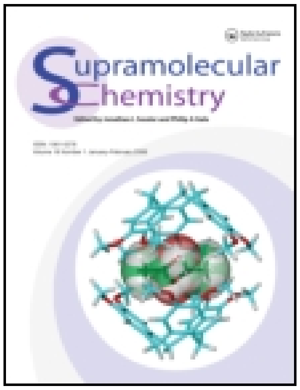

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Functional significance of molecule–ion interactions between a series of inorganic salts and β-cyclodextrin

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In the present work, β-cyclodextrin (CD) was employed to form molecule–ion adducts with a series of inorganic salts, in order to investigate whether there is a relation between the change in thermal behaviour of β-CD and the presence and properties of inorganic salts. Our results indicated that all the adducted β-CDs decomposed earlier than free β-CD. In particular, significant changes in maximum decomposition temperature (T_m) and maximum decomposition rate (V_m) of β-CD upon adduct had a close connection with the nature of inorganic salts. For example, the effects of chlorides and sodium oxysalts on T_m of β-CD decreased in the order: $CaCl_2 > LiCl > KCl > NaCl$ and $Na_3PO_4 > Na_2CO_3 > NaNO_3$, respectively. Interestingly, the orders were in good accord with the effects of β-CD on the molar conductivities of the salt solutions. Furthermore, mass spectral data indicated that the thermal release behaviour of the adducted products was quite different not only from one another but also from free β-CD based on comparisons of relative abundances of decomposed fragments at the same heating times. We believe that the results obtained from this study provide a new understanding of how the nature of inorganic salts relates to the thermal degradation of a carbohydrate.

Keywords: β-cyclodextrin; inorganic salts; molecule–ion interaction; thermal degradation

Introduction

The thermal behaviour of carbohydrates is of great significance because it has a close relation with the everyday life of human beings, such as the thermal stability of biomaterials and catalytic degradation of waste carbohydrates. β-Cyclodextrin (CD), one of the most important carbohydrates, is a cyclic oligosaccharide with an apolar cavity that shows a certain degree of selectivity in binding organic compounds (*1–4*). And this binding phenomenon has wide applications in many areas of organic chemistry (*5–8*). Also, there were a few reports on weak binding affinities of β-CD to inorganic ions in solutions (*9–12*). And the weak molecule–ion interactions between them were recently found to be able to improve the crystal growth of inorganic nanoparticles (*13–16*). Very recently, we reported two important findings: (1) The thermal decomposition of sodium arsenite ($NaAsO_2$) was largely changed by the presence of β-CD, leading to a release of four forms of gaseous arsenic (As^+, As_2^+, As_3^+ and As_4^+) in different relative abundances (RA, %) at lower temperatures (*17*) and (2) The existence of lithium carbonate (Li_2CO_3) dramatically changed the degradation mechanism of β-CD, producing many interesting fragments such as $C_6H_6O^+$, $C_7H_7^+$, $C_5H_5^+$ and $C_3H_3^+$ ions (*18*).

At present, all that can be confidently asserted is that there is a mutual influence between inorganic salts and β-CD, and the influence plays a dominant role in mediating crystal formation of β-CD and modulating distribution of inorganic ions in crystallisation processes (*19*). However, the relationship between the nature of inorganic salts and the change in spectral characteristics of β-CD is still not clear. This is the reason why a series of experiments was designed and carried out in this project.

Initially, molar conductivity experiments of several chlorides and sodium oxysalts in the presence of β-CD were performed to measure the molecule–ion interactions between these salts and β-CD and to detect the degree of the interactions. Then, solid adducts of β-CD with a series of salts were prepared. Three analysis methods: thermogravimetry (TG), gas chromatography coupled to time-of-flight mass spectrometry (GC-TOF-MS) and calcination measurements were performed to examine the difference in thermal properties of β-CD before and after interaction, with the task of evaluating what is the difference between the effects of inorganic salts on the spectral characteristics

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of β-CD. Our results showed a significant phenomenon that the presence of inorganic salts led to an earlier decomposition of all the adducted β-CDs, and that the magnitude of the salt effects was dependent on the nature of the salts used.

Next, field-emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD) indicated that the surface structure and crystal packing of β-CD were changed upon adduct, and the changes observed were in close relation to the nature of the salts. That is to say, different salts have different influences on the crystal growth of β-CD.

We believe that the results obtained from this work have consolidated our finding on the differences in spectral characteristics and decomposition behaviour of β-CD induced by inorganic salts (*17*, *20*, *21*). These findings are useful for a better understanding of crystal design and growth of hybrid particles formed by similar inorganic and the organic components, especially the disposal of waste carbohydrates.

Experimental section

Materials

β-CD was purchased from Shanghai Chemical Reagent Company (Shanghai, China) and recrystallised twice using deionised water. Analytically pure lithium chloride ($LiCl·H_2O$), sodium chloride (NaCl), potassium chloride (KCl), calcium chloride ($CaCl_2$), sodium nitrate ($NaNO_3$), sodium carbonate (Na_2CO_3) and sodium phosphate decahydrate ($Na_3PO_4·10H_2O$) were commercially available and used as received without further purification. All other chemicals were of general-purpose reagent grade unless otherwise stated.

Preparation of solid adducts

A total of 1 mmol β-CD (1.135 g) and 1 mmol (0.058 g) NaCl were dissolved in 120 ml deionised water, and stirred at 333.2 K for 6 h in a round-bottomed flask. After water was removed from the solution by rotary evaporation under vacuum below 323.2 K, a white adduct NaCl–β-CD (1.102 g) was prepared. Other adducts were obtained in white solid form as a crystal powder in this manner. Mechanical mixtures were prepared by mixing an equimolar ratio of β-CD with each of the salts.

Preparation of solution samples

Aqueous solutions of 1.00×10^{-3} mol dm^{-3} of the salts in the absence and presence of β-CD (from 0.00 to 1.00×10^{-2} mol dm^{-3}) were prepared to measure their molar conductivities (Λ_m). Each value of Λ_m was obtained from an average of three measurements.

Sintering experiments

A small amount of samples of β-CD and its adducts was dried to constant weight at 393.2 K under vacuum. After cooling to 298.2 K in evacuated desiccators over P_2O_5, the samples were weighed and calcined for 10 min at 423.2, 473.2, 523.2, 573.2 and 603.2 K under ambient atmosphere in a muffle furnace. Each residue was weighed after it was cooled to 298.2 K in a desiccator.

TG and GC-TOF-MS experiments

Considering different thermal stabilities of these salts, two methods were adopted to dry the adducts of β-CD in order to remove crystal water from the products. Method 1, the β-CD adduct of $LiCl·H_2O$ was dried at 333.2 K for 2 h under vacuum to prevent the decomposition of $LiCl·H_2O$ during the drying process. Method 2, all other adducts were dried at 393.2 K for 2 h under vacuum. In view of the fact that these salts have a very low mass fraction in the adducts, it is reasonable to assume that the strongest signal in each curve of derivative thermogravimetry (DTG) or total ionic current (TIC) analyses should be regarded to determine the maximum decomposition process of β-CD after adduct.

Instruments and methods

The values of Λ_m of solutions were measured using a Leici DDS-11D conductivity meter (Shanghai Leici Instrument Factory, Shanghai, China) with automatic temperature compensation at 298.2 K and automatic calibration. A conductance cell with a cell constant of around 1.083 cm^{-1} was used. The Λ_m values of aqueous solutions of β-CD itself at different concentrations served as a standard of reference for all the data concerning β-CD. ^{1}H nuclear magnetic resonance (^{1}H NMR) data of free β-CD and a mixed sample of the salts with β-CD in D_2O (20:1, molar ratio, with stirring at 333.2 K for 6 h) were obtained on a Bruker NMR spectrometer at 300 MHz using $CDCl_3$ with 0.03% v/v TMS as an external reference at 298.2 K.

Crystal morphologies of β-CD and its several adducts were observed using a Supra 40 FE-SEM operated at 5 kV. Powder XRD patterns were obtained in a Philips X'Pert Pro X-ray diffractometer using monochromatised CuKα radiation in the 2θ range $5° \leq 2\theta \leq 40°$. Tube voltage and current was 40 kV and 40 mA, respectively.

TG and DTG analyses were recorded on a Shimadzu TGA-50 thermogravimetric analyser at a constant heating rate of 10 K min^{-1} under a nitrogen atmosphere with a gas flow of 25 ml min^{-1}. GC-TOF-MS measurements with a programmed temperature operation were carried out with a Micromass GCT-MS spectrometer using a standard direct insertion probe for samples (*22*).

Results and discussion

Intensity of molecule–ion interactions

Figure 1 clearly displays that there is a change ($\Delta\Lambda_m$) of Λ_m values of several chlorides and sodium oxysalts in the absence and presence of β-CD. In addition, the $\Delta\Lambda_m$ values are associated with initial molar ratio (IMR) of β-CD to the salts. That is to say, the $\Delta\Lambda_m$ values increase with the increase in concentration of β-CD when the concentration of the salts is kept at a constant value of 1.00×10^{-3} mol dm^{-3}.

The results give a true picture of the actual mobility state of ions in solutions of the salts. On the one hand, the differences in mobility behaviour of ions with and without β-CD suggest that there is a molecule–ion interaction between β-CD and ions, because β-CD itself, as a neutral molecule, presents a slightly increasing trend in conductivity with increasing concentration. On the other hand, the concentration dependence of the molecule–ion interaction means that the stronger the interaction between ions and β-CD, the more the decrease in the mobility of the ions in solutions. Furthermore, β-CD shows a pronounced effect on the Λ_m values of $CaCl_2$ and Na_3PO_4, and the effect decreases in the orders: $CaCl_2 > LiCl > KCl > NaCl$ and $Na_3PO_4 > Na_2CO_3 > NaNO_3$. These orders draw a complete picture of the relative strength of the molecule–ion interaction. From this we can deduce that the effects of β-CD on the chlorides and sodium oxysalts are possibly related to the polarisation of the cations: $Ca^{2+} > Li^+ > K^+ > Na^+$ and the negative charge number of the anions: $PO_4^{3-} > CO_3^{2-} > NO_3^-$, respectively.

^1H NMR measurements are employed to further determine such an interaction and its intensity (*23*, *24*). Figure 2 illustrates ^1H NMR spectra of free β-CD and mixed samples of the salts with β-CD (20:1, molar ratio).

As seen in Figure 2, addition of the salts to β-CD leads to changes in chemical shifts (δ) of the proton resonances of the hydrogen atoms on the carbon atoms (C-2 to C-6) of β-CD. The direction and magnitude of such changes were not uniform. For example, the signals of the protons (HC-2, HC-4 and HC-6) in β-CD shift downfield for KCl, LiCl, $CaCl_2$ and $NaNO_3$, but upfield for NaCl, Na_2CO_3 and Na_3PO_4. It is important to note that the order of the salt effect on the δ values for the protons is consistent with the result obtained from the conductivity experiments. The conductivity experiments display the effect of β-CD on the salts, and the ^1H NMR measurements reveal the effect of the salts on β-CD. Hence, this observation may imply a functional relationship between action and reaction.

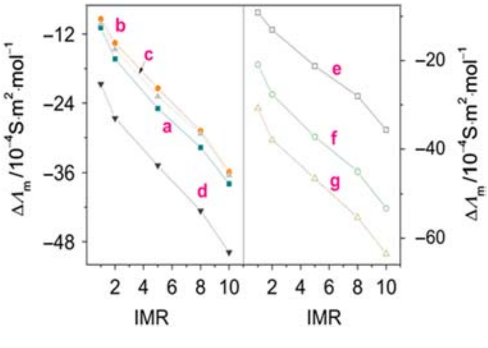

Figure 1. $\Delta\Lambda_m$ values of aqueous solutions of LiCl (a), NaCl (b), KCl (c), $CaCl_2$ (d), $NaNO_3$ (e), Na_2CO_3 (f) and Na_3PO_4 (g) as a function of IMR of β-CD (0.00–1.00×10^{-2} mol dm^{-3}) to the salts (1.00×10^{-3} mol dm^{-3}).

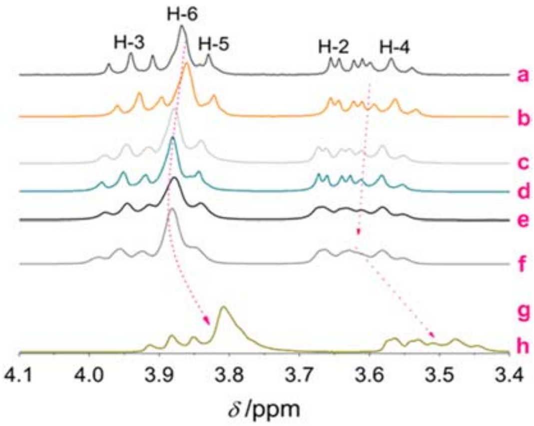

Figure 2. ^1H NMR spectra of free β-CD (a) and mixed samples of β-CD with NaCl (b), KCl (c), LiCl (d), $CaCl_2$ (e), $NaNO_3$ (f), Na_2CO_3 (g) and Na_3PO_4 (h) in D_2O.

Surface structures and stacking behaviours

FE-SEM images show that β-CD has a geometric shape of hexagonal prism. However, its adducts of LiCl, NaCl, $CaCl_2$, Na_2CO_3 and Na_3PO_4 are in the shape of bent tiles, biscuits, potato chips, sponge leafs and fungus stones, respectively, as seen in Figure 3. The fact that the solid adducts exhibit completely different morphologies from one another and from β-CD gives a strong impression that the surface structure of β-CD is likely to have a close relation with the presence and nature of inorganic salts. For example, according to the orders obtained from the conductivity experiments, we find that the stronger the interaction between a salt and β-CD, the worse the morphology in FE-SEM images. This difference of salt effects probably implies that the salts can be used to modulate the crystal growth pattern and crystal size of β-CD.

In order to determine whether the change in surface structure is accompanied by a change in spatial arrangement, XRD measurements were done under the same conditions. The results of these experiments are summarised in Table 1. Apparently, the characteristic peaks of β-CD at lower 2θ angles from free state to the adducted states give rise to different shifts (see the

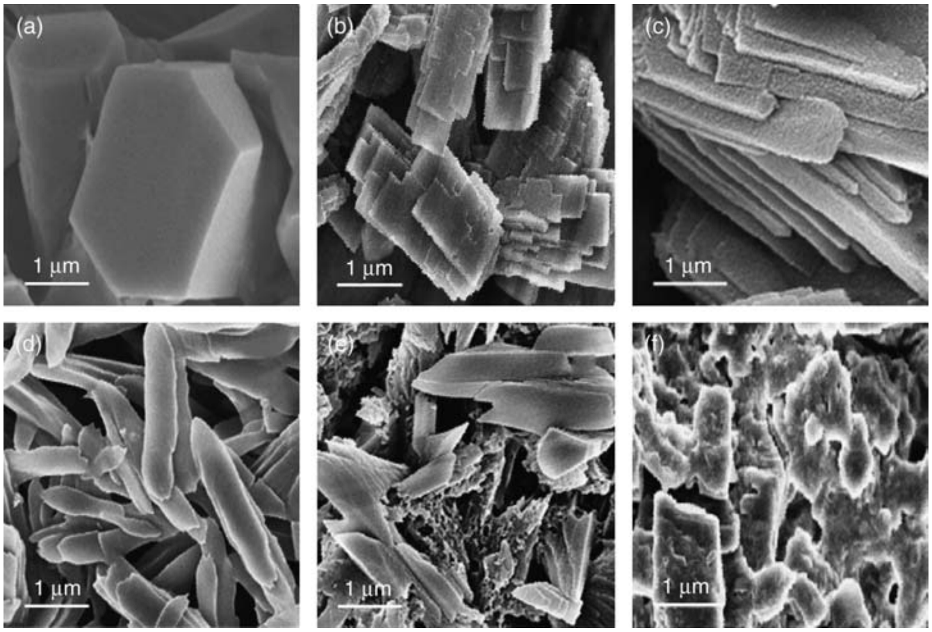

Figure 3. FE-SEM images of (a) β-CD and its adducts of (b) LiCl, (c) NaCl, (d) $CaCl_2$, (e) Na_2CO_3 and (f) Na_3PO_4.

Table 1. Positions (2θ) of several diffraction peaks of β-CD and its adducts in XRD patterns.

Samples	Several characteristic peaks in XRD spectra, 2θ (°)
β-CD	6.4 (w), 9.1 (m), 12.5 (s), 15.5 (m), 19.3 (s)
LiCl−β-CD	6.5 (w), 9.2 (m), 12.6 (s), 15.5 (m), 19.2 (m)
NaCl−β-CD	6.5 (w), 9.3 (m), 12.7 (s), 15.6 (m), 19.6 (m)
KCl−β-CD	6.5 (w), 9.3 (m), 12.4 (s), 15.6 (m), 19.7 (s)
$CaCl_2$−β-CD	6.6 (w), 9.5 (w), 12.8 (m), 13.5 (m), 18.4 (s)
$NaNO_3$−β-CD	6.5 (w), 9.5 (s), 12.5 (s), 15.5 (m), 19.5 (m)
Na_2CO_3−β-CD	6.6 (w), 9.7 (m), 12.8 (s), 15.7 (m), 18.4 (m)
Na_3PO_4−β-CD	6.6 (w), 9.8 (m), 12.6 (s), 15.6 (m), 18.3 (m)

Note: Alphabets s, m and w represent strong, moderate and weak peaks, respectively.

Table 2. α Values of β-CD before and after adduct at different temperatures in air.

Samples	α (%)		
	523.2 K	573.2 K	603.2 K
β-CD	56.67	62.00	75.33
LiCl−β-CD	54.49	79.42	81.74
NaCl−β-CD	63.44	95.70	97.30
KCl−β-CD	65.09	91.90	95.37
$CaCl_2$−β-CD	74.68	84.14	90.51
$NaNO_3$−β-CD	64.28	95.60	97.80
Na_2CO_3−β-CD	87.03	93.50	97.83
Na_3PO_4−β-CD	50.29	82.45	83.63

Supporting Information, available online). For example, the two characteristic peaks of β-CD at 6.4° and 9.1° shift to higher 2θ angles upon adduct in all cases. The result means that the molecule–ion interaction between β-CD and the salts causes a closer arrangement of the β-CD molecules.

The change in molecular arrangement of β-CD leads us to further examine what differences in thermal behaviours, if any, exist between β-CD and its adducts, as well as between these adducts.

Decomposition degrees under ambient atmosphere

Changes in decomposition degree (α, %) of β-CD before and after adduct are demonstrated by sintering experiments under ambient atmosphere. Table 2 indicates the relationship between heating temperatures and α values of β-CD in the forms of free and adducted states. The α values are calculated based on the initial mass percentage of β-CD in these states and the final residual mass at each temperature. It should be mentioned that inorganic salts do not decompose in the detected temperatures.

As seen from Table 2, the α values of β-CD in the presence of different inorganic salts differ from one another, and from those of free β-CD at the same temperatures, reflecting the salt effect on the decomposition process of β-CD in air. Furthermore, at a lower temperature (523.2 K), most of the salts such as NaCl, KCl, $CaCl_2$ and, especially, Na_2CO_3 virtually promote the decomposition of β-CD. And at a higher temperature, all the salts further improve the decomposition efficiency of β-CD. For example, at 573.2 K, the salt effect causes an increase ($\Delta\alpha$) of at least 17%.

Table 3. Relationship between heating times and release signals in TIC curves of β-CD and its adducts.

Samples	Heating times (min)		
	R_1	R_2	R_3
β-CD	–	25.63 (s)	27.23 (m)
LiCl–β-CD	18.58 (w)	25.35 (s)	31.65 (w)
NaCl–β-CD	18.22 (w)	25.24 (s)	31.64 (m)
KCl–β-CD	20.05 (m)	25.07 (s)	31.49 (m)
$CaCl_2$–β-CD	17.17 (s)	25.32 (m)	31.72 (w)
$NaNO_3$–β-CD	17.89 (m)	25.34 (s)	31.60 (w)
Na_2CO_3–β-CD	18.00 (w)	25.37 (s)	31.72 (w)
Na_3PO_4–β-CD	18.35 (m)	25.27 (s)	31.65 (w)

Note: Alphabets s, m and w represent strong, moderate and weak peaks, respectively.

The results of Table 2 give a strong impression on the complexity of the salt effect on thermal degradation behaviour of β-CD. In order to examine whether the salt effect is related to the decomposition products of β-CD, GC-TOF-MS measurements are performed in this study.

Decomposition products under vacuum

Data of TIC (see Table 3) from GC-TOF-MS show that the salt effect results in three outstanding features: (1) an extra release signal (R_1) occurring in the time range from 17.17 to 20.05 min, (2) an earlier main release signal (R_2) from 25.63 min in free β-CD to no more than 25.37 min and (3) a delayed release signal (R_3) from 27.23 min in free β-CD to no less than 31.49 min. This finding not only provides evidence for the earlier decomposition of β-CD upon adduct, but also reveals differences in decomposition routes between β-CD and its adducts.

Furthermore, a change in the decomposition route of β-CD before and after adduct is reflected by the difference in decomposition products in the light of the mass spectra at the same stages. Figures 4 and 5 illustrate the signals of two release stages (R_1 and R_2) in β-CD adducts of $NaNO_3$, Na_2CO_3 and Na_3PO_4.

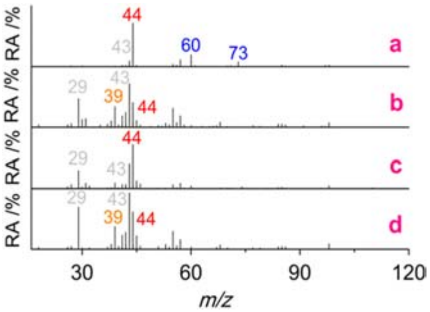

Figure 4. Mass spectra of (a) β-CD at 17.33 min and its adducts of (b) $NaNO_3$, (c) Na_2CO_3 and (d) Na_3PO_4 at R_1.

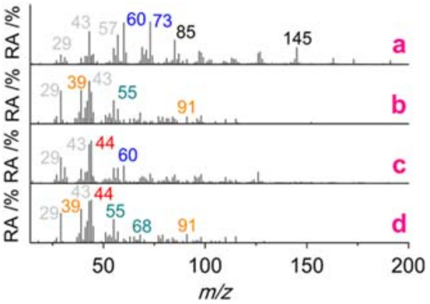

Figure 5. Mass spectra of (a) β-CD and its adducts of (b) $NaNO_3$, (c) Na_2CO_3 and (d) Na_3PO_4 at R_2.

As seen from Figure 4, more signals are present in these adducts than in free β-CD. Although all the four characteristic fragments at m/z 29.002 (CHO^+), 43.018 ($CHCH_2O^+$), 60.021 ($C_2H_4O_2^+$) and 73.027 ($C_2H_4CHO_2^+$) appear in the mass spectra, only smaller fragments such as m/z 29.002 and 43.018 occur in these adducts in a higher RA value and vice versa. These provide direct evidence for the salt effect on the decomposition products of β-CD. The difference of the salt effect also can be clearly seen from the comparison of decomposition products in this figure. For example, $C_3H_3^+$ at m/z 39.023, the smallest of a series of tropylium ions ($C_nH_n^+$), only can be observed in the adduct of β-CD with $NaNO_3$ and Na_3PO_4, as well as with Li_2CO_3 (*18*), in higher RA values.

Figure 5 shows that the main release process (R_2) of free β-CD produces some larger molecule ions such as m/z 85.028 ($C_4H_5O_2^+$) and 145.051 ($C_6H_9O_4^+$) in higher RA values, and the two fragments at m/z 60.021 and 73.027 give very strong signals in the case of free β-CD. However, the relative intensities of all the signals are weak or very weak in the adducts. It gives us a strong hint that the ions scattered in these adducts could affect the chemical bonds of β-CD, which also explains the reason why the salts could promote the decomposition of β-CD in air.

It should be noted that the release of CO_2^+ (m/z 43.989) means the cleavage of 1,4-glycosidic bonds of β-CD molecules (see the Supporting Information, available online). Therefore, the results shown in Figures 4 and 5 together present the dependence of the cleavage extent of 1,4-glycosidic bonds on the following factors: (1) heating time (e.g. Figures 4(a) and 5(a)) and (2) nature of inorganic salts adducted (e.g. $Na_2CO_3 > Na_3PO_4 > NaNO_3$ at R_1 and $Na_2CO_3 = Na_3PO_4 > NaNO_3$ at R_2). The quantitative response of these factors is also indicated in the case of the presence of several chlorides. Figure 6 illustrates mass spectra of NaCl–β-CD at several different release stages to trace the cleavage behaviour of 1,4-glycosidic bonds within an adducted β-CD during the whole decomposition process.

As shown in Figure 6(A), at the beginning of the decomposition (18.22 min), the rupture of C—C and C—O

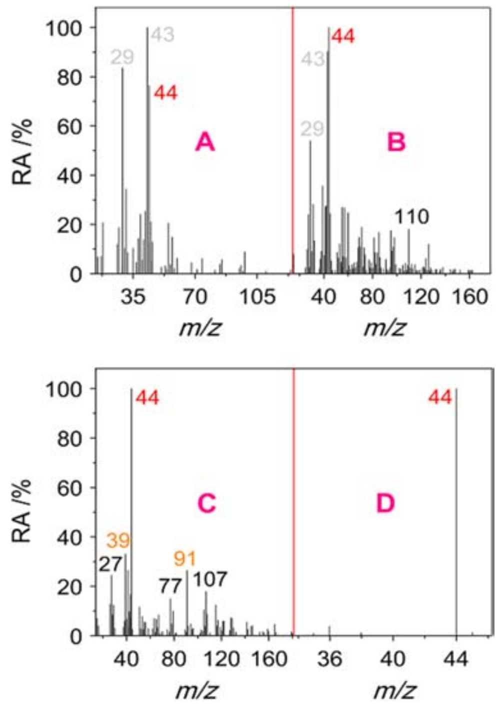

Figure 6. Mass spectra of NaCl–β-CD at (A) 18.22, (B) 25.24, (C) 31.64 and (D) 35.90 min.

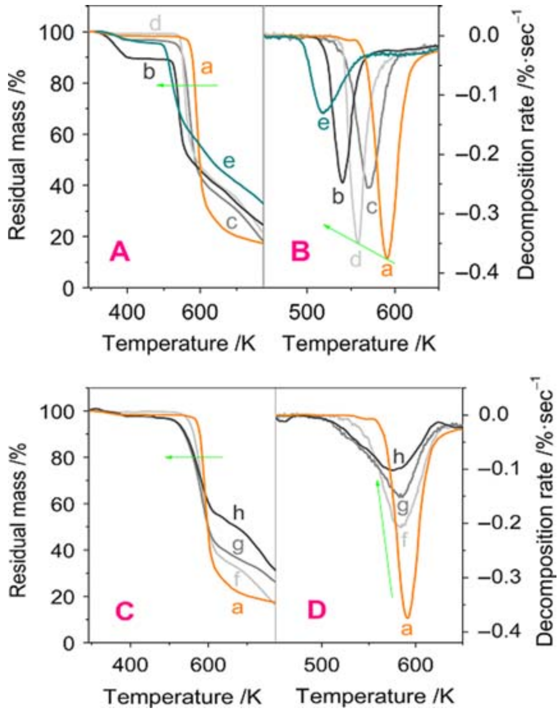

Figure 7. (A,C) TG and (B,D) DTG profiles of (a) β-CD and its adducts of (b) LiCl, (c) NaCl, (d) KCl, (e) $CaCl_2$, (f) $NaNO_3$, (g) Na_2CO_3 and (h) Na_3PO_4.

bonds in glucopyranose units of β-CD is in a dominant position, which produces CHO^+ and $CHCH_2O^+$. With the increase of heating time (at 25.24 and 31.64 min), 1,4-glycosidic bonds rupture more frequently than do C—C and C—O bonds (see Figure 6(B),(C)). Finally, at the end of decomposition (35.90 min, Figure 6(D)), there is only a strong signal at *m/z* 43.989, which is related to the CO_2^+ ion, indicating the thorough decomposition of β-CD.

Additionally, several peaks at *m/z* 27.023, 77.040 and 107.053, corresponding to $C_2H_3^+$, $C_6H_5^+$ and $C_7H_7O^+$, respectively, are clearly observed at 31.64 min, which also appear in other adducts except $CaCl_2$–β-CD. They are also present in the case of Li_2CO_3–β-CD (*18*), but are absent in the case of $NaAsO_2$–β-CD (*17*). The results suggest that molecule–ion interactions have a diverse effect on the decomposition of β-CD.

Two key phenomena occurring in the process of decomposition

TG/DTG measurements under nitrogen atmosphere reveal that the salt effects result in two key phenomena: an earlier decomposition and a weaker decomposition, occurring in the decomposition process of β-CD.

Initially, from Figure 7(A),(B), we note that the presence of the chlorides induces an earlier decomposition of β-CD in the light of the difference (ΔT_m) in the maximum decomposition temperature (T_m) between β-CD and its adducts. Actually, this phenomenon also occurs in the cases of $NaNO_3$, Na_2CO_3 and Na_3PO_4 (see Figure 7(C),(D)). The result provides direct evidence that the inorganic salts decrease the decomposition temperature of β-CD.

Next, an obvious decrease (ΔV_m) in the maximum decomposition rate (V_m) of β-CD upon adduct with the chlorides, especially, the sodium oxysalts is found from Figure 7(B),(D). In other words, the presence of the inorganic salts results in a diminution of the decomposition rate of β-CD.

In addition, there is also an apparent $\Delta\alpha$ values of β-CD between, before and after adduct at higher temperatures. Table 4 summarises the data of $\Delta\alpha$ at T_m (α_1) and 773.2 K (α_2). They are determined based on an

Table 4. Thermal decomposition parameters of the adducts of β-CD under TG/DTG conditions.

Samples	ΔT_m (K)	ΔV_m (% s^{-1})	$\Delta\alpha_1$ (%)	$\Delta\alpha_2$ (%)
LiCl–β-CD	−50.9	−0.127	−12.90	−8.46
NaCl–β-CD	−21.6	−0.119	−4.03	3.01
KCl–β-CD	−33.2	−0.026	−9.09	0.75
$CaCl_2$–β-CD	−73.1	−0.243	−20.05	−10.30
$NaNO_3$–β-CD	−7.7	−0.167	1.04	6.50
Na_2CO_3–β-CD	−8.8	−0.222	3.69	−2.58
Na_3PO_4–β-CD	−16.5	−0.271	−5.75	−4.68

evaluation of two factors: contents of crystal water and initial mass fractions of the salts in the samples. The water contents are calculated by TG curves.

On the basis of values of ΔT_m in Table 4, we find that the effect of the chlorides and the oxyacid salts on the T_m of β-CD decreases in the order: $CaCl_2 > LiCl > KCl > NaCl$ and $Na_3PO_4 > Na_2CO_3 > NaNO_3$, respectively. Interestingly, the decreasing orders caused by the salt effect are in good accordance with the decreasing orders of Λ_m of the salts induced by β-CD. This implies that there is a relation between the molecule–ion interaction in solution and the crystallisation of the interacting components from the solution. These results forcefully support the view that there is a relation between the stability of the adducts and the degree of molecule–ion interaction between β-CD and the ions, which could be approximately explained by the same orders of ionic potential of the cations and charges of the anions in the salts.

The data in Table 4, together with the results of molar conductivity and crystal structural measurements, indicate that the extent of the salt effect is dependent on the salt type (see Figure 8).

The fact that the effects of the chlorides and oxyacid salts are mainly reflected by the decreases of T_m and V_m values of β-CD, respectively, strongly suggests different contributions of cations and anions to the changes in the decomposition process of β-CD. In our opinion, the significant changes in the decomposition behaviour of β-CD can be explained as follows.

On the one hand, as seen from Figure 8(B), the H—O and C—O bonds of β-CD can be weakened because the occurrence of the cations (Li^+, Na^+, K^+ and Ca^{2+}) near the oxygen atoms will cause the deformation of the electron clouds of the oxygen atoms, leading to a decrease in electron density of the C—O and O—H bonds due to the charge transferred from the oxygen atoms to these cations. The weakening of these bonds may be responsible for the decrease in T_m of β-CD.

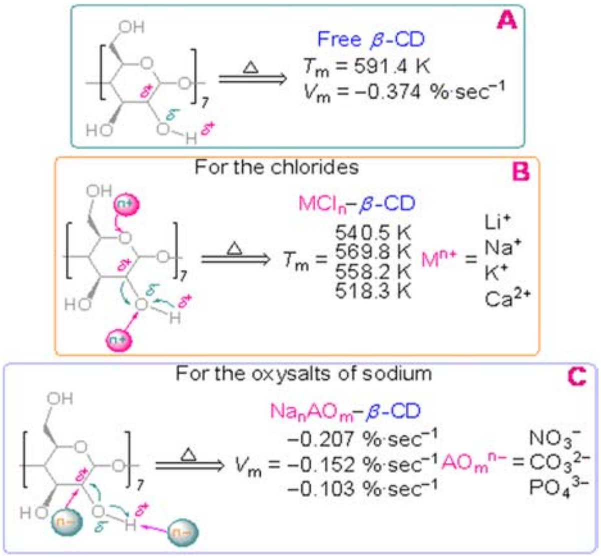

Figure 8. Proposed causes of decreases in T_m and V_m of β-CD in the presence of several chlorides and oxyacid salts, respectively.

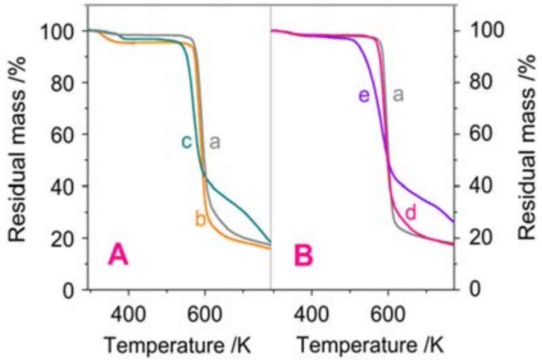

Figure 9. The TG curves of (A) (a) β-CD, (b) the physical mixture and the adduct of (c) NaCl and β-CD, and (B) (a) β-CD, (d) the physical mixture and (e) the adduct of Na_2CO_3 and β-CD.

On the other hand, as shown in Figure 8(C), the anions (NO_3^-, CO_3^{2-} and PO_4^{3-}) may prefer to act on the carbon and hydrogen atoms of β-CD, which increases the electron density of the C—H and C—C bonds. This will result in a more moderate decomposition of β-CD, in favour of the decrease of V_m of β-CD.

Such an explanation is supported by the observation in decomposition products of β-CD upon adduct with the salts based on mass spectra at the same heating temperatures. In a word, there are similarity and difference among the decomposition processes of the adducts, which relate to the universality and particularity of such an interaction between carbohydrates and inorganic salts.

Finally, we need to answer the following question: what is the difference between an adduct behaviour in aqueous solution and a physical mixing behaviour in solid state? The answer is summarised in Figure 9. Clearly, the TG curves of the mechanical mixtures are highly similar to that of free β-CD, but largely different from those of the adducts. This result demonstrates that an adduct behaviour generated by β-CD and the salts in solutions cannot be performed by a simple mechanical mixing behaviour.

Conclusions

In the present work, the molecule–ion interaction between β-CD and a series of inorganic salts and the degree of the interaction were detected in solution. The surface structure and stacking behaviour of β-CD upon adduct with the salts would produce observable changes. Also, such an interaction led to an important difference in decomposition degree, decomposition temperature and decomposition rate of β-CD before and after adduct. All of these reflected the importance of the salt effect. Furthermore, the similarity and difference of the salt effect on the decomposition behaviour of β-CD were found to be dependent on the salt type. A qualitative description based on the molecule–ion interaction was proposed to account for different contributions of cations and anions to the decreases of T_m and V_m values of β-CD. And the description was well supported by the nature of the decomposition fragments of β-CD upon adduct. We consider that the lower decomposition temperatures and the higher decomposition degrees of β-CD induced by inorganic salts could provide a new insight into the understanding of thermal degradation of carbohydrates.

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Supplementary Information

The details of (1) XRD patterns, (2) Heating programme in GC-TOF-MS experiments, (3) TIC curves and (4) mass spectra of the samples are available online.

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