

Dielectric relaxation of α -cyclodextrin–polyiodide complexes $(\alpha\text{-cyclodextrin})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-cyclodextrin})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$

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(Received 18 July 2001; revised version accepted 3 October 2001)

The frequency and temperature dependence of real (ϵ') and imaginary (ϵ'') parts of the dielectric constant of polycrystalline complexes $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$ ($\alpha\text{-CD} = \alpha\text{-cyclodextrin}$) has been investigated over the frequency and temperature ranges of 0–100 kHz and 120–300 K. The dielectric behaviour is described well by Debye type relaxation (α -dispersion). Both systems exhibit an additional Ω dispersion at low frequencies which is attributed to ionic conductance and is much greater in the case of Li due to the greater mobility of cations Li^+ . The temperature dependence of ϵ' reveals the existence of two kinds of water molecule in the case of the $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$ complex; these can be classified as tightly bound and easily movable water molecules that cause two steps in ϵ' versus T plots. In the case of the $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ complex the water molecules are tightly bound and as a result only one step is observed in these graphs. These findings are also confirmed from the ϵ''_{max} versus T plots, which exhibit the same number of steps with ϵ' , and from calorimetric measurements. The order–disorder transition or the transformation of normal hydrogen bonds to flip-flop type has been observed as a peak in ϵ'' versus T plots that is more intense and narrow in the case of Li and less high but more broad in Cd. The relaxation time varies in a \wedge -like curve (from 120 K to 240 K) and rises rapidly for temperatures greater than 240 K, indicating the existence of a new process involving the breaking of hydrogen bonds (normal or flip-flop type). The calculated values of activation energy ($0.35\text{--}0.62 k_{\text{B}}T_{\text{trans}}$) reveal the greater stability of the Li compared with the Cd complex. The starting value of $8.2\text{--}8.4 \mu\text{s}$ for τ is the same as observed in $\beta\text{-CD}$ complexes with guest 4-*t*-butylbenzyl alcohol (TERB). However, the activation energies of these are greater ($1.1\text{--}1.7 k_{\text{B}}T_{\text{trans}}$), indicating greater stability for $\beta\text{-CD}$ complexes.

1. Introduction

When α -cyclodextrin ($\alpha\text{-CD}$) is crystallized from aqueous solution with metal iodides, channel-type complexes are formed in which dimers of two $\alpha\text{-CD}$ molecules (head to head) are stacked like coins in a roll, and in the tubular cavity polyiodide chains are developed [1].

In the case of Li^+ the X-ray crystal structure [2] of the inclusion complex $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ has shown that in each $\alpha\text{-CD}$ dimer the polyiodide chain consists of five iodine atoms. Four of them, well ordered, form two I_2 units that are located within the cavities of the two $\alpha\text{-CD}$ molecules. The remaining iodine atom, located between the large sides of opposing $\alpha\text{-CD}$ molecules, is disordered in two positions with occupancies 69% and 31%. Each of the I_2 units binds to one of the two dis-

ordered iodine sites to form I_3^- anions and so each $\alpha\text{-CD}$ dimer accommodates two units $\text{I}_3^- \text{I}_2$ or $\text{I}_2 \text{I}_3^-$. Seven of the eight water molecules per dimer bridge (via hydrogen bonding) the O(6)H groups of adjacent dimers; the eighth can interact with the Li^+ cation that is located outside the $\alpha\text{-CD}$ channels and is coordinated to four hydroxyl groups O(2), O(3), O(2'), O(3') of $\alpha\text{-CD}$ molecules joined in the dimer.

In the case of Cd^{2+} the X-ray crystal structure [2] of the inclusion complex $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$ has shown that the situation is somewhat different. The $\alpha\text{-CD}$ molecules of the dimer are rotated relative to each other by 13° and are stabilized by the hydrogen bonds O(2)··O(2') and O(3)··O(3'). Direct hydrogen bonds O(6)··O(6') are developed between adjacent dimers, in contrast to the Li^+ complex where these hydrogen bonds are not direct but mediated by one or two water molecules O(6)·· H_2O ··O(6') and O(6)·· H_2O ·· H_2O ··O(6') in alternating sequence. As

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in Li^+ the four iodine atoms are well ordered but the fifth can be found in two statistically equivalent sites in the ratio 50/50, so that no discrete units I_3^- , I_2 can be found but instead a nearly linear I_5^- unit. Additionally, the 26 water molecules that correspond to this form are located inside the large spaces between the α -CD endless stacks. In contrast to the Li^+ complex, the Cd^{2+} cations are not in direct contact with the α -CD hydroxyls but are surrounded by hydration shells.

It has been shown that a transition temperature is exhibited when the flip-flop-type hydrogen bonds in β -CD \cdot 12H $_2$ O (according to Saenger *et al.* [3–5]) are transformed into the normal state. The transition temperature was indicated by a peak in the imaginary part of the dielectric constant ϵ'' and by a minimum in the phase shift component φ [6]. In the α -CD crystal structures [7–9] no flip-flop-type hydrogen bonds were observed, and this was confirmed by dielectric spectroscopy and by Raman spectroscopy [10]. Neither method reveals a transition temperature in any form of α -CD, in contrast to β -CD for which both methods reveal an order–disorder transition.

In the present work we investigate the dielectric properties of two α -cyclodextrin–polyiodide inclusion complexes, $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$, named Li and Cd, respectively, in the following text, over the frequency range 0–100 kHz and temperature range 120–300 K.

2. Experimental

α -CD, iodine, lithium iodide and cadmium iodide were purchased from Fluka Chemika. The procedure that follows took place in the preparation of both samples according to [2]. A few grams of α -cyclodextrin were dissolved in water at RT until the solution became almost saturated (<14.5 g per 100 ml). Then it was heated to 70°C for 20–25 min, after the addition of iodide salt and iodine in ratio 1.3/1, with a total iodine/iodide concentration of 5×10^{-2} M. The hot solution was filtered and left in a Dewar flask containing water at the same temperature. After 1 or 2 days, dark brown-black thin crystals, like needles, had grown. The water content of the two types of crystal was determined by the use of thermogravimetric analysis (TGA Instruments 2050, heating rate 10°C min $^{-1}$). The Li complex was found to contain 8 water molecules and the Cd complex 26 molecules. Thus, the general compositions are $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$. The dielectric measurements were taken using a low frequency (0–100 kHz) dynamic signal analyser (Hewlett-Packard 3561A), over the temperature range 120–300 K, that was connected to a PC for further processing of the data stored in the analyser. An analytical description of the

process is given in [6]. Finally, the differential scanning calorimetry method (Perkin Elmer DSC-4) was used, with a TADS system, for all calorimetric measurements.

3. Results

3.1. Temperature dependence of ϵ' , ϵ'' and phase shift

The temperature dependence of ϵ' and ϵ'' over the range 120–300 K at 200 Hz is shown in figures 1 and 2

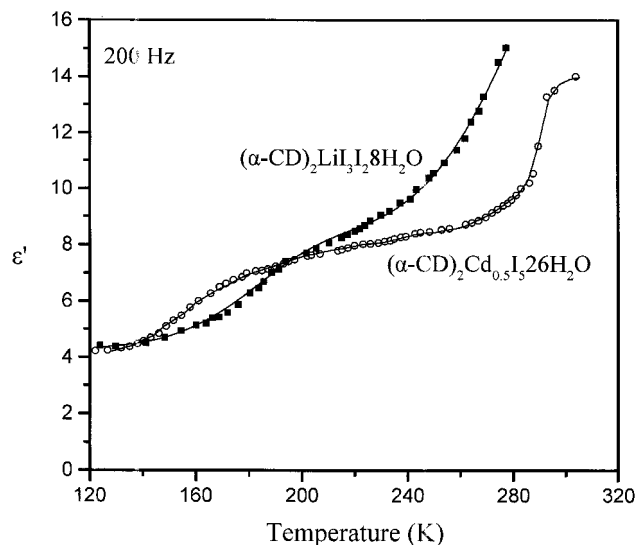


Figure 1. Temperature dependence of the real (ϵ') part of the dielectric constant of $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$ at 200 Hz.

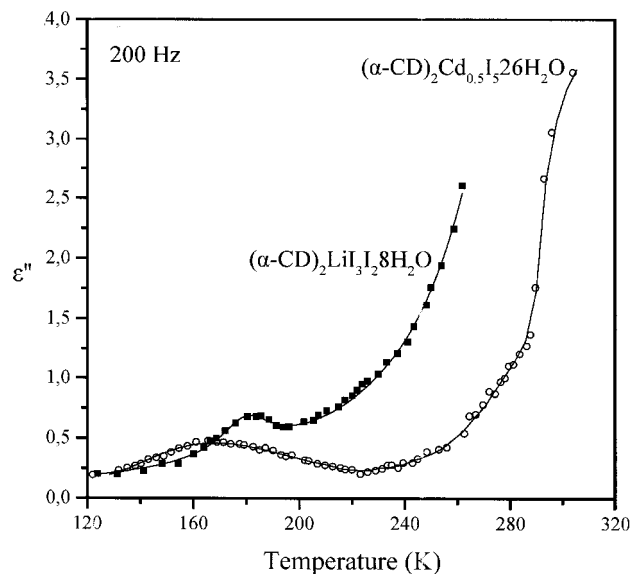


Figure 2. Temperature dependence of the imaginary (ϵ'') part of the dielectric constant of $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$ at 200 Hz.

for the two complexes $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$. The same qualitative picture is observed for the other, higher fixed frequencies over the range 100 Hz–100 kHz.

In the $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ complex ϵ' increases in a step-like form, from 4.41 at low temperatures to 8.46 at 220 K, with the inflection point observed at 180 K. Above 240 K, ϵ' increases more rapidly almost in an exponential way, so that $\epsilon' = 15.02$ at 277 K and $\epsilon' = 35.10$ at 302.5 K. The variation in dielectric loss ϵ'' with temperature gives a bell-shape curve with a maximum value 0.68 at 180 K, and the values around this point are narrowly distributed with a half-width of ~ 30 K. For higher temperatures $T > 240$ K the ϵ'' values increase rapidly, so that $\epsilon'' = 2.59$ at 262.1 K and $\epsilon'' = 54$ at 302.5 K.

In the $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$ complex ϵ' increases with temperature in a double-step fashion from 4.21 at low temperatures to 8.44 at 250.4 K and then to 13.98 at 305.6 K. The inflection point of the first step is at 165 K and that of the second step is located at 290 K. The ϵ'' versus T curve is a broad-bell shape with maximum value $\epsilon'' = 0.50$ at temperature 165 K, which coincides with the inflection point of the first step, and a half-width of ~ 50 K. For higher temperatures $T > 240$ K, ϵ'' increases rapidly so that $\epsilon'' = 3.5$ at 300 K.

The ϵ''_{max} value of the loss peak of the Li complex increases with temperature in a single sigmoid shape as in figure 3, from 2.22 at 123 K to 4.07 at 241.1 K and then increases to 5.59 at 279.4 K. In the case of the complex with Cd, a plot of ϵ''_{max} versus T exhibits a

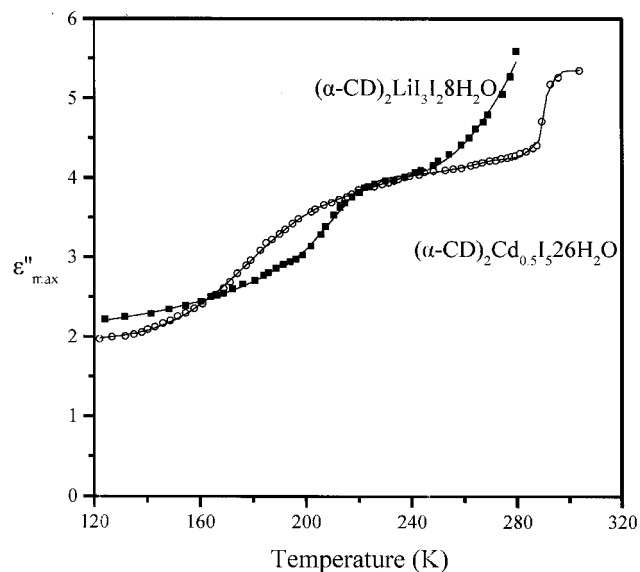


Figure 3. Plot of ϵ''_{max} versus temperature for $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$ at frequency 200 Hz.

double-step character, the first step from 1.99 at 122 K to 4.02 at 240 K and the second step to 5.34 at 304.1 K, with an inflection point at 290.0 K.

The phase shift φ of $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ at a fixed frequency of 200 Hz (figure 4) over the range 120–300 K, drops from 88.5° at 124 K to 84.1° at 180.5 K; then it increases to 85.1° at 201.7 K and decreases rapidly to 75.8° at 264.1 K. The transition temperature shifts to higher and φ_{min} to lower values as the frequency is increased. Similarly, the plots of phase shift versus T for the $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$ complex behave the same way, and the value of T for the minimum of φ is 165 K ($\varphi_{\text{min}} = 85.24^\circ$) at a fixed frequency of 200 Hz. Finally, for both samples ϵ' and ϵ'' showed thermal hysteresis during a cooling–heating cycle, for all fixed frequencies examined. Representative results are shown in figures 5 and 6 for the $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ inclusion complex.

3.2. Relaxation time

The relaxation time ($\tau = 1/2\pi f_{\text{max}}$) of the Li complex is 8.39 μs at 124.0 K and by increasing the temperature reaches a maximum of 9.49 μs at the transition temperature $T_{\text{trans}} = 205.6$ K; then it drops to 8.97 μs at 239.9 K, see figure 7. For higher temperatures $T > 240$ K the relaxation time increases rapidly with temperature to 10.58 μs at 276.7 K. Similar behaviour is observed for the Cd complex; τ starts at 8.17 μs at 121.2 K and increases with temperature to the maximum, 9.36 μs , $T_{\text{trans}} = 182.7$ K, then decreases to 8.32 μs at 256.0 K and increases again to 8.99 at 304.1 K. The deviations

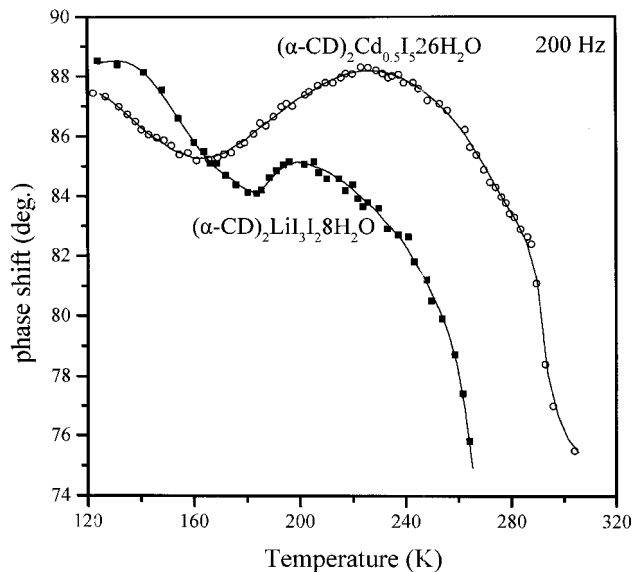


Figure 4. Temperature dependence of the phase shift for $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$ at 200 Hz.

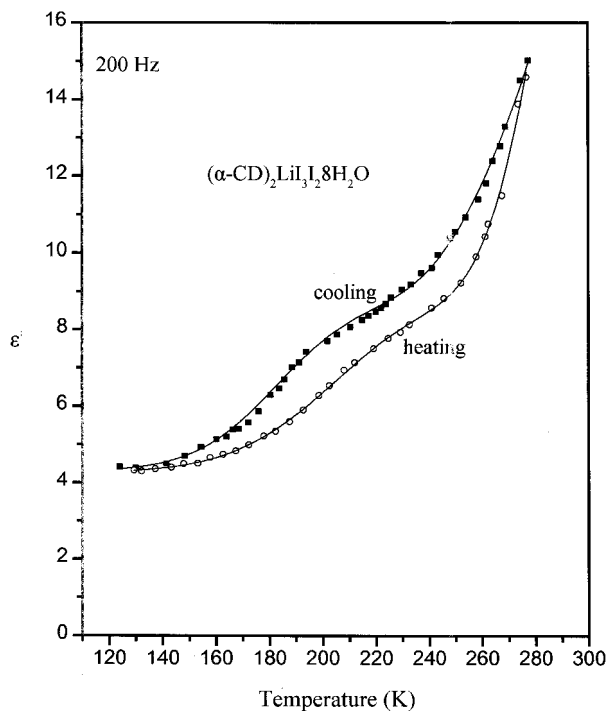


Figure 5. Thermal hysteresis of the real (ϵ') part of the dielectric constant of $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ at 200 Hz.

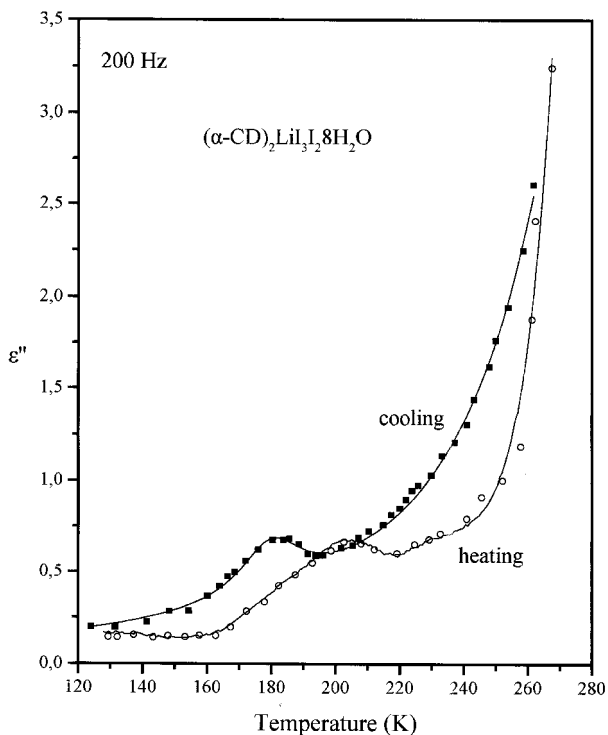


Figure 6. Thermal hysteresis of the imaginary (ϵ'') part of the dielectric constant of $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ at 200 Hz.

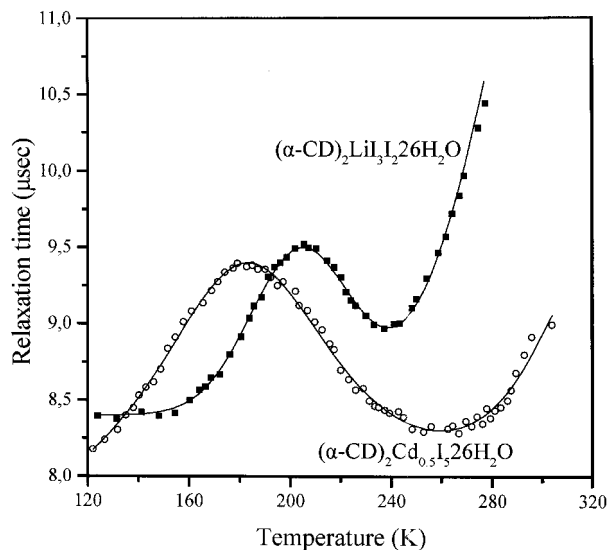


Figure 7. Relaxation time versus temperature for $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 26\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$.

in the values of both curves are very great at high temperatures $T > 240$ K, starting from $0.50 \mu\text{s}$ up to $2.05 \mu\text{s}$.

3.3. Calorimetric measurements

The DSC trace of $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ (figure 8), with scan rate 10 deg min^{-1} , shows one distinct endothermic peak with onset temperature 105°C over a temperature range of 35 K, while this peak for $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$ (figure 9), with scan rate

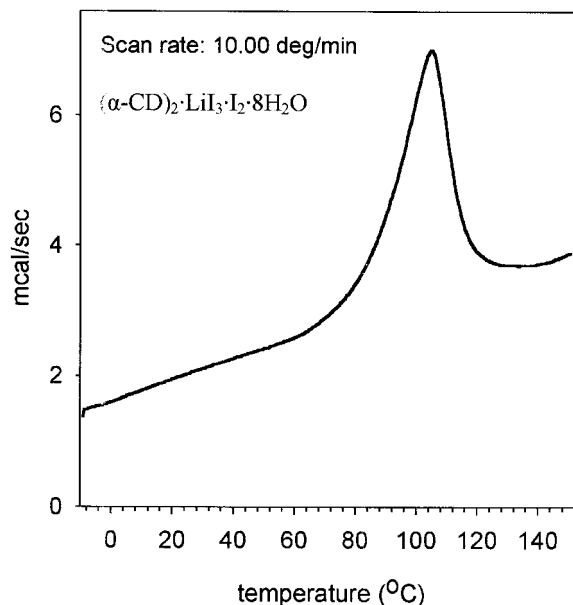


Figure 8. DSC thermogram of $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$; the heating rate 10 deg min^{-1} .

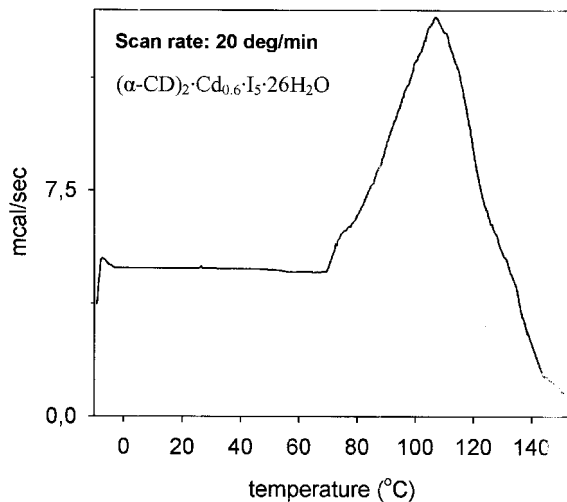


Figure 9. DSC thermogram of $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$; the heating rate 20 deg min^{-1} .

20 deg min^{-1} , is not so distinct, having many shoulders and extending over a range of 70 K that is twice the 35 K range of Li.

4. Discussion

It is already known [7–9] that ‘empty’ $\alpha\text{-CD} \cdot 6\text{H}_2\text{O}$ molecules are in a collapsed state because two of the six hydrogen bonds are broken and no flip-flop hydrogen bonds occur. In a previous paper [10], we confirmed this finding, since ‘empty’ $\alpha\text{-CD}$ did not show any order–disorder transition. By contrast, both samples examined in the present article exhibit such a transition.

The plots of dielectric loss and phase shift versus temperature show a maximum and a minimum, respectively, because of the transformation of the normal hydrogen bonds to flip-flop ones, in both samples. The height (or the depth) of these peaks is greater for Li, but the half-width is greater for Cd. This suggests that the transition between the two states is more rapid in the case of Li, taking place over the short range $\Delta T = 40 \text{ K}$ at 200 Hz; on the other hand, this process is much slower for the Cd complex. These findings can be explained if we consider the different nature and connections of the water molecules that participate in the two structures: in the Li complex the eight water molecules per dimer are located between adjacent dimers and bridge via hydrogen bonding the O(6) hydroxyl groups at the narrow sides of the $\alpha\text{-CD}$ molecules. All the eight water molecules seem to occupy equivalent positions, and therefore are activated almost at the same temperature. By contrast, the 26 water molecules of Cd are located in the large interstices between the infinite

stacks of $\alpha\text{-CD}$ dimers. Some of them are in general less tightly bound than the water molecules in Li. Furthermore some others are bonded to $\alpha\text{-CD}$ hydroxyl groups or form two different hydration shells surrounding the Cd sites. Since these water molecules do not occupy equivalent positions and have different surroundings, they do not have the same energies; consequently, each molecule or group of equivalent molecules is activated at a different temperature. Therefore, the order–disorder transition of water molecules and $\alpha\text{-CD}$ hydroxyl groups in the case of Cd occurs over a wide temperature range (125–225 K at 200 Hz). The ϵ' versus T plots of the Cd complex exhibit two steps while those of the Li complex exhibit only one. The second step at high temperatures ($\sim 290 \text{ K}$) corresponds to the remaining water molecules (of the total of 26) that may move easily in contrast to those that are more tightly bound and cause the first step at low temperature (125–225 K). The latter are entirely responsible for the above-mentioned peak in ϵ'' versus T plots, i.e. the order–disorder transition, as the easily movable water molecules do not contribute to this transition and are activated only at high temperatures, associated with proton conductance (Ω dispersion). By contrast, in the case of the Li complex the water molecules cannot be separated but are tightly bound and movable and there is only a single step.

The abrupt increase in ϵ'' at 200 Hz above 240 K, which reaches the value of 54 at 302.5 K, is due to the large ionic conductance, which is unusual for inclusion complexes of cyclodextrins and cannot be attributed only to the movement of the H^+ and OH^- ions. The ionic conductance is attributed mainly to the activation and movement of the metallic cations, and is inversely proportional to their mass. On the other hand, the corresponding value $\epsilon'' = 3.58$ of the Cd complex at 200 Hz ($T = 305.6 \text{ K}$) suggests that the ionic conductance of Cd^{2+} ions is small relative to Li^+ ions because of their large mass, and the water molecules not incorporated in the $\alpha\text{-CD}$ dimer stacks play a less important role. This aspect is in agreement with the results on other $\alpha\text{-CD}$ complexes with Ba^{2+} and K^+ ions [11].

The plots of ϵ''_{max} versus T confirm the hypothesis that there are two kinds of water molecule in Cd because ϵ''_{max} exhibits a double step: the first occurs at 185 K (inflection point) due to the strongly bound molecules, and the second has an inflection point at 290 K as a result of the less tightly bound molecules. The Li complex shows only one step, whose inflection point is located at 205 K.

The calorimetric measurements (figures 8 and 9) also are in agreement with the fact that there are two kinds of water molecule in Cd and only one in Li. Heating of the samples with various scan rates gives a distinct peak

for Li, which is associated with loss of water, over a temperature range of 35 K, while this peak for Cd is not so distinct, having many shoulders and extending over a range of 70 K, i.e. double the 35 K range of Li.

The thermal hysteresis (figures 5 and 6) that appears in both samples is a result of hydrogen bond transformation from flip-flop to normal type. Therefore it appears in a temperature range around the transition temperature. The area bounded by the two curves ε'' (cooling–heating), i.e. the area of hysteresis loop, is equal to the energy dissipated within the material. Thermal hysteresis of this type makes these materials valuable as thermal absorbers for the appropriate temperature range.

The relaxation time τ versus temperature plot is sharply peaked from 120 K to 240 K and then presents a new rising segment for temperatures higher than 240 K in both samples. In the Li complex τ is 8.39 μs at 124 K and 9.49 μs at 205.6 K (maximum of the peak). Then it decreases to 8.97 μs at 240 K, similar to that found for other complexes [6], but above this temperature τ increases up to 10.58 μs at 276.7 K, behaviour not observed previously. The same behaviour is also displayed by the Cd complex: τ has the value of 8.17 μs at 121.2 K, 9.36 μs at 184 K (maximum), which is the transition temperature, 8.3 μs at 260 K, and finally increases to 9.0 μs at 300 K. Use of the Arrhenius equation $\tau = \tau_0 \exp(-E/RT)$ gives the activation energies on both sides of the transition temperature. These energy values and the corresponding temperatures are listed for both samples in table 1.

These activation energies have small absolute values in the range 0.35–0.62 $k_{\text{B}}T_{\text{trans}}$, where k_{B} is the Boltzmann constant, and correspond to the heights of the intrinsic barriers shown in [10], figure 12. The negative activation energy suggests that the activation processes involve the breaking of hydrogen bonds and the formation of more stable bonds, and indicates the greater stability of the Li complex against the Cd one. This can be understood if we consider the structure of the two complexes. In Li all the water molecules are accommodated between adjacent dimers, bridging them via a number of hydrogen bonds that form an extensive net

which stabilizes the complex. Furthermore, many hydrogen bonds participate in the bridging of the two α -CD molecules that constitute a dimer, since the two α -CD molecules are eclipsed relative to each other and the number of bonds created is a maximum. On the other hand, the staggered orientation of the α -CD molecules of the dimer in Cd prohibits the existence of some of these bonds; additionally the 26 water molecules located outside the dimer stacks do not participate in the bridging of the dimers and, as a consequence, the stabilization of the complex is lower than in Li. The temperatures of the above order–disorder transitions are higher for the Li than for the Cd samples, which is expected since a large number of less tightly bonded water molecules in the Cd samples facilitates reorientation of hydrogen bonding.

The new increase in relaxation time τ for temperatures above 250–260 K exhibits a second activation process involving (i) the breaking of hydrogen bonds (normal or flip-flop type) and (ii) the release of metal cations and hydroxyl groups that help give rise to ionic conductance. This process needs to be investigated furthermore.

5. Conclusions

Debye's equations provide a sufficient description of the dielectric properties of the two complexes under study. The temperature dependence of ε' reveals the existence of two kinds of water molecule in the case of the $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$ complex, and these may be classified as tightly bound and easily movable water molecules that cause two steps in ε' versus T plots. The first step at low temperatures has been attributed to the strongly bound water, while the second step is caused by the less tightly bound water molecules. By contrast, in the case of the $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ complex such a distinction cannot be made, since the eight water molecules are tightly bound, occupying almost equivalent positions bridging hydroxyl groups of adjacent α -CD dimers. As a result only one step is observed in these graphs. These findings are confirmed by the $\varepsilon''_{\text{max}}$ versus T plots, which exhibit the same number of steps with ε' , and from calorimetric measurements. The order–disorder transition or, according to Saenger [3–5], ordering of the flip-flop hydrogen bonds, has been observed as a loss peak in ε'' versus T plots, with the difference more intense and narrow in the case of Li and less high but more broad in Cd. This is caused by the above-mentioned equivalent energies of dipoles in Li and the dispersion of energies in Cd. In the latter, only the tightly bound water molecules contribute to the transition. The easily movable water molecules (second step in the ε' versus T plots) contribute only to ionic conductance, which is much

Table 1. Activation energies (in kJ mol^{-1}) for the Li and Cd complexes.

	T_{trans}	$E(T < T_{\text{trans}})$	$E(T > T_{\text{trans}})$
Li	205.6 K	0.95	–1.05
Cd	182.7 K	0.54	–0.88

greater in the case of Li due to the greater mobility of cations Li^+ . The relaxation time varies in a \wedge -like curve and rises rapidly for temperatures greater than 240 K, indicating the existence of a new process involving the breaking of the hydrogen bonds (normal or flip-flop type). The calculated values of the activation energy ($0.35\text{--}0.62 k_{\text{B}}T_{\text{trans}}$) reveal the greater stability of the Li compared with the Cd complex. The starting value of $8.2\text{--}8.4\ \mu\text{s}$ for τ is the same as observed in β -CD complexes with guest 4-t-butylbenzyl alcohol [6]. However, the activation energies of these are greater ($1.1\text{--}1.7 k_{\text{B}}T_{\text{trans}}$), indicating greater stability compared with the α -CD complexes discussed here. The thermal hysteresis that appears in both samples is a result of hydrogen bond transformation from flip-flop to normal type.

This work was partly supported by Grant No. 70/4/3347 SARG, NKUA.

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