmonochromated AlK_{α} radiation (1486.6 eV). The source was operated at 14 kV and 20 mA. The energy scale of the spectrometer was calibrated by using Cu $2p_{3/2}$ and Au $4f_{7/2}$ at 932.7 and 84.0 eV.

Results and discussion

IR spectra

All characteristic bands of the zeolite in the products containing natural zeolitic material or synthetic zeolite were conserved. There were no essential changes in the IR spectra of either products containing α CD or β CDen (in the role of G_1), or those enclosing salicylic acid or iodine (in the role of G_2). All products conserved their zeolitic peaks belonging to the host component as the strongest. The peaks of both forms of CD acting as the guest either overlapped with those of the zeolite or were of very weak intensity. Iodine as guest G_2 is not active in the IR spectra, and therefore it could not be checked by this method. Salicylic acid exhibited its characteristics in a clear way in the products with α CD. In the products with β CDen as guest the intensities of the salicylic acid peaks were very weak. The cavity of β CDen is more spacious than that of CD (inner diameters: α CD=4.7–6.0 Å, β CD=8.0 Å) [4], and therefore a difference in enclosing capacities as concerns new guests (G_2) may explain this phenomenon.

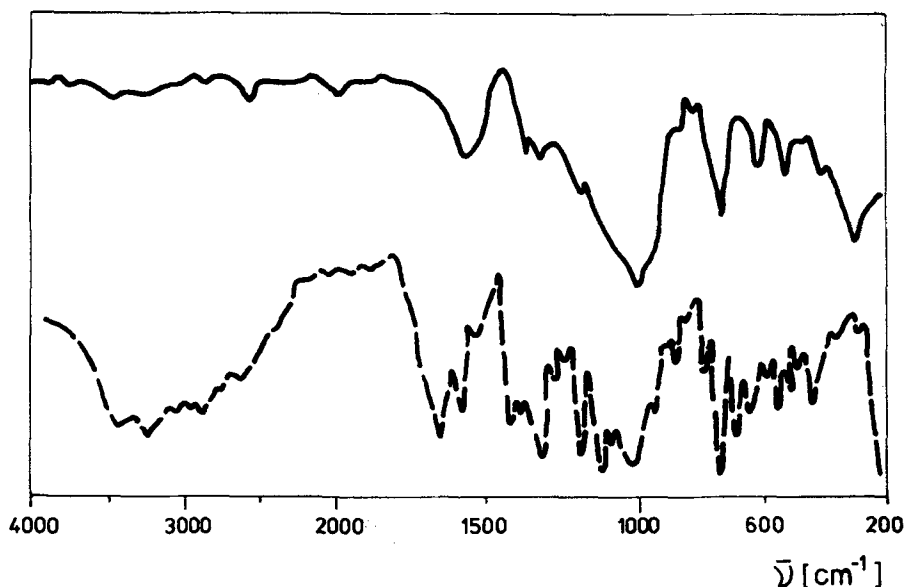


Fig. 1 IR spectra of the product CTCu- α CD-salic. (—) and its analogous physical mixture CTCu + α CD + salic (---)

There were distinct differences between the products and their physical mixtures, as can be seen in Fig. 1.

Thermal analysis

Derivatographic measurements

All products were studied by heating up to 900°C. The characteristics found in the derivatographic measurements are illustrated in Table 1.

The DTA curves revealed two main processes in the decomposition of the products. Depending on the guest G_1 , the CDs are liberated from the zeolite in the interval 150–420°C.

In the case of products containing a second enclosed guest G_2 , this component is liberated first, at the starting temperature of decomposition of the product.

Table 1 Thermal characteristics of products according to derivatographic measurements

Products	Desorption of G_1		Desorption of G_2	
	Temp. interval/°C	Δm / %	Temp. interval/°C	Δm / %
CTCu- α CD	250-405	8		
CTCu- β CDen	250-390	5		
NaY- α CD	170-410	12		
NaY- β CDen	150-420	13		
CTCu- α CD-salic.	210-410	10	70-210	21
CTCu- β CDen-salic.	220-405	7	60-240	16
CTCu- α CD-iodine	240-410	7	70-240	10
CTCu- β CDen-iodine	270-420	3	80-270	6
NaY- β CDen-iodine	140-400	13	60-140	14
NaY- α CD-salic.	240-360	7	65-220	20
	360-500	7		
NaY- β CDen-salic.	200-360	8	65-200	15
	360-610	9		

Salicylic acid is liberated up to the temperature when the CDs start to decompose. The same process is observed in the case of iodine, but iodine is lost in an exothermic process. The loss of G_2 is reflected by a greater amount in the TG curve (6–21%) than that for G_1 (3–13%). The temperature range in which the CDs alone are liberated from a product is somewhat different from the case when the CDs enclose the guest G_2 .

All derivatographic curves show that the component G_2 is released first, the CDs as G_1 then start to decompose, and this leaves the zeolitic host structure.

Table 2 lists the amounts of CDs and salicylic acid sorbed in zeolites. α CD is better sorbed in CTCu (19.82 wt%), as is β CDen in the NaY zeolite (20.33 wt%). Salicylic acid is most easily sorbed (9.63 wt%) in the CTCu- α CD product and least easily (5.54 wt%) in the NaY- β CDen product. The CTCu zeolitic form provided more convenient conditions for the sorption of salicylic acid than did the NaY zeolite. The latter zeolite is a better sorptive material for iodine (present as guest G_2). The lower amount of sorbed iodine is due to its volatility during preparation, drying and standing. A certain amount of iodine is sorbed on the surface of the zeolite [7].

The physical mixtures of starting materials differ from the analogous products (Figs 2 and 3), especially as concerns the DTA curves, where numerous thermal processes were observed. A series of simultaneous thermal decompositions occur, because the material made by simple physical mixing of the starting materials in the solid state liberates its components continuously. All of our combinations were prepared from the starting materials with the guest component in solution, in contrast with physical mixtures.

Depending on the natures of G_1 and G_2 , (in Table 2), our products may be described as follows:

CTCu-0.25 α CD	NaY-0.14 β CDen
CTCu-0.14 β CDen	NaY-0.26 β CDen
CTCu-0.28 α CD-0.14salic.	NaY-0.29 β CDen-0.14iodine
CTCu-0.16 β CDen-0.15salic.	NaY-0.20 α CD-0.08salic.
CTCu-0.26 α CD-0.06iodine	NaY-0.27 α CD-0.07salic.
CTCu-0.15 β CDen-0.04iodine	

DSC measurements

Differential scanning calorimetric measurements were performed on products containing CTCu zeolite (Fig. 4).

When α CD was the only guest component in the inclusion compound, only one peak was observed ($T=293.2^\circ\text{C}$; $\Delta H=35.74$ J/g). This peak represents the process of liberation of α CD from the product. When there were two guest components in the product (CD and salicylic acid), two DSC peaks were observed. For CTCu- α CD-salic., the first peak ($T=228.86^\circ\text{C}$; $\Delta H=18.62$ J/g) represents the process of melting and liberation of salicylic acid, with DTA maximum at 160°C (melting point 159°C) [2]. The value of $\Delta H=330.25$ J/g for this process is relatively high and can be ascribed to the process of some new host formation, which is seen as the glass transition process. For the product CTCu- β CDen-salic., two peaks were again observed, with much lower values

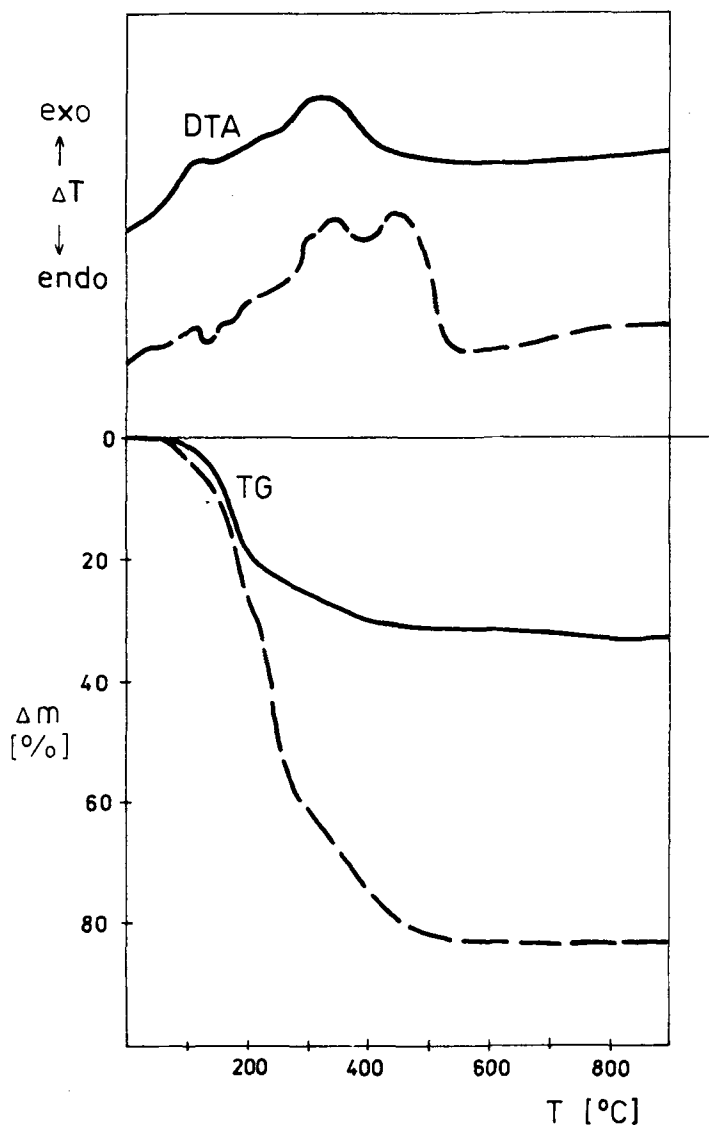


Fig. 2 DTA and TG curves of the product CTCu- α CD-salic. (—) and its physical mixture CTCu+ α CD+salic. (---)

of energy. At $T=157.12^{\circ}\text{C}$, we found $\Delta H=7.66$ J/g for salicylic acid release (DTA maximum at 160°C), and at $T=211.6^{\circ}\text{C}$, $\Delta H=37.03$ J/g connected with the liberation of β CDen.

The physical mixture of CTCu+ α CD+salicylic acid was likewise examined. It showed differences from the analogous product in the peak intensities and their parameters ($T=160.12^{\circ}\text{C}$; $\Delta H=48.17$ J/g vs. $T=241.47^{\circ}\text{C}$; $\Delta H=$

247.04 J/g). Some weak sublimation was found at about $T=76^{\circ}\text{C}$ (sublimation temperature of pure salicylic acid). A strong difference was found for the melting of salicylic acid not enclosed in the physical mixture. There was also a clear difference in the ease of release of salicylic acid.

A further difference in the behaviour of the physical mixture related to the sorbed CD. The glass transition was not found in the analogous temperature in-

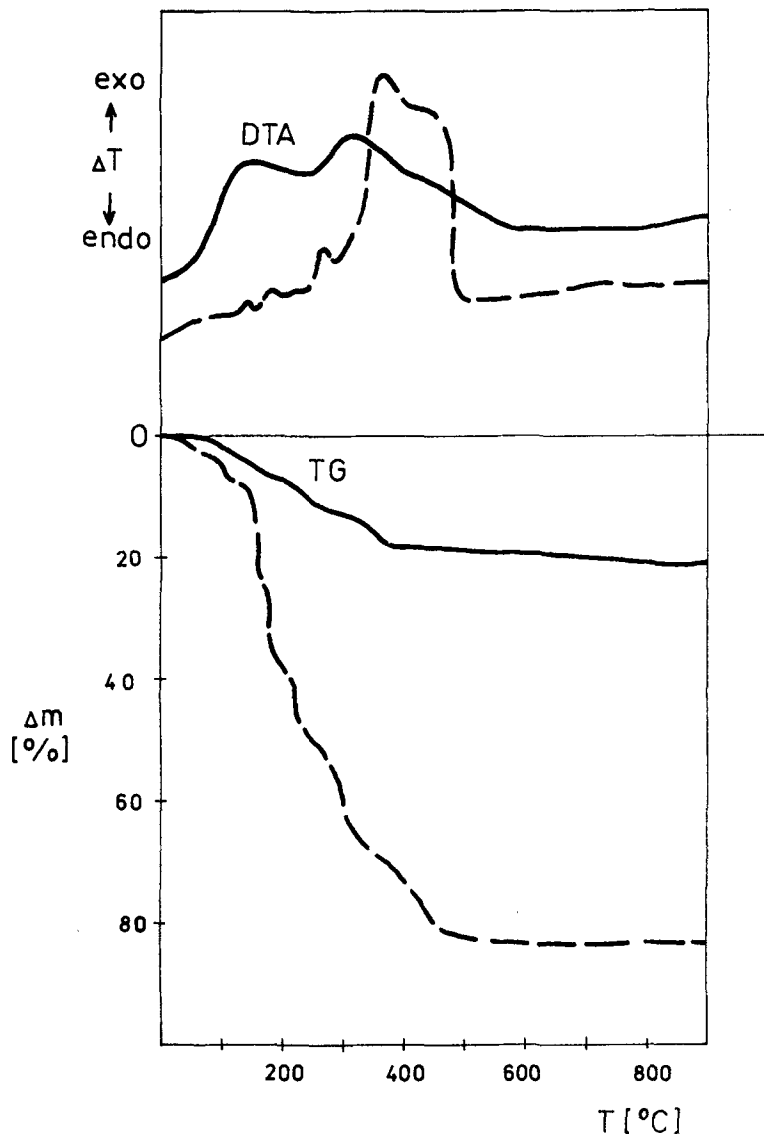


Fig. 3 DTA and TG curves of the product CTCu- α CD-iodine (—) and its physical mixture CTCu+ α CD+iodine (---)

terval for the physical mixture. The process of CD liberation is connected with a ΔH value about one-fifth lower and a lower temperature. We may suppose a freer mobility of the CD in the physical mixture relative to the limited motion of the enclosed CD in the product.

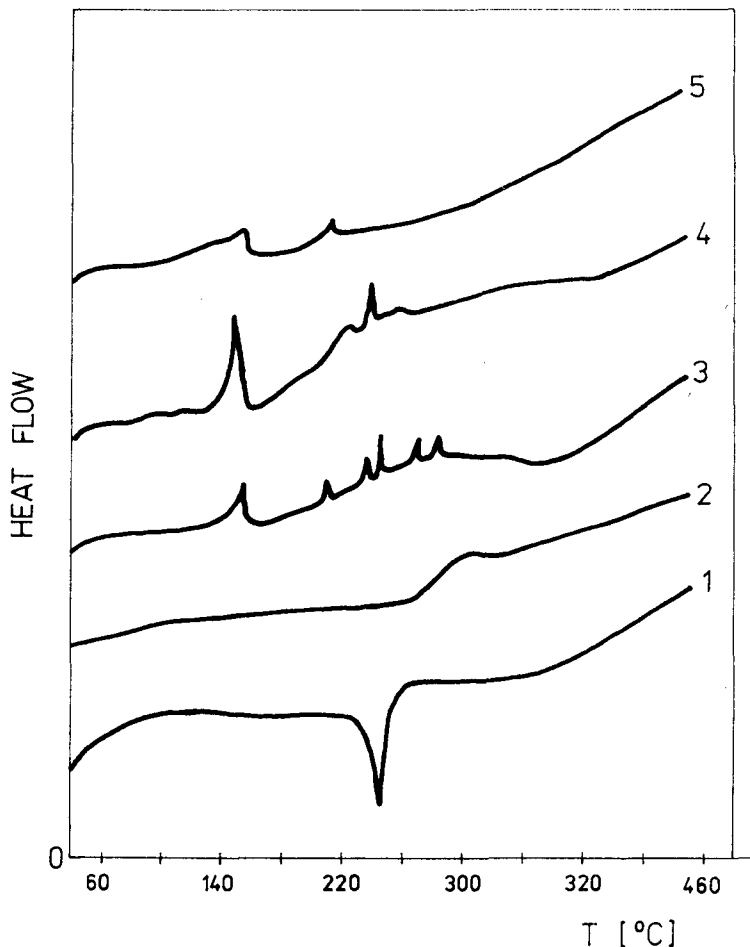


Fig. 4 DSC curves of CTCu zeolite (1), products CTCu- α CD (2), CTCu- α CD-salic. (3), CTCu- β CDen-salic. (5) and the physical mixture CTCu+ α CD+ salic. (4)

This phenomenon was also investigated via the results of preliminary measurements of the NMR relaxation time T_1 . The physical mixture of CTCu zeolite and CD showed striking differences (2 orders of magnitude) from the product prepared from the same starting compounds. Two kinds of channels in the zeolite were differentiated. The longer T_1 may be ascribed to the liberation from the less spacious channels.

X-ray diffractographic and ESCA measurements

Diffractographic measurements were performed on our starting materials and products. It was observed that the crystalline character of the zeolite in the products decreased due to the presence of CDs anchored in the cavities of the zeolite or partly sorbed on the surface of the zeolite. A comparison of the diffractographic patterns of the starting materials and products suggests that the CD molecules, as guest component in the zeolite, are dispersed in the mineral phase, similarly as in other products [1].

ESCA measurements confirmed the weak interactions between the zeolitic structure and its guest components. In the case of CTCu zeolite modified by Cu(II) ions, some of the Cu(II) ions were reduced to Cu(I) and Cu(0) forms in the products. The higher value of the ratio Cu(0)+Cu(I)/Cu(II) (0.68) was observed for the CTCu- α CD product, and the lower value (0.608) was observed for the CTCu zeolite. As concerns the peak areas of the atoms present in the zeolite and therefore also in the products (Cu, O, C, K, Si and Al), a difference was observed for carbon. This is obviously because of its increase due to the sorption of CDs in the zeolites.

Conclusions

The new products were prepared by the sorption of CDs and of salicylic acid or iodine in zeolites.

The combinations of $H_1-H_2-G_1$ or $H_1-G_1-G_2$ type are based on the possible double role of CDs in the zeolitic host. The products differ from the analogous physical mixtures prepared from the corresponding starting compounds. The derivatographic TG curves helped to confirm the mode of liberation of the guest components from the zeolite. The most striking phenomenon revealed by the DSC measurements contributed to the changes occurring in the newly-formed more complex host. A glass transition occurs between the CDs and natural zeolite, but not in the physical mixture.

* * *

The authors wish to thank Prof. J. Szejtli for the samples of cyclodextrins and Ing. P. Imón, CSc. for carrying out the calorimetric measurements.

References

- 1 A. Sopková, *J. Incl. Phenom.*, 14 (1992) 5.
- 2 A. Sopková, P. Mondík and M. Šingliar, *J. Incl. Phenom.*, 13 (1992) 233.
- 3 P. Mondík, A. Sopková, G. Suchár and T. Wadsten, *J. Incl. Phenom.*, 13 (1992) 109.
- 4 J. Szejtli, *Cyclodextrins and their Inclusion Complexes*, Akadémiai Kiadó, Budapest 1982.
- 5 D. Duchene and D. Wousesidjewe, *J. Coord. Chem.*, 27 (1992) 223.

- 6 A. Sopková, E. Hanzelová, Z. Ondříková, E. Búciová and J. Hviždák, Proc. 4th Intern. Seminar Inclusion Compounds, Stará Lesná, June 1991, p. 49–52.
- 7 M. Reháková, M. Casciola, A. Sopková and Z. Bastl, Solid state Ionocs, 66 (993) 189.
- 8 Y. Matsui, T. Yokoi and K. Mochida, Chem. Lett., (1976) 1037.

Zusammenfassung — Zur Untersuchung der thermischen Eigenschaften von kombinierten Ein-schlußverbindungen vom Zeolith-Cyclodextrin-Typ und vom Zeolith-Cyclodextrin-Arzneimittel-Typ wurden derivatografische und kalorimetrische Messungen verwendet. Es gabe Unterschiede bei den charakteristischen Zersetzungstemperaturintervallen sowie in der Art der Freisetzung von Cyclodextrin und Arzneimittel aus den Produkten. Kalorimetrische Messungen zeigten, daß der Prozeß im neugebildeten Komplexwirt mit einer Glasumwandlung verknüpft ist. Die Produkte sind für einen Einsatz in der Veterinärmedizin vorgesehen.