

Dielectric relaxation of β -cyclodextrin–polyiodide complexes (β -cyclodextrin) $_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ and (β -cyclodextrin) $_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$

JOHN C. PAPAIOANNOU*

Department of Chemistry, Laboratory of Physical Chemistry, National and Kapodistrian
University of Athens, PO Box 64004, 157 10 Zografou, Athens, Greece

(Received 13 November 2003; revised version accepted 5 January 2004)

The frequency and temperature dependence of real (ϵ') and imaginary (ϵ'') parts of the dielectric constant of polycrystalline complexes (β -CD) $_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ and (β -CD) $_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ (β -CD = β -cyclodextrin) have been investigated over the frequency and temperature ranges of 0–100 kHz and 120–300 K. The temperature dependence of ϵ' , ϵ'' and phase shift ϕ showing two steps, two peaks and two minima respectively, reveals 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 $\phi(T)$ present the transformation of flip-flop hydrogen bonds to the normal state. The second $\epsilon''(T)$ peak or $\phi(T)$ minimum correspond to the easily movable water molecules or to a partial transformation of tightly bound to easily movable water molecules. Both samples for $T > 275$ K show semiconductive behaviour with energy gaps 0.72 eV for the (β -CD) $_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ and 0.58 eV for the (β -CD) $_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ complex. The conductivity at temperatures $T > 220$ K is greater for the Li complex and at $T < 220$ K both complexes have similar conductivity values. The relaxation time varies in a Λ -like curve (from 180 K to 260 K) and rises rapidly for temperatures greater than 260 K, indicating the process of ionic movements. The activation energies around the transition temperature 0.40 – $0.50 k_{\text{B}}T_{\text{trans}}$ for the (β -CD) $_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ and 0.78 – $1.00 k_{\text{B}}T_{\text{trans}}$ for the (β -CD) $_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ reveal the greater stability of the β -K complex against that of the β -Li complex.

1. Introduction

When α - and β -cyclodextrins (α -CD, β -CD) are crystallized from aqueous solutions with metal iodide/iodine, channel-type complexes are formed in which two α -CD or β -CD molecules (head to head) are stacked like coins in a roll, and in the tubular cavity polyiodide chains are developed [1]. The α -CD complexes are packing in four different lattice types (triclinic, tetragonal, pseudo hexagonal, hexagonal) depending on the nature of the metal. In contrast, the β -CD displays only one crystal lattice type (monoclinic) for a variety of metals.

The polyiodide chain of the α -CD complexes with Li^+ (or K^+), Cd^{2+} and Ba^{2+} metal are best described as alternating units $\text{I}_3^- \cdot \text{I}_2^- \cdot \text{I}_3^- \cdot \text{I}_2^- \dots$, $\text{I}_5^- \cdot \text{I}_5^- \cdot \text{I}_5^- \dots$ and $\text{I}_3^- \cdot \text{I}_3^- \dots$ respectively [1], whereas in the complex of β -CD with K^+ the polyiodide chain consists of I_7^- units which can be formulated as $\text{I}_2 \cdot \text{I}_3^- \cdot \text{I}_2 \dots$ shaped into a Z-like structure in which both I_2 units are nearly perpendicular to the I_3^- unit [2].

We have investigated the dielectric relaxation properties of the α -CD complexes with lithium, cadmium, barium and potassium metals, (α -CD) $_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$, (α -CD) $_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$, (α -CD) $_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and (α -CD) $_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ named α -Li, α -Cd, α -Ba and α -K respectively [3, 4]. The temperature dependence of the dielectric constant (real part ϵ' and imaginary part ϵ'') reveals the existence of two kinds of water molecule (tightly bound and easily movable) in the case of the α -Cd, α -Ba and α -K complexes, and only one kind of water molecule (tightly bound) in the case of the α -Li complex. All systems also show the order–disorder transition that according to Saenger *et al.* [5, 6] 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 [3, 4]. All systems showed ionic conductivity at room temperature which decreases in the order: α -Ba $^{2+} > \alpha$ -Li $^+ > \alpha$ -K $^+ > \alpha$ -Cd $^+$.

In the present work we investigate the dielectric properties of two β -cyclodextrin–polyiodide inclusion complexes (β -cyclodextrin) $_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ and

*e-mail: jpapaio@cc.uoa.gr

$(\beta\text{-Cyclodextrin})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ named $\beta\text{-K}$ and $\beta\text{-Li}$ respectively, over the frequency range 0–100 kHz and temperature range 120–300 K.

2. Experimental

$\beta\text{-Cyclodextrin}$, iodine, lithium iodide and potassium iodide were purchased from Fluka Chemica. The preparation of both samples was carried out according to [1]. One gram of $\beta\text{-CD}$ was dissolved in 80 ml water at room temperature until the solution became almost saturated. Then 0.38 g potassium iodide and 0.44 g solid iodine were added to the solution and it was heated to 70°C for 20–25 min. The hot solution was filtered and left in a Dewar flask containing water at the same temperature. After one or two days, brown thin crystals of $\beta\text{-K}$ were grown. For $\beta\text{-Li}$ we used 2 g $\beta\text{-CD}$, 0.3 g lithium iodide and 0.45 g solid iodide and brown thin crystals $\beta\text{-Li}$ were grown in a similar way to the $\beta\text{-K}$ case. 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 $\beta\text{-K}$ and $\beta\text{-Li}$ complexes were found to contain eight water molecules. So, the general compositions are $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ and $(\beta\text{-CD})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$.

The dielectric measurements were taken using a low-frequency (0–100 kHz) dynamic signal analyser (DSA-Hewlett-Packard 3561A), at the temperature range of 120–300 K, which was connected to a personal computer for further processing of the data stored in the DSA. An analytical description of the process is given in a previous article [7].

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 $(\beta\text{-CD})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ and $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$.

In the $(\beta\text{-CD})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ complex ϵ' increases in a double-sigmoid fashion from 3.4 at low temperatures $T < 160$ K to 7.8 at 219 K and then to 11.8 at temperature 243.5 K. The inflection point of the first sigmoid is observed at 195.4 K ($\epsilon' = 5.9$) and that of the second sigmoid at 231.4 K ($\epsilon' = 10.1$). Above 245 K, ϵ' increases more rapidly, so that $\epsilon' = 39.0$ at 285.7 K. The variation in dielectric loss ϵ'' with temperature gives a single bell-shaped curve with peak value $\epsilon'' = 0.7$ observed at 195.4 K and a shoulder with $\epsilon'' = 5.7$ at 251.3 K. For $T > 260$ K ϵ'' increases rapidly so that at 292.2 K $\epsilon'' = 24.9$. By increasing the frequency of the applied field to 1 kHz, only the first sigmoid curve in the ϵ' versus T plot and the corresponding bell-shape curve in the ϵ'' versus T plot are distinguished. The same

situation is observed for higher applied frequencies (10–100 kHz), the second sigmoid of ϵ' versus T and the corresponding shoulder of ϵ'' versus T are absent.

In the $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ complex, the temperature dependence of ϵ' and ϵ'' is similar to the $(\beta\text{-CD})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ complex. The ϵ' values increase in a double-step fashion from 3.4 at low temperatures $T < 140$ K to 10.4 at 247 K and then to 13.7 at temperature 265 K. The inflection point of the first step is at 197.0 K, $\epsilon' = 5.9$ and that of the second step is located at 253.6 K, $\epsilon' = 11.5$. Above 265 K ϵ' increases rapidly in an exponential way, so that at temperature 300 K the value of ϵ' is 27.3. The ϵ'' versus T plot shows, as before, a single bell-shaped curve with peak value 0.9 at 203.0 K and a shoulder with value 3.7 at 262 K, which coincide with the corresponding temperatures of

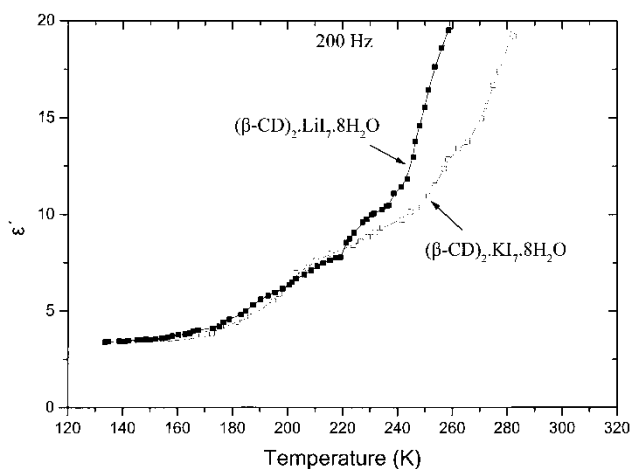


Figure 1. Temperature dependence of real (ϵ') part of the dielectric constant of $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ and $(\beta\text{-CD})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ at frequency 200 Hz.

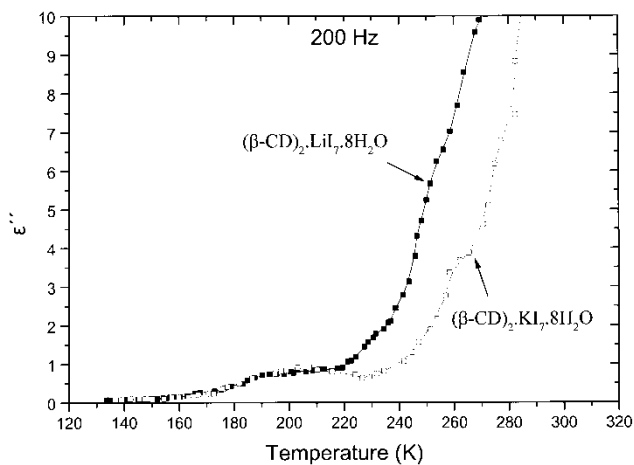


Figure 2. Temperature dependence of imaginary (ϵ'') part of the dielectric constant of $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ and $(\beta\text{-CD})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ at frequency 200 Hz.

the inflection point and shoulder in the ε' versus T plots. Above the temperature 262 K, ε'' increases fast with temperature so that at 300.9 K $\varepsilon'' = 16.1$. By increasing the frequency of the applied field to 1 kHz, the second sigmoid of the ε' versus T plot and the corresponding shoulder of the ε'' versus T plot are absent, only the first sigmoid remained, with the inflection point shifted to a higher temperature. The same qualitative picture is observed for the other, higher fixed frequencies in the range 10–100 kHz.

The phase shift φ of $(\beta\text{-CD})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ at a fixed frequency of 200 Hz (figure 3) over the range 120–300 K, presents one topical minimum value and one plateau-like temperature region; specifically it drops from 88.9° at 134 K to a minimum value of 82.7° at 195 K, then it increases to 83.4° and decreases rapidly to 70.7° at 251.3 K; then in a step-like form it decreases slightly to 69.8° at 275.7 K and then it drops rapidly to 59.1° at 289.6 K. At higher fixed frequencies it is observed that the low temperature minimum is shifted to higher temperatures but the plateau of the higher temperature is not distinguished. Similarly, the plots of phase shift versus T for the $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ complex behave in the same way and the value of T for the minimum of φ is 197.0 K ($\varphi_{\min} = 82.2^\circ$) and a slightly distinguished plateau of value 75.2° at 258.3 K, at a fixed frequency of 200 Hz. For higher fixed frequencies, as in the case of the $(\beta\text{-CD})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ complex, only the first characteristic (minimum) remains unaffected, shifted to higher temperatures, and the second one (plateau) disappears completely.

3.2. Temperature dependence of conductivity

The variation with temperature of ac conductivity ($\ln\sigma$ versus $1/T$) of the β -Li complex at 200 Hz is shown in figure 4 during the cooling process. This plot shows two sigmoid curves (a) and (b) in the temperature ranges $4.56 \text{ K}^{-1} < 10^3/T$ and $3.63 \text{ K}^{-1} < 10^3/T < 4.56 \text{ K}^{-1}$ respectively, and a linear part (c) in the temperature range $10^3/T < 3.63 \text{ K}^{-1}$. Similar results are found for the β -K complex, figure 4. The conductivity values of the β -K and β -Li samples are almost the same over the temperature range 130–220 K, but at higher temperatures the β -Li values are considerably higher than those of β -K. Both samples show thermal hysteresis for fixed frequency 200 Hz.

3.3. Relaxation time

The relaxation time ($\tau = 1/2\pi f_{\max}$) of the β -Li complex is 8.0 μs at 140 K and by increasing the temperature reaches a maximum of 10.1 μs at $T = 221.3$ K; then it drops to 9.8 μs at 254 K (figure 5). For higher temperatures $T > 260$ K the relaxation time increases

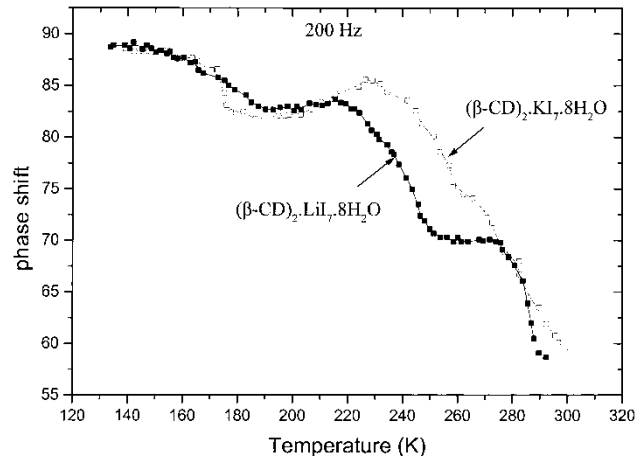


Figure 3. Temperature dependence of phase shift for $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ and $(\beta\text{-CD})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ at frequency 200 Hz.

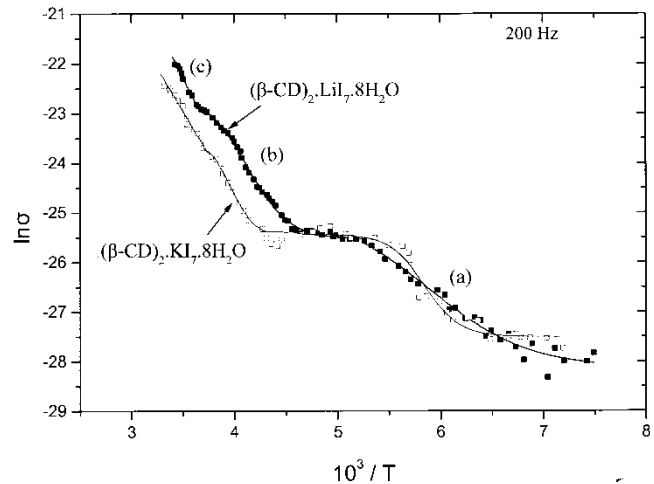


Figure 4. Temperature dependence of ac conductivity ($\ln\sigma$ versus $1/T$) for the $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ and $(\beta\text{-CD})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ complexes at frequency 200 Hz.

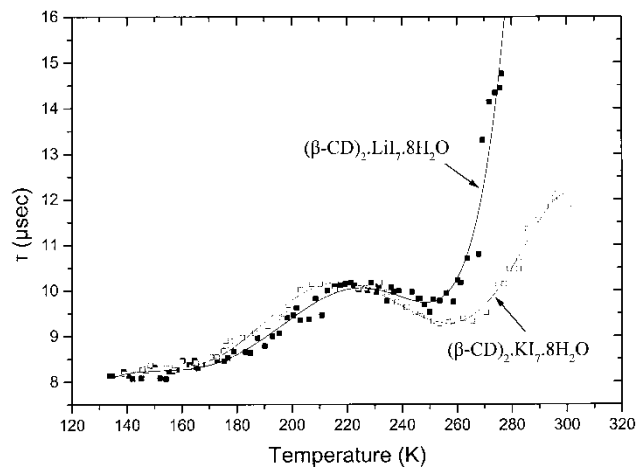
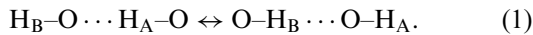


Figure 5. Relaxation time (τ) against temperature for $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ and $(\beta\text{-CD})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$.

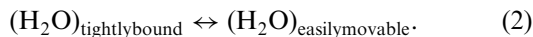
rapidly with temperature to 44.7 μs at 276.3 K. Similar behaviour is observed for the β -K complex; r starts at 8.2 μs at 140 K and increases with temperature to the maximum, 10.2 μs , with temperature $T = 221.0$ K, then decreases to 9.4 μs at 262 K and increases again to 12.2 μs at 296.7 K.

4. Discussion

The main dielectric characteristics of $(\beta\text{-CD})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ and $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ are the following: in both complexes, at applied frequency 200 Hz, the ϵ' versus T plots show two sigmoids, the ϵ'' versus T plots exhibit two loss peaks of which the second one is degenerated in a shoulder, and the φ versus T plots show two minima of which the second one is degenerated in a plateau region. The same behaviour was found previously for the complexes $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$ [3], $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ [4]. The first sigmoid at low temperatures has been attributed to the strongly bound water molecules, while the second one to the less tightly bound (easily movable) water molecules. Both systems exhibit the already known order-disorder transition which is caused by the transformation of the normal hydrogen bonds to flip-flop bonds, according to the scheme [5, 6]:



This transition is shown as the first peak in the plots ϵ'' versus T and as the first minimum in the plots φ versus T in the temperature region (190–200 K). The second peak of $\epsilon''(T)$ or the second minimum of $\varphi(T)$ in the temperature region 240–250 K is related to the easily movable water molecules. The transformation of some bound water molecules to easily movable water molecules is also possible, according to the scheme:



In the temperature dependence of conductivity ($\ln \sigma$ versus $1/T$) of $(\beta\text{-CD})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ and $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ three temperature domains are distinguished, indicated by (a), (b), (c) in figure 4, as in the case of $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ [4]. In the β -Li complex the low temperature sigmoid (a), $T < 219$ K ($10^3/T > 4.56 \text{ K}^{-1}$), is due to the H^+ and OH^- of the normal hydrogen bonds and the tightly bound water molecules. The high temperature sigmoid (b), $275 \text{ K} > T > 219 \text{ K}$ ($3.63 \text{ K}^{-1} < 10^3/T < 4.56 \text{ K}^{-1}$), is caused by the H^+ and OH^- of the flip-flop-type hydrogen bonds and the easily movable water molecules. The difference $\Delta \ln \sigma$ (from -25.4 to -22.8) between the upper plateau values of the two sigmoids 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 $T > 275$ K ($10^3/T < 3.63 \text{ K}^{-1}$) is due to the ionic movements in the crystal channels and shows semiconductive behaviour, with energy gap $E_w = 0.58$ eV as calculated from the Arrhenius equation $\sigma = \sigma_0 \exp(-E_w/2k_B T)$. In a similar way the $\ln \sigma$ versus $1/T$ plot of the $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ complex gives the energy gap $E_w = 0.72$ eV for the linear domain (c), $T > 270$ K ($10^3/T < 3.7 \text{ K}^{-1}$) and also gives the two sigmoid curves (a) and (b) in the temperature ranges $T < 234$ K ($10^3/T > 4.27 \text{ K}^{-1}$) and $T > 234$ K ($10^3/T < 4.27$) respectively (figure 4). The rise in conductivity of both complexes for temperatures $T > 270$ K is caused mainly by the activation and movement of metallic cations, Li^+ or K^+ , which is inversely proportional to their mass, and less by the movement of the H^+ and OH^- ions. This aspect is in agreement with the results on α -CD complexes with Li^+ , Cs^+ , K^+ and Ba^{2+} [3, 4]. The conductivity of $(\beta\text{-CD})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ is higher than that of $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ because the lighter cation Li^+ is transported easier than the K^+ under applied field, that is:

$$\sigma_{\beta\text{-Li}} > \sigma_{\beta\text{-K}} \quad \text{for } T > 220 \text{ K}.$$

The fact that in the low temperature region $T < 220$ K the conductivity variation with temperature is the same for both the β -Li and β -K complexes, is caused by the same number of β -CD hydroxyl groups and water molecules contained in the same crystal structure, that is:

$$\sigma_{\beta\text{-Li}} = \sigma_{\beta\text{-K}} \quad \text{for } T < 220 \text{ K}.$$

Comparing the absolute values of conductivity of the β -Li and β -K complexes with the corresponding values of α -Li [3] and α -K [4] it is seen that in the temperature region $T > 250$ K the conductivity of β -CD complexes is greater than that of the α -CD complexes with the same alkali metal Li or K, that is:

$$\sigma_{\beta\text{-Li}} > \sigma_{\alpha\text{-Li}} > \sigma_{\beta\text{-K}} > \sigma_{\alpha\text{-K}} \quad \text{for } T > 250 \text{ K}.$$

This happens because the diameter of the β -CD channels is larger than that of the corresponding α -CD channels and the ions move relatively freely in the first case. In the low temperature region $T < 240$ K where the ions are not movable, all the complexes have almost the same conductivity values, that is:

$$\sigma_{\beta\text{-Li}} \cong \sigma_{\alpha\text{-Li}} \cong \sigma_{\beta\text{-K}} \cong \sigma_{\alpha\text{-K}} \quad \text{for } T < 240 \text{ K}.$$

The relaxation time r versus temperature plot is sharply peaked from 180 K to 260 K and then presents

Table 1. Activation energies (in kJ mol^{-1}) and transition temperatures of $(\beta\text{-CD})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ and $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ complexes.

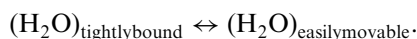
Sample	$T_{\text{trans}}(\text{K})$	$E(T < T_{\text{trans}})$	$E(T > T_{\text{trans}})$
$(\beta\text{-CD})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$	221	0.92 (or $0.50 k_{\text{B}} T_{\text{trans}}$)	-0.75 (or $0.40 k_{\text{B}} T_{\text{trans}}$)
$(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$	215	1.4 (or $0.78 k_{\text{B}} T_{\text{trans}}$)	-1.8 (or $1.00 k_{\text{B}} T_{\text{trans}}$)

a new rising segment for temperatures higher than 260 K in both samples. The same behaviour was also found for the α -Li, α -Cd, α -Ba and α -K complexes [3, 4]. Use of the Arrhenius equation $r = r_0 \exp(-E/k_{\text{B}}T)$ 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 $0.50\text{--}1.00 k_{\text{B}} T_{\text{trans}}$, 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 β -K complex against the β -Li. The new increase in relaxation time r for temperatures above 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 dependence of ε' , ε'' and phase shift φ showing two steps, two peaks and two minima respectively, reveals the existence of two kinds of water molecule in both complexes $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ and $(\beta\text{-CD})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$, namely the tightly bound and the easily movable water molecules, as was found in the cases of $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5} \cdot \text{I}_5 \cdot 26\text{H}_2\text{O}$, $(\alpha\text{-CD})_2 \cdot \text{BaI}_2 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2 \cdot \text{KI}_3 \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ [3, 4].

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 $\varepsilon''(T)$ or second minimum of $\varphi(T)$ is related to the easily movable water molecules. It is also possible 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 0.58 eV for $(\beta\text{-CD})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ and 0.72 eV for $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ in the temperature regions $T > 275$ K and $T > 270$ 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 rising segment for $T > 250$ K which is caused by the ionic conductivity. The calculated activation energies around the transition temperature have small absolute values in the range $0.40\text{--}1.00 k_{\text{B}} T_{\text{trans}}$ and reveal the greater stability of the $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 8\text{H}_2\text{O}$ compared with the $(\beta\text{-CD})_2 \cdot \text{LiI}_7 \cdot 8\text{H}_2\text{O}$ complex.

Acknowledgement

This work was partly supported by Grant No. 70/4/3347 Special Account for Research Grants, National and Kapodistrian University of Athens.

References

- [1] NOLTEMAYER, M., and SAENGER, W., 1980, *J. Am. Chem. Soc.*, **102**, 2710.
- [2] BETZEL, C., HINGERTY, B., NOLTEMAYER, M., WEBER, G., and SAENGER, W., 1983, *J. Incl. Phenom.*, **1**, 181.
- [3] GHIKAS, T., and PAPAIOANNOU, J., 2002, *Molec. Phys.*, **100**, 673.
- [4] PAPAIOANNOU, J., and GHIKAS, T., 2003, *Molec. Phys.*, **101**, 2601.
- [5] BETZEL, C., SAENGER, W., HINGERTY, B. E., and BROWN, G. M., 1984, *J. Am. Chem. Soc.*, **106**, 7545.
- [6] ZABEL, V., SAENGER, W., and MASON, S. A., 1986, *J. Am. Chem. Soc.*, **108**, 3664.
- [7] PAPAIOANNOU, J., PAPADIMITROPOULOS, N., and MAVRIDIS, I., 1999, *Molec. Phys.*, **97**, 611.