

Dielectric relaxation of α -cyclodextrin–polyiodide complexes (α -cyclodextrin) $_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and (α -cyclodextrin) $_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$

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The frequency and temperature dependence of the real (ϵ') and imaginary (ϵ'') parts of the dielectric constant of the polycrystalline complexes (α -CD) $_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and (α -CD) $_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ (α -CD = α -cyclodextrin) have been investigated over the frequency and temperature ranges 0–100 kHz and 120–300 K, respectively. The temperature dependences of ϵ' , ϵ'' and the phase shift φ show two steps, two peaks and two minima, respectively, revealing the existence of two kinds of water molecule, the tightly bound and the easily movable water molecules, in both complexes. The first peak of $\epsilon''(T)$ or the first minimum of $\varphi(T)$ presents the transformation of flip-flop hydrogen bonds to the normal state. The second $\epsilon''(T)$ peak or $\varphi(T)$ minimum corresponds to the easily movable water molecules or to a partial transformation of tightly bound to easily movable water molecules. For $T > 270$ K both samples show semiconductive behaviour with energy gaps of 1.84 eV for the (α -CD) $_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ complex and 1.36 eV for the (α -CD) $_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ complex. The conductivity at room temperature decreases in the order: (α -CD) $_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O} > (\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O} > (\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O} > (\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$. The relaxation time varies in a Λ -like curve (from 120 to 250 K) and rises rapidly for temperatures greater than 250 K, indicating the process of ionic movements. The activation energies around the transition temperature $0.98\text{--}1.09 k_{\text{B}} T_{\text{trans}}$ for (α -CD) $_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $1.06\text{--}1.55 k_{\text{B}} T_{\text{trans}}$ for (α -CD) $_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ reveal the greater stability of the α -K complex against that of the α -Ba complex.

1. Introduction

When metal iodides (M^+I^-) are added to an aqueous solution of α -cyclodextrin (α -CD), channel-type complexes with polyiodide chains of disordered I_3^- and I_2 units are formed [1]. In a previous paper we investigated the dielectric relaxation properties of two α -cyclodextrin–polyiodide complexes with lithium and cadmium metals, (α -CD) $_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and (α -CD) $_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$ [2]. The temperature dependences of their dielectric constants (real part ϵ' and imaginary part ϵ'') reveal the existence of two kinds of water molecule (tightly bound and easily movable) in the case of the α -Cd complex, and only one kind of water molecule (tightly bound) in the case of the α -Li complex. Both systems also show the order–disorder transition that according to Saenger *et al.* [3–5] is caused by the transformation of flip-flop hydrogen bonds to 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 [2, 6–8].

In the present work we investigate the dielectric properties of two more α -cyclodextrin polyiodide inclusion complexes, (α -cyclodextrin) $_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and (α -cyclodextrin) $_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$, named α -Ba and α -K, respectively, in the following, over the frequency range 0–100 kHz and temperature range 120–300 K.

2. Experimental

α -cyclodextrin, iodine, barium iodide and potassium iodide were purchased from Fluka Chemica. The preparation of both samples was done according to [9]. A few grams of α -cyclodextrin were dissolved in water at room temperature until the solution became almost saturated ($< 14.5 \text{ g}(100 \text{ ml})^{-1}$). Then the solution was heated to 70°C for 20–25 min, after the addition of iodide salt and iodine in the ratio 1.3:1, with total iodine/iodide concentration being $5 \times 10^{-2} \text{ M}$. The hot solution was filtered and left in a Dewar flask containing water at the same temperature. After one or two days, bronze rectangular thin crystals were grown in

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the case of Ba metal and dark-black thin crystals in the case of K metal. The water content of the crystals was determined by the use of thermogravimetric analysis (TGA Instruments 2050, heating rate $10^{\circ}\text{C min}^{-1}$). The α -Ba and α -K complexes were found to contain eight water molecules each. So, the general compositions are $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$.

The dielectric measurements were taken using a low-frequency (0–100 kHz) dynamic signal analyser (DSA-Hewlett-Packard 3561A), at the temperature range 120–300 K, which was connected to a PC for further processing of the data stored in the analyser. An analytical description of the process is given in a previous article [6]. Finally, the differential scanning calorimetry (DSC) method (Perkin Elmer DSC-4 instrument) was used with a thermal analysis data station (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 frequency 200 Hz is shown in figures 1 and 2 for both complexes $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$.

In the $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ complex ϵ' increases in a double sigmoid fashion from 5.0 at low temperatures $T < 160$ K to 10.0 at 190 K and then to 20 at temperature 250 K. The inflection point of the first sigmoid is observed at 170 K ($\epsilon' = 7.9$) and that of the second sigmoid at 240 K ($\epsilon' = 19.5$). Above 270 K, ϵ'

increases more rapidly, so that $\epsilon' = 32$ at 278 K and $\epsilon' = 93$ at 297 K. The variation in dielectric loss ϵ'' with temperature gives a double-bell-shaped curve with peak values $\epsilon'' = 1.5$ observed at 172 K and $\epsilon'' = 3.9$ at 243 K. For $T > 260$ K ϵ'' increases rapidly so that at 275 K $\epsilon'' = 10.3$ and at 297 K $\epsilon'' = 126$. By increasing the frequency of the applied field to 1 kHz, both sigmoid curves in the ϵ' versus T plot and the corresponding bell-shaped curves in the ϵ'' versus T plot are distinguished with the inflection points shifted to 180 K for the first and 250 K for the second. For higher applied frequencies (10–100 kHz) the second sigmoid of the plot of ϵ' versus T and the corresponding bell-shaped curve of ϵ'' versus T are absent.

In the case of the $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ complex, the temperature dependence of ϵ' and ϵ'' is similar to that of the $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ complex. The ϵ' values increase in double-step fashion from 4.2 at low temperatures $T < 150$ K to 9.0 at 200 K and then to 15.0 at temperature 261 K. The inflection point of the first step is at 175 K and that of the second step is at 233 K. Above 265 K ϵ' increases rapidly in an exponential way, so that at temperature 290 K the value of ϵ' is 19.0 and at 303 K $\epsilon' = 25.0$. The ϵ'' versus T plot shows, as before, a double-bell-shaped curve with peak values 1.1 and 2.0 located at temperatures 178 K and 235 K, respectively, which coincide with the corresponding temperatures of inflection points in the ϵ' versus T plots. Above the temperature 260 K, ϵ'' increases rapidly with increasing temperature so that at 290 K $\epsilon'' = 4.3$ and 303 K

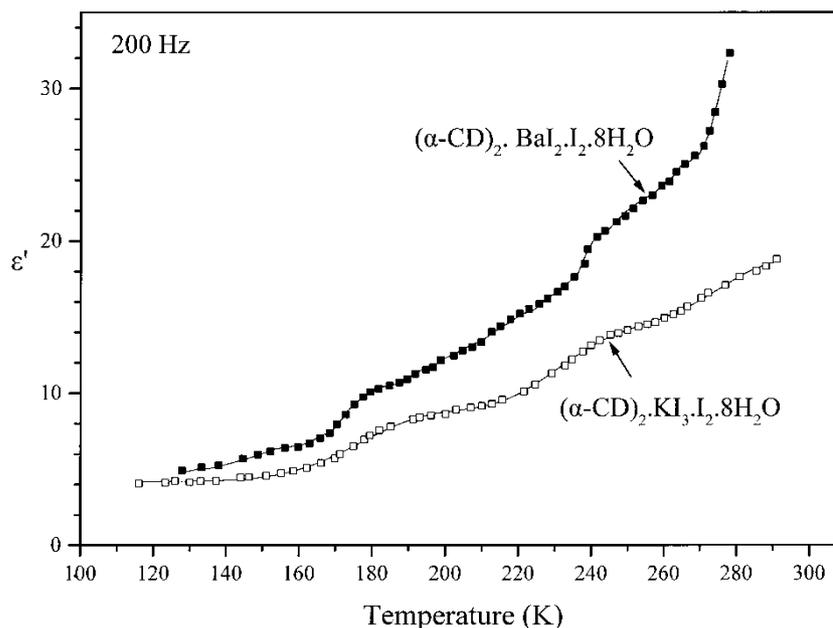


Figure 1. Temperature dependence of real (ϵ') part of the dielectric constant of $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ at frequency 200 Hz.

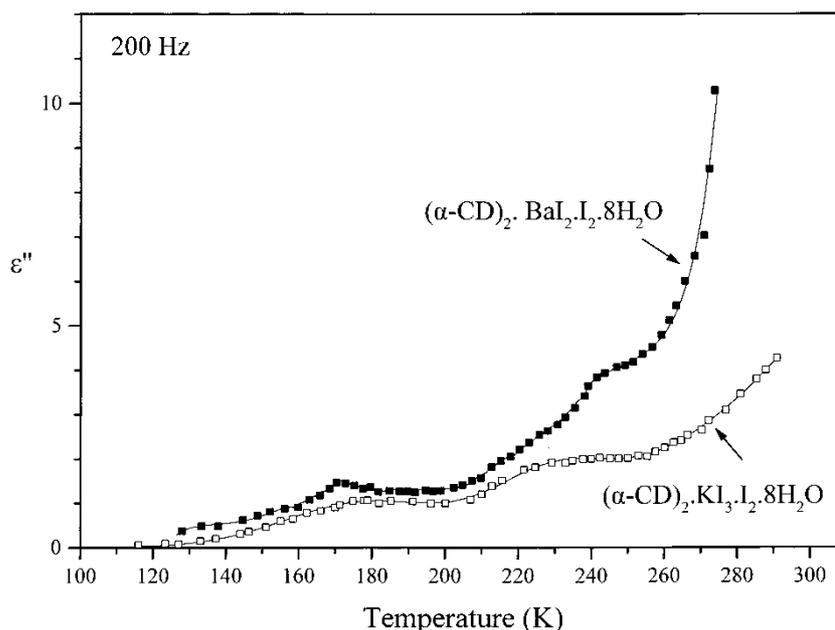


Figure 2. Temperature dependence of imaginary (ϵ'') part of the dielectric constant of $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ at frequency 200 Hz.

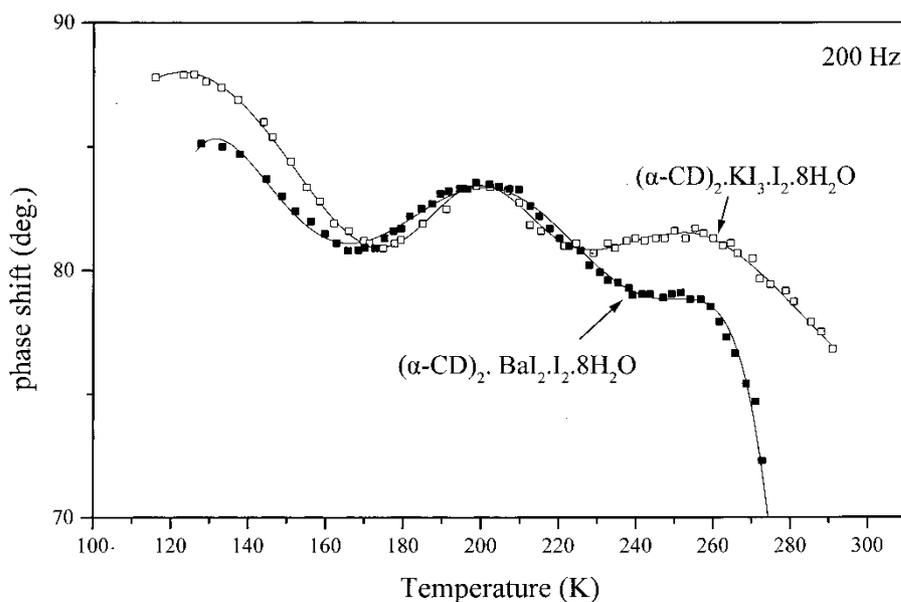


Figure 3. Temperature dependence of phase shift for $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ at frequency 200 Hz.

$\epsilon'' = 17.5$. By increasing the frequency of the applied field to 1 kHz, the second sigmoid of the ϵ' versus T plot and the corresponding bell-shaped curve of the ϵ'' versus T plot are absent. Only the first sigmoid still remains, with the inflection point shifted to the higher temperature of 185 K. The same qualitative picture is observed for the other, higher fixed frequencies in the range 10–100 kHz.

The phase shift φ of $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ at a fixed frequency of 200 Hz (figure 3) over the range 120–300 K, presents two minimum values, specifically it drops from 85.0° at 130 K to a minimum value of 80.8° at 168 K; it then increases to 84.0° at 200 K and decreases to a second minimum value of 79.0° at 242 K; it then increases again to 80.5° at 260 K and decreases rapidly to 58° at 280 K or 35° at 297 K. The same picture is observed for a fixed

frequency of 1 kHz with the φ minimum values 76.5° and 74.0° located at shifted temperatures 180 K and 255 K, respectively. At higher fixed frequencies it is observed that the first minimum is shifted to higher temperatures but the second minimum is not distinguished. Similarly, the plots of phase shift versus T for the $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ complex behave in the same way and the values of T for the two minima of φ are 175 K ($\varphi_{\min} = 81.0^\circ$) and 225 K ($\varphi_{\min} = 80.5^\circ$) at a fixed frequency of 200 Hz. For a fixed frequency of 1 kHz the first minimum is located at 185 K ($\varphi_{\min} = 78.5^\circ$) and the second at 250 K ($\varphi_{\min} = 77.5^\circ$). For higher fixed frequencies, as in the case of the $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ complex, only the first minimum remains, shifted to higher temperatures, and the second one disappears.

3.2. Temperature dependence of conductivity

The variation with temperature of ac conductivity ($\ln \sigma$ versus $1/T$) of the $\alpha\text{-K}$ complex at 200 Hz is shown in figure 4 during the cooling and heating process. This plot shows two sigmoid curves (a) and (b) at the temperatures $4.75 \text{ K}^{-1} < 10^3/T$ and $3.5 \text{ K}^{-1} < 10^3/T < 4.75 \text{ K}^{-1}$, respectively, and a linear part (c) at temperatures $10^3/T < 3.5 \text{ K}^{-1}$. Similar results are found for the $\alpha\text{-Ba}$ complex (figure 5). Both samples show thermal hysteresis for fixed frequency 200 Hz.

3.3. Relaxation time

The relaxation time ($\tau = \frac{1}{2\pi f_{\max}}$) of the $\alpha\text{-Ba}$ complex is $9.0 \mu\text{s}$ at 125 K and on increasing the

temperature reaches a maximum of $11.5 \mu\text{s}$ at the transition temperature $T_{\text{trans}} = 187.6 \text{ K}$; it then drops to $10.0 \mu\text{s}$ at 230 K (figure 6). For higher temperatures $T > 240 \text{ K}$ the relaxation time increases rapidly with increasing temperature to $13.5 \mu\text{s}$ at 278 K. Similar behaviour is observed for the $\alpha\text{-K}$ complex; τ starts at $8.4 \mu\text{s}$ at 115 K and increases with increasing temperature to the maximum, $11.0 \mu\text{s}$ $T_{\text{trans}} = 202.5 \text{ K}$, then decreases to $9.5 \mu\text{s}$ at 240 K and increases again to $11.6 \mu\text{s}$ at 302 K.

3.4. Calorimetric measurements

The DSC trace of $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ (figure 7), with scan rate 10 deg min^{-1} , shows two distinct endothermic peaks with onset temperatures 102 K and 120 K over a temperature range of 70 K, while in the case of $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ (figure 8) the DSC trace, with scan rate 20 deg min^{-1} , shows one slab endothermic peak at 120 K extending over a range of 55 K.

4. Discussion

The main dielectric characteristics of $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ are the following: in both complexes the ϵ' versus T plots show two steps, the ϵ'' versus T plots exhibit two loss peaks and the φ versus T plots show two minima. The same behaviour was found previously for the complex $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$ [2]. The first step at low temperatures has been attributed to the strongly bound water, the second step to the less tightly bound

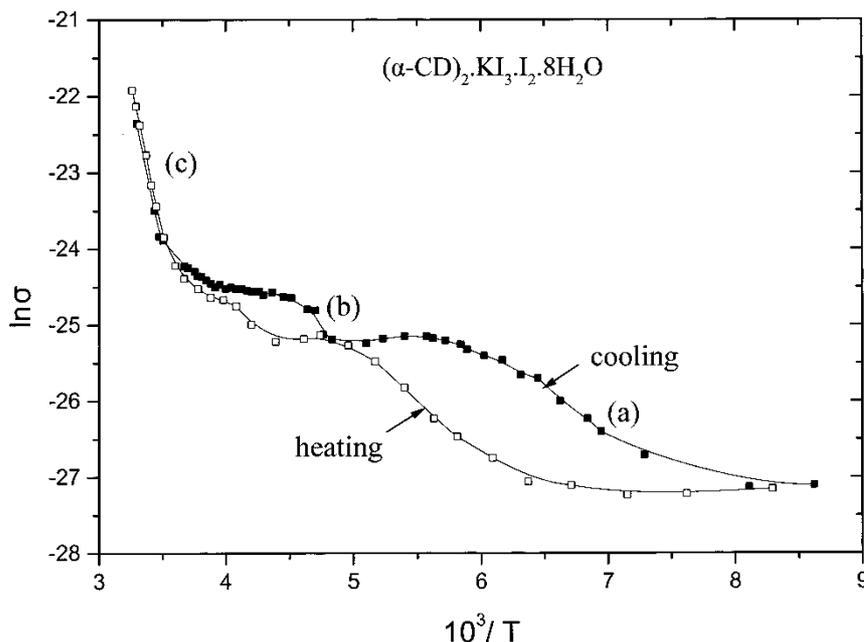


Figure 4. Temperature dependence of ac conductivity ($\ln \sigma$ versus $1/T$) for the complex $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ at frequency 200 Hz.

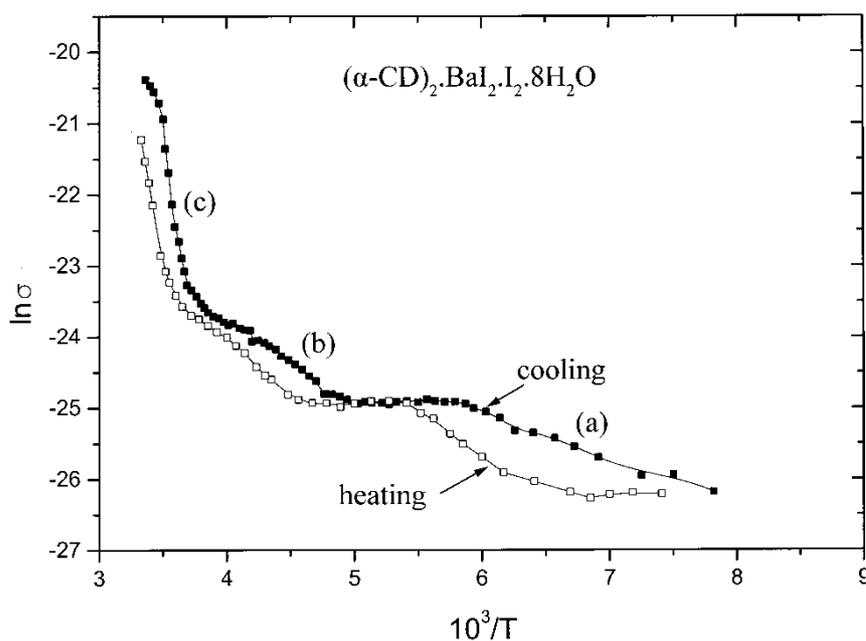


Figure 5. Temperature dependence of ac conductivity ($\ln \sigma$ versus $1/T$) for the complex $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ at frequency 200 Hz.

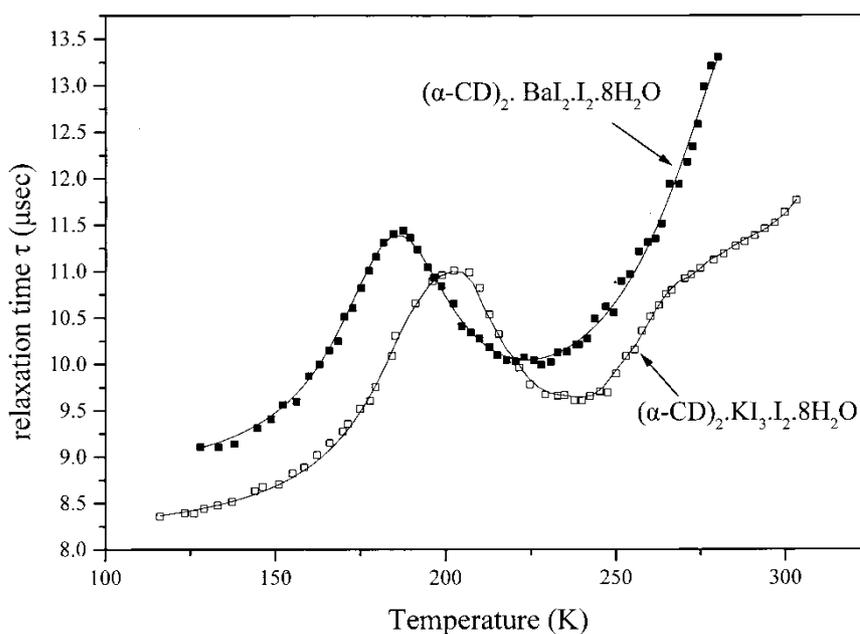
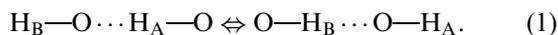


Figure 6. Relaxation time (τ) against temperature for $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$.

(easily movable) water molecules. Both systems exhibit the already known order-disorder transition that is caused by the transformation of the normal hydrogen bonds to flip-flop bonds, according to the scheme [4, 5]:



This transition is shown as the first peak in the plots of ϵ'' versus T and as the first minimum in the plots of φ versus T in the temperature region 160–170 K. The second peak of $\epsilon''(T)$ or the second minimum of $\varphi(T)$ in the temperature region 220–240 K is related to the easily movable water molecules. The transformation of some bound water molecules to easily movable water

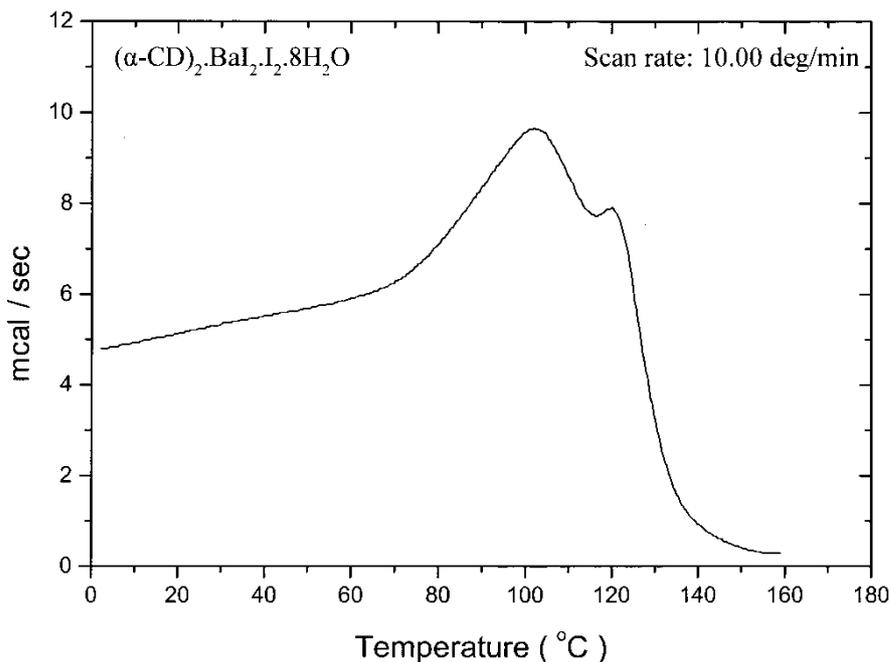


Figure 7. DSC thermogram of $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$: the heating rate was 10 deg min^{-1} .

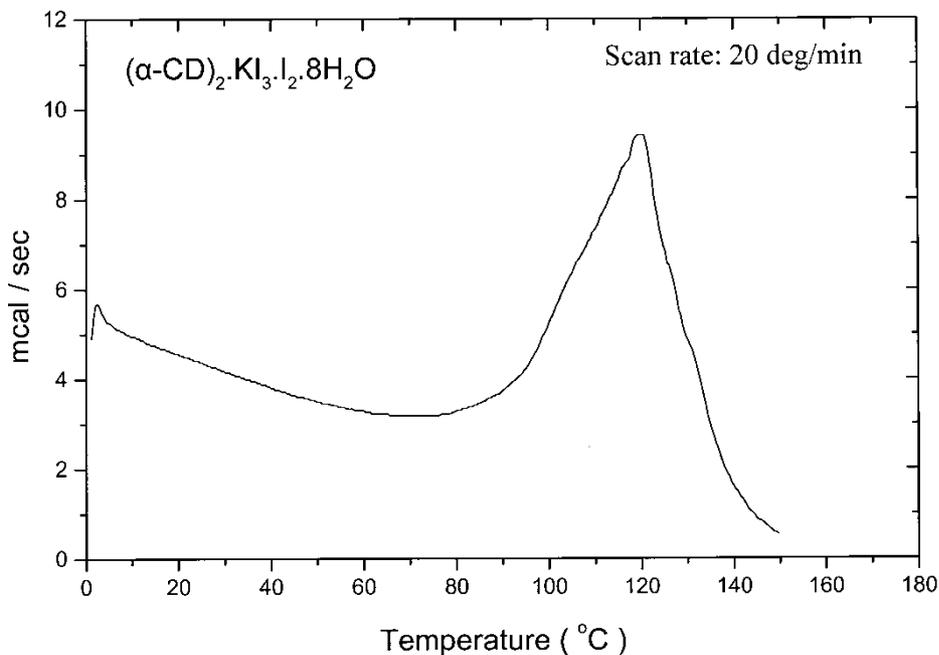
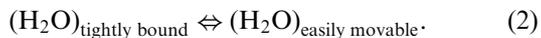


Figure 8. DSC thermogram of $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$: the heating rate was 20 deg min^{-1} .

molecules is also possible, according to the scheme:



The calorimetric measurements (figures 7 and 8) are in agreement with the fact that there are two kinds of water molecule. On heating the samples, two distinct peaks are found in the case of $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and one

slab peak in the case of $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$, similar to that of $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$ [2].

In the temperature dependence of conductivity ($\ln \sigma$ versus $1/T$) of $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ three temperature domains can be distinguished, indicated by (a), (b), (c) in figures 4 and 5, respectively. In the $\alpha\text{-K}$ complex the low temperature

Table 1. Activation energies (in kJ mol^{-1}) and transition temperatures of the $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ complexes.

Sample	T_{trans} (K)	$E(T < T_{\text{trans}})$	$E(T > T_{\text{trans}})$
$(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$	187	1.53 (or $0.98 k_{\text{B}} T_{\text{trans}}$)	−1.70 (or $1.09 k_{\text{B}} T_{\text{trans}}$)
$(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$	202	1.78 (or $1.06 k_{\text{B}} T_{\text{trans}}$)	−2.60 (or $1.55 k_{\text{B}} T_{\text{trans}}$)

sigmoid (a), $T < 210 \text{ K}$ ($10^3/T > 47.5 \text{ K}^{-1}$), is due to H^+ and OH^- of the normal hydrogen bonds and the tightly bound water molecules. The high temperature sigmoid (b), $285 \text{ K} > T > 210 \text{ K}$ ($3.5 \text{ K}^{-1} < 10^3/T < 4.75 \text{ K}^{-1}$), is caused by H^+ and OH^- of the flip-flop-type hydrogen bonds and the easily movable water molecules. The increase $\Delta \ln \sigma$ (from -25.5 to -24.5) of the second sigmoid is the net contribution to the conductivity from the transformation of flip-flop hydrogen bonds to normal state, equation (1), and from the transformation of water molecules according to equation (2). The linear part (c) for $T > 285 \text{ K}$ ($10^3/T < 3.5 \text{ K}^{-1}$) is due to the ionic movements in the crystal channels and shows semiconductive behaviour, with energy gap $E_w = 1.36 \text{ eV}$ as calculated from the Arrhenius equation $\sigma = \sigma_0 \exp(-E_w/2k_{\text{B}}T)$. In a similar way the $\ln \sigma$ versus $1/T$ plot of the $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ complex gives an energy gap $E_w = 1.84 \text{ eV}$ for the linear domain (γ), $T > 270 \text{ K}$ ($10^3/T < 3.7 \text{ K}^{-1}$) and two sigmoid curves (a) and (b) in the temperature ranges $T < 202 \text{ K}$ ($10^3/T > 4.95 \text{ K}^{-1}$) and $T > 202 \text{ K}$ ($10^3/T < 4.95$), respectively (figure 5).

The rise in conductivity of both complexes for temperatures $T > 270 \text{ K}$ is caused mainly by the activation and movement of metallic cations, K^+ or Ba^{2+} (which is inversely proportional to the cation mass) and to a lesser extent by the movement of the H^+ and OH^- ions. This aspect is in agreement with the results on α -CD complexes with Li^+ and Cs^+ ions [2]. The conductivity at frequency 200 Hz and room temperature decreases in the order: $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O} > (\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O} > (\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O} > (\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$. This is explained if we consider that the atomic weight of the cations increases in the reverse order ($AW_{\text{Li}} < AW_{\text{K}} < AW_{\text{cd}} < AW_{\text{Ba}}$), and that the lighter cations, Li^+ and K^+ , are transported easily under applied field. In the case of the cation Ba^{2+} the difficulty of movement is balanced by the double charge ($2+$) with the consequence of a greater conductivity. The thermal hysteresis that appears in both the α -Ba and α -K samples is a result of hydrogen bond transformation from flip-flop to normal type.

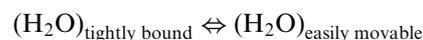
The plot of relaxation time τ versus temperature is sharply peaked from 120 to 240 K and then presents a new rising segment for temperatures higher than 240 K in both samples. The same behaviour was also found for

the Li and Cd complexes [2]. Use of the Arrhenius equation $\tau = \tau_0 \exp(-E/k_{\text{B}}T)$ 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 0.98 – $1.55 k_{\text{B}} T_{\text{trans}}$, where k_{B} is the Boltzmann constant. The negative activation energies suggest the breaking of hydrogen bonds and the formation of more stable bonds, and indicate the greater stability of the α -K complex compared with the α -Ba complex. The new increase in relaxation time τ for temperatures above 250 – 260 K exhibits the activation process involving the release of metal cations and hydroxyl groups that cause the ionic conductivity and give the semiconductive character to the materials.

5. Conclusions

The temperature dependences of ϵ' , ϵ'' and the phase shift φ show two steps, two peaks and two minima, respectively, revealing the existence of two kinds of water molecule in both the complexes $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$, namely the tightly bound and the easily movable water molecules, as was found for $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$.

Both samples present the order–disorder transition which is caused by the transformation of flip-flop hydrogen bonds to the normal state. The second peak of ϵ'' (T) or the second minimum of $\varphi(T)$ is related to the easily movable water molecules. It is also possible that the transformation of some bound water molecules to easily movable water molecules occurs according to the scheme:



Both samples show ionic conductivity and semiconductive character with energy gaps of 1.84 eV for the $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and 1.36 eV for the $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ in the temperature regions $T > 270 \text{ K}$ and $T > 285 \text{ K}$, respectively.

The temperature dependence of the relaxation time shows the characteristic Λ -like curve for most of the α -CD or β -CD complexes and a new rising segment for $T > 250 \text{ K}$ which is caused by the ionic conductivity. The calculated activation energies around the transition temperature have small absolute values in the range

$0.98\text{--}1.55 k_B T_{\text{trans}}$ and reveal the greater stability of the $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ complex compared with the $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ complex.

Since the samples that we examined were polycrystalline, the ionic conductivity was restricted because of the grain boundaries. Therefore it is necessary to use single crystals that probably have the properties of one-dimensional organic conductors, owing to their channel structure.

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