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Dielectric Relaxation of the β-Cyclodextrin Complexes with Tridecanoic Acid and 1,13-Tridecanedioic Acid

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Abstract

The frequency and temperature dependence of the real (ϵ') and imaginary (ϵ'') parts of the dielectric permittivity of the polycrystalline complex β-cyclodextrin-tridecanoic acid in two hydration forms (with 16.2 and 10.7 water molecules) and β-cyclodextrin-1,13-tridecanedioic acid with 16.4 and 10.5 water molecules have been investigated, in the frequency range 0.1–100 kHz and temperature range 120–310 K. The dielectric behavior is described well by Debye-type relaxation α dispersion. All systems except for the complex of partially dehydrated monocarboxylic acid, exhibit an additional Ω-dispersion, at low frequencies ($f < 1000$ Hz). Only one-step was found in the ϵ' vs. T plots of both complexes in the two hydration forms, a fact indicating that the water molecules cannot be divided into strongly bound and easily movable molecules. The ϵ''vs. T plots, at a fixed frequency (200 Hz), show the characteristic peak attributed to a transition between ordered and disordered β-CD hydroxyl groups and water molecules. The transition temperature was 202.7 K for all systems examined except for the complex β-CD-tridecanoic acid.16.2 H_2O (214.5 K). This means that the order to disorder transformation process was unaffected by the dehydration process in the case of the dicarboxylic acid complex, whereas in the case of the monocarboxylic acid, it was unexpectedly facilitated. The relaxation time varies with temperature, in a Λ like curve (in the range 8–14 μs), with maximum values located at the corresponding order-disorder transition temperatures. The activation energies of the fully hydrated complexes have absolute values of ~5 kJ/mol in the range 1.98–3.82 $K_B T_{\text{transition}}$ which are higher than the corresponding values of ~2 kJ/mol of the dehydrated complexes. A thermal hysteresis observed in all complexes is a result of the order-disorder transformation.

Introduction

The X-ray, room temperature crystal structure of the inclusion complex of β-cyclodextrin (β-CD) with the aliphatic monoacid tridecanoic acid (TRIMO) [1, 2] has shown that two β-CD molecules are held together (head to head), while one molecule of the monoacid threads through them thus forming [3]pseudorotaxanes. The aliphatic acid is disordered over two orientations (A and B) of almost equal occupation factors. In 3-D the complexes are organized in channels along the *c* axis. In two adjacent β-CD dimers along the channel the two aliphatic acid orientations (A and B) are antiparallel and hydrogen bonds are developed between the two carboxylic groups. 19.5 water molecules distributed over 28 sites have been located, and form two separate water networks, one connecting the primary hydroxyl side and another the secondary side.

The X-ray crystal structure determination of the β-CD complex with the aliphatic diacid 1,13-tridecanedioic acid (TRIDI) [3–4], at 173 K, showed also [3]pseudorotaxane formation. Two β-CD molecules form a dimer and one molecule of diacid, disordered in two positions A and B (50% each), threads through them. However, in this case the β-CD dimers pack in a type called intermediate mode (IM), since it is intermediate between the channel mode, where the dimers align in channels and the chessboard mode, where they are isolated [5]. In the IM mode two consecutive dimers are laterally shifted by 6.2 Å and their cavity is partially blocked. Their carboxylic groups do not interact directly but through water molecules. In the crystal structure of β-CD·TRIDI, 24.5 water molecules have been located distributed over 42 sites, and form two separate and independent water networks, one connecting the primary hydroxyl side and the other the secondary [5, 6] as in the complex β-CD·TRIMO.

It has been shown [7–9] that when the disordered β-CD hydroxyl groups change into an ordered state, a transition temperature is exhibited in which, according to Saenger *et al.* [10–11], the flip-flop type hydrogen bonds are transformed into the normal type. The transition temperature was indicated by a peak of the imaginary part (ϵ'') of the dielectric permittivity ($\epsilon = \epsilon' - i\epsilon''$) and as a minimum of the phase shift component φ at the current passing through the sample relative to the applied signal. The frequency

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dependence of the real (ϵ') and imaginary (ϵ'') parts is described well by Debye-type relaxation [12, 13] according to Equations (1) and (2):

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2 T^2}, \tag{1}$$

$$\epsilon'' = \frac{(\epsilon_s - \epsilon_\infty)\omega T}{1 + \omega^2 T^2}, \tag{2}$$

where ϵ_s is the static and ϵ_∞ the high frequency permittivity, $\omega = 2\pi f$ the applied frequency and $T = 1/2\pi f_{\max}$ the relaxation time. Generally the ϵ' versus frequency curves are of sigmoidal shape. The frequency variation of ϵ'' has the form of a loss peak (α-dispersion). Figure 2 of ref. [7], centered at a characteristic frequency $f_{\max}$. If the system exhibits dc conductivity (σ), i.e., ionic motion, there is a “dc contribution” to ϵ'' which is proportional to σ and inversely proportional to the frequency ω. So at low frequencies $\omega \ll 1/T$ the contribution of conductivity to ϵ'' will be significant, and this gives rise to the Ω-dispersion (Figure 3 of ref. [7]) and

$$\epsilon'' = \frac{(\epsilon_s - \epsilon_\infty)\omega T}{1 + \omega^2 T^2} + \frac{\sigma}{\omega \epsilon_0}, \tag{3}$$

where ϵ_0 is the vacuum dielectric permittivity. The temperature dependence of ϵ' and $\epsilon''_{\max}$ exhibits two steps in some α-CD and β-CD complexes but only a single step in some others [7–9]. The low temperature step is due to the tightly bound water molecules, whereas that at higher temperatures is due to easily removable water. The dynamics of water molecules in complex geometries is a matter of intense debate [14].

In the present work we investigate the dielectric properties of two polycrystalline inclusion complexes in two hydration forms [$(\beta$-CD$)_2$·TRIMO·16.2H_2O, $(\beta$-CD$)_2$·TRIMO·10.7H_2O] and [$(\beta$-CD$)_2$·TRIDI·16.4H_2O $(\beta$-CD$)_2$·TRIDI·10.5H_2O] over the frequency range 0.1–100 kHz and temperature range 120–310 K.

Experimental

The βCD·TRIMO complex was prepared [2] by mixing 26 μmol β-cyclodextrin (Fluka) dissolved in 1 mL H_2O with a solution of 28 μmol solid tridecanoic acid (Aldrich) in 0.3 mL ethanol. The β-CD·TRIMO complex precipitated immediately. It was left stirring for 1–2 hours and then it was filtered and dried in air. Thermogravimetric analysis (TA instruments 2050, heating rate 5 °C $\min^{-1}$) was used to determine the water content which was 16.2 water molecules per β-CD dimer (TRIMO16.2). A second sample was dried in an oven kept at 45 °C for two days. Thermogravimetric analysis, as before, showed that the water content was 10.7 water molecules per β-CD dimer (TRIMO10.7). The complex β-CD·TRIDI was prepared [4] by adding 30 μmol solid 1,13-tridecanedioic acid (Aldich) to an aqueous solution of β-cyclodextrin (Fluka) (26 μmol β-CD in 1.0 mL H_2O). The complex precipitated after stirring of the solution over a period of 24 hours at RT then it was filtered and dried in air. The water content, determined as before was 16.4 water molecules per β-CD dimer (TRIDI16.4). In a separate sample dried in an oven at 45 °C for two days, the water content was found to be 10.5 water molecules per β-CD dimer (TRIDI10.5). The dielectric permittivity measurements were made using a low frequency (0.1–100 kHz) dynamic signal analyzer (DSA-Hewlett-Packard 3561A), in the temperature range of 120–310 K. The analytical experimental procedure is described elsewhere [7]. The uncertainty interval of the measured permittivity values is less than 3%.

Results

Variation of ϵ' and ϵ'' with temperature

The temperature dependence of ϵ' and ϵ'' over the range 120–310 K is shown in Figure 1 for TRIMO16.2 and TRIDI16.4 and in Figure 2 for the samples TRIMO10.7 and TRIDI10.5.

The ϵ' values of TRIMO16.2, at 200 Hz, increase in a sigmoid shape from 3.21 at low temperatures to 16.23 at 281 K and then increase rapidly to 19.46 at 306 K. The corresponding values of TRIDI16.4 coincide with those of TRIMO16.2 for temperatures $T < 186$ K, and deviate to higher values ($\Delta\epsilon' \approx 1.9$) for temperatures $T > 186$ K, Figure 1. The same qualitative picture is observed for the other higher fixed frequencies.

The ϵ'' vs. T plots, at a fixed frequency of 200 Hz, of both TRIMO16.2 and TRIDI16.4 show the characteristic peak of the order-disorder transition, with half-width $\cong$ 26 K, and peak values of 2.28 and 2.55 located at temperatures of 214.5 K and 202.7 K respectively. They show also an abrupt increase of ϵ'' from the value of 0.77 at 243 K to 7.61 at 306 K for the TRIMO16.2 sample, and from the value of 0.53 at 241 K to 7.58 at 300 K for the TRIDI16.4 sample. In the ϵ'' vs. T curve of TRIMO16.2 the maximum is shifted to higher T by $\cong$ 10 K relative to that of TRIDI16.4.

For TRIMO10.7 and TRIDI10.5 the ϵ' vs. T and ϵ'' vs. T plots have the same characteristics as TRIMO16.2 and TRIDI16.4 but with smaller absolute values. In the curves of ϵ' vs. T, the ϵ' values increase from 3.03 at 130 K to 9.16 at 266 K and then rapidly to 11.46 at 303 K for TRIMO10.7. For TRIDI10.5 the ϵ' values increase from 3.27 at 130 K to 12.59 at 249.7 K and then rapidly to 16.67 at 306 K. The temperature range for which the ϵ' values of TRIMO10.7 and TRIDI10.5 coincide, is smaller ($T < 160$ K) than that of TRIMO16.2 and TRIDI16.4 ($T < 186$ K). The ϵ'' vs. T plots of TRIMO10.7 and TRIDI10.5 have similar shapes as in the TRIMO16.2 and TRIDI16.4 samples. The peaks are located at the same temperatures for both samples but the peak values of ϵ'' are 0.78 for TRIMO10.7 with half-width 60 K and 1.31 for the TRIDI10.5 with half-width 55 K. In TRIMO10.7 the abrupt increase of ϵ'' starts from the value 0.19 at 267 K and reaches the value 0.74 at 303 K. In TRIDI10.5 the abrupt increase of ϵ'' starts from the value of 0.31 at 259 K and reaches the value of 2.21 at 303 K. We note that differences of the ϵ' and ϵ'' values between

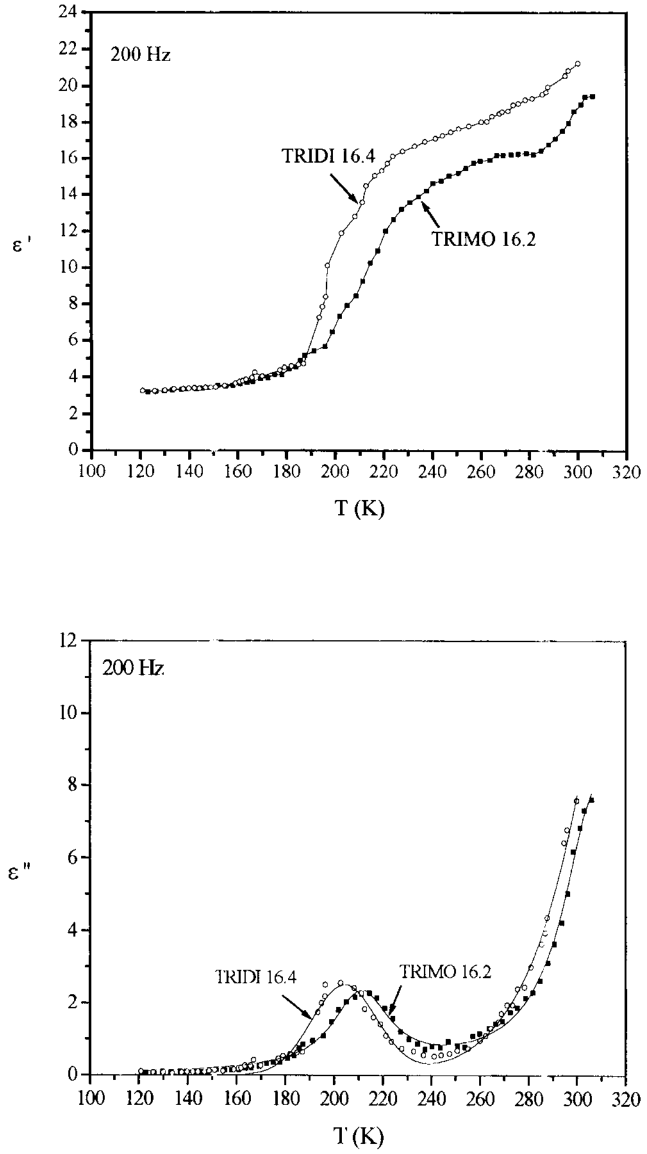

Figure 1. Temperature dependence of the real (ϵ') and imaginary (ϵ'') parts of the dielectric permittivity of TRIMO16.2 and TRIDI16.4 at a frequency of 200 Hz.

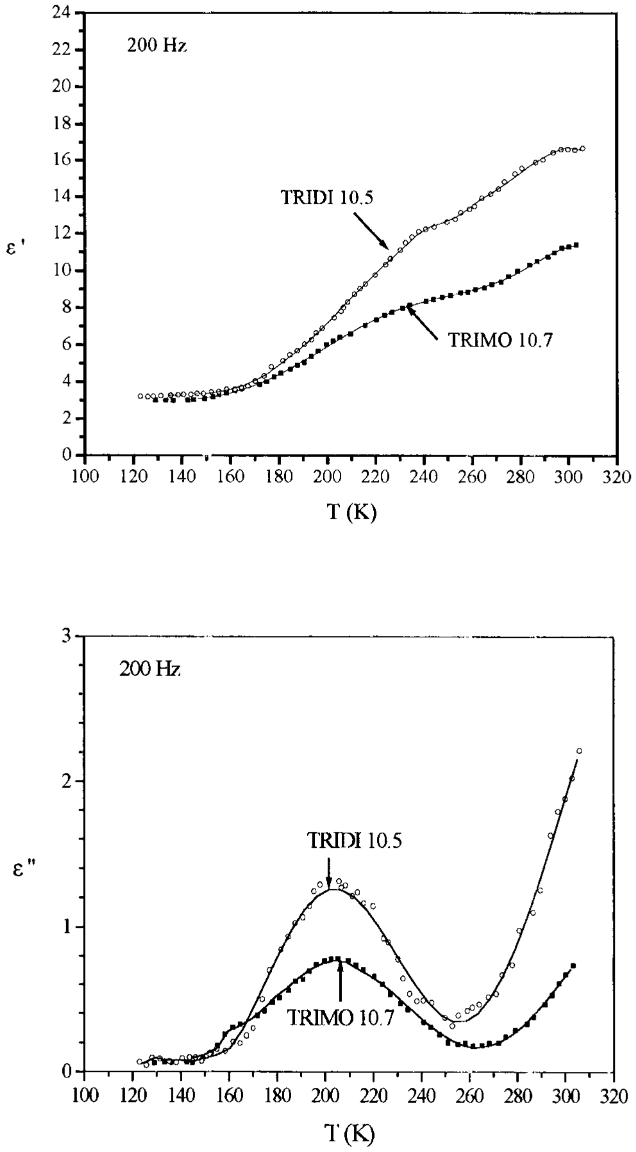

Figure 2. Temperature dependence of the real (ϵ') and imaginary (ϵ'') parts of the dielectric permittivity of TRIMO10.7 and TRIDI10.5 at a frequency of 200 Hz.

TRIMO10.7 and TRIDI10.5 differ more than the corresponding difference between TRIMO16.2 and TRIDI16.4. All samples investigated showed a “thermal hysteresis” in the temperature range 260–180 K, for every fixed frequency examined. Representative examples are shown in Figures 3 and 4 for TRIMO16.2 and TRIDI16.4, respectively. It is observed that in the case of TRIMO16.2, Figure 3, the heating and cooling processes are completely reversible, for both ϵ' and ϵ'', in the temperature regions $T < 170$ K and $T > 275$ K. A thermal hysteresis of about 14 K is observed in the vicinity of the transition. In the case of TRIDI16.4, Figure 4, the ϵ' and ϵ'' values are completely reversible in the temperature region $T < 170$ K but at temperatures $T > 250$ the heating values are slightly smaller than the corresponding cooling values. The thermal hysteresis is about 19 K in the vicinity of the transition. Similar results are found for the other samples which differ in that the cooling and heating curves superimpose at $T < 150$ K only.

Frequency dependence of ϵ' and ϵ'

The frequency dependence of ϵ' and ϵ'' in the range 0.1–100 kHz for fixed temperatures, during the cooling experiment, are shown in Figure 5 for TRIMO16.2 and in Figure 6 for TRIDI16.4. In the low frequency range (100–1000 Hz) the slope of the curves of TRIMO16.2 increase with decreasing frequencies (with rate $\Delta\epsilon \sim 3$/octave) for temperatures between 123 K and 285 K, whereas the curves are almost flat close to those temperatures. In the case of TRIDI16.4 the corresponding slopes of ϵ' increase with a rate of $\Delta\epsilon' \sim 4.17$/octave. The absolute values of ϵ' at low temperatures are almost the same for both samples, i.e., $\epsilon' = 3.18$ at 123 K for TRIMO16.2 and $\epsilon' = 3.23$ at 121 K for TRIDI16.4. At high temperatures, $\epsilon' = 22.36$ (306 K) for TRIMO16.2 and $\epsilon' = 23.05$ (300.1 K) for TRIDI16.4 at 100 Hz. The frequency variation of ϵ'' of TRIMO16.2, TRIDI16.4 and TRIDI10.5 exhibit both α- and Ω-dispersions and they follow Equations

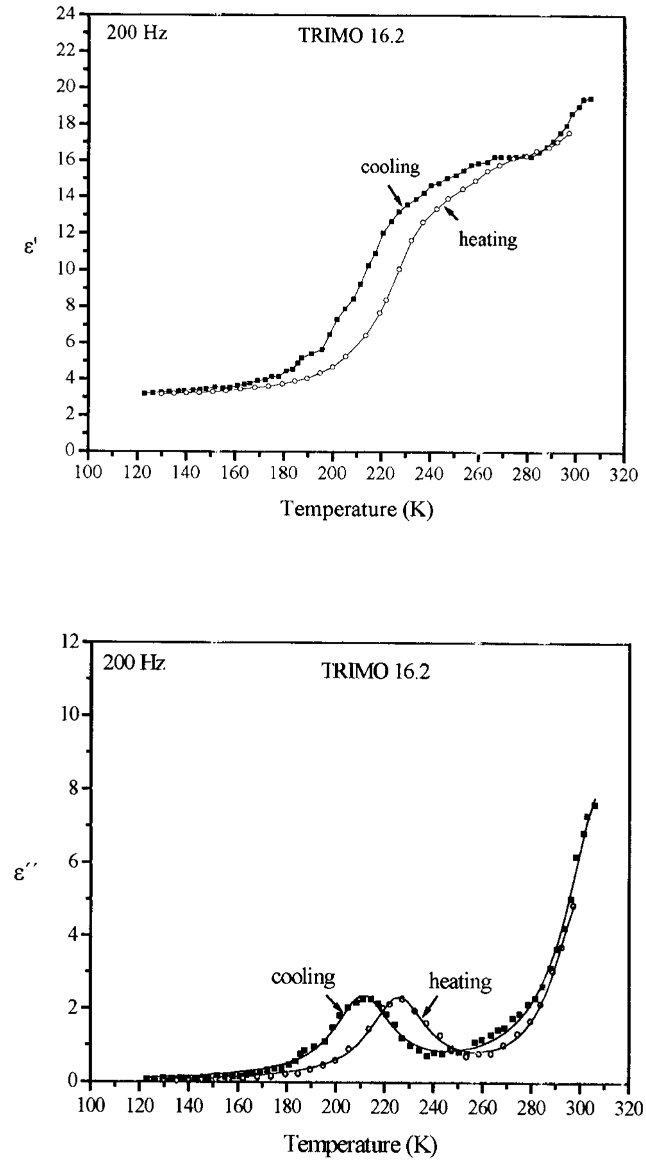

Figure 3. Thermal hysteresis of TRIMO16.2.

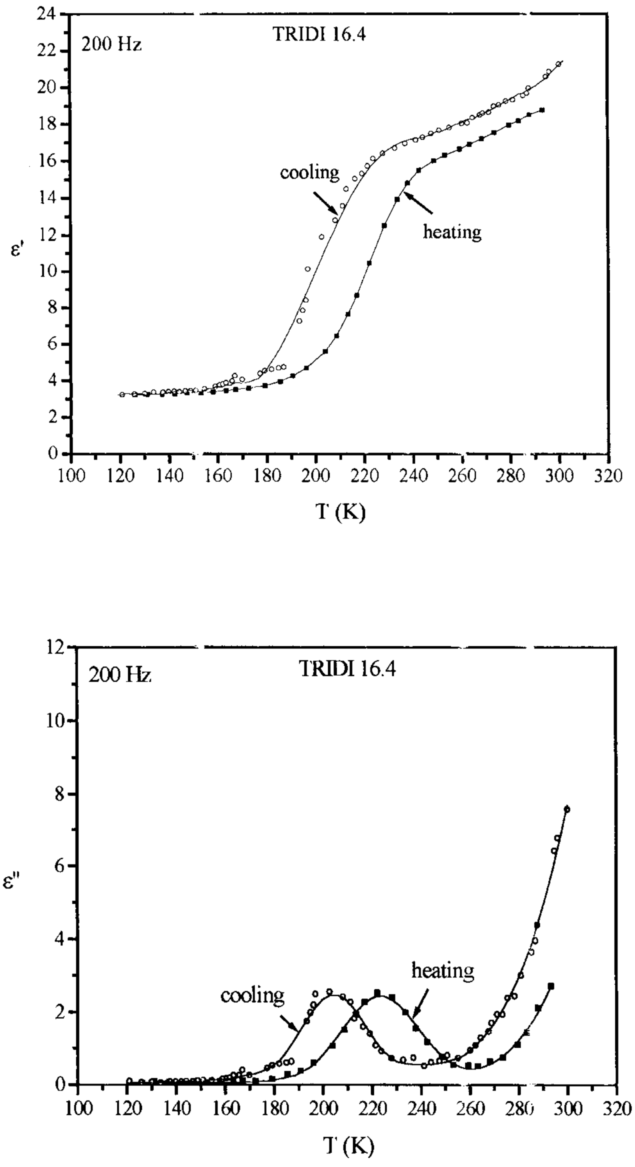

Figure 4. Thermal hysteresis of TRIDI16.4.

(1) and (3). The Ω-dispersion as already mentioned is directly connected to ionic movements or dc conductivity (σ). TRIMO10.7, shows only α-dispersion and it is characterized by Equations (1) and (2) since the dc conductivity is zero.

The $\epsilon''_{\mathrm{max}}$ values of the loss peaks of all samples increase with temperature, Figure 7, i.e., for TRIMO16.2, from 1.55 at 122 K to 8.44 at 306 K. The $\epsilon''_{\mathrm{max}}$ values of TRIDI16.4 coincide with those of TRIMO16.2 for $T < 185$ K and then increase to the value 9.65 at 300 K. TRIMO10.7 and TRIDI10.5 have smaller $\epsilon''_{\mathrm{max}}$ values and as the temperature increases the deviation among themselves ($\Delta\epsilon''_{\mathrm{max}}$) increase from 0 to 2.5. The sigmoid shape is still clear in the case of TRIDI10.5 but the horizontal part at high temperatures has disappeared in the case of TRIMO10.7.

The relaxation time ($T = 1/2\pi f_{\mathrm{max}}$), Figure 8, in both TRIMO16.2 and TRIDI16.4 starts at 8.2 μs at low T, peaks at 13.5 μs by increasing the temperature and then drops to the value 8.2 μs again. Maxima of 13.5 μs occur at the transition temperatures 230 K and 216 K for TRIMO16.2 and TRIDI16.4 respectively. In TRIMO10.7 and TRIDI10.5 a similar behavior is observed but the maximum values are 10.5 μs and 11.2 μs respectively. The transition temperature for both curves is at 216 K, the same temperature as for TRIDI16.4, Table 1.

Discussion

It has been shown that the β-CD dimer is a very stable entity [6] and that the H-bonding network it forms with water molecules around it is semi-invariant. Specifically, the H-bonds around the secondary hydroxyls O(2) and O(3) are invariant in all structures and these at the primary interface present some differences depending on the crystal packing.

In both inclusion complexes the dimers formed consist of two truncated cones which have their wide rim in contact, stabilized by the OA3n ... OB3(8-n) hydrogen bonds between the O(3) secondary hydroxyl groups of the independent β-CD monomers A and B [6]. These barrel-like

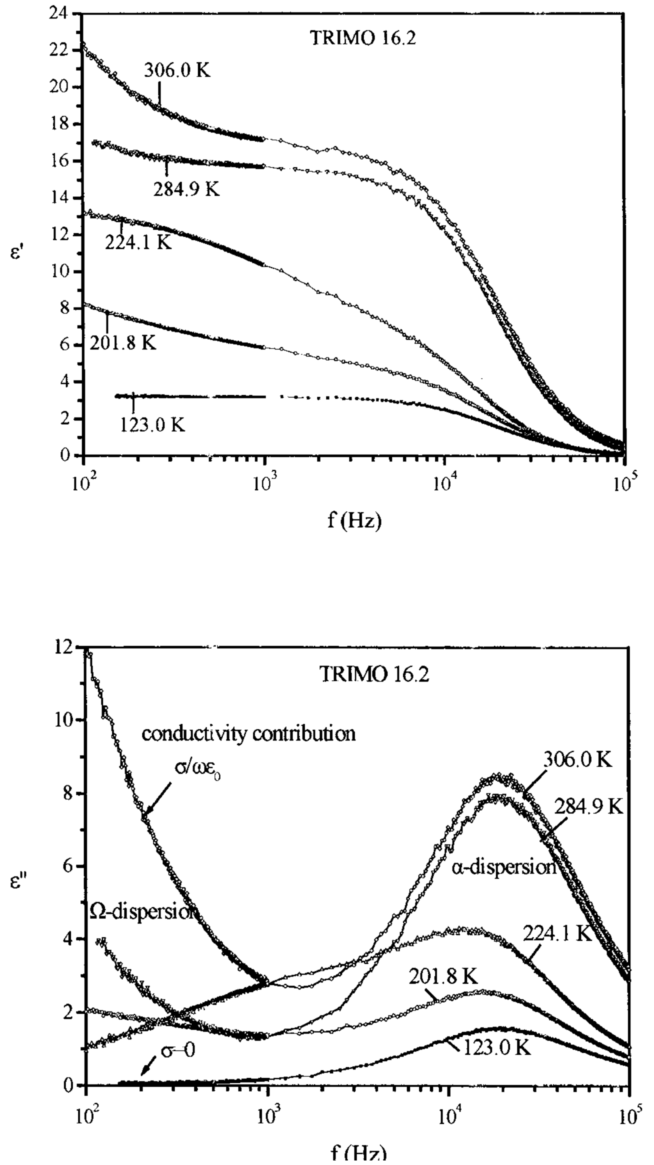

Figure 5. Frequency dependence of the real (ϵ') and imaginary (ϵ'') parts of the dielectric permittivity of TRIMO16.2.

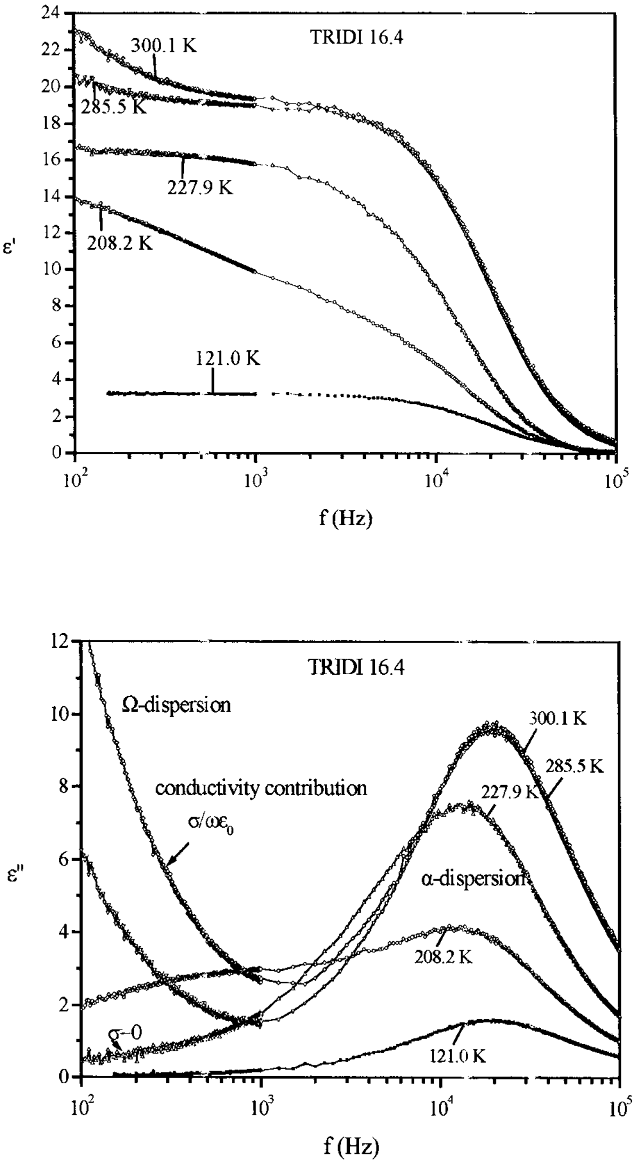

Figure 6. Frequency dependence of the real (ϵ') and imaginary (ϵ'') parts of the dielectric permittivity of TRIDI16.4.

units are common in both inclusion complexes and they are not expected to have any difference in their dielectric properties. The guest molecules, which are accommodated in these units, emerge from the two primary faces of the dimer. So both ends of the guest molecule affect only the narrow rims occupied by the primary O(6) hydroxyl groups. In the β-CD.TRIMO case the primary faces form direct H-bonds and align in channels isolating the guest from the water environment. Thus at one end the hydrophobic group (–CH_3) is protected from the aqueous environment inside the channel and at the opposite end, the carboxyl groups of two adjacent dimers come close and develop a carboxylic dimer which behaves like a non-polar entity and has no contribution to the polarization of the total system. In contrast, the structure of the inclusion complex β-CD·TRIDI has the carboxyl groups, at both ends of the guest, hydrated and directly connected by H-bonds with the water networks of primary O(6) hydroxyl groups. We believe that the difference in the hydration at the primary faces is consistent with the dielectric behavior.

The main dielectric characteristics of β-CD·TRIMO and β-CD·TRIDI are the following: (a) in both complexes the ϵ' versus T plots show a single step and the ϵ'' vs. T plots exhibit a loss peak. The ϵ' and ϵ'' values show a thermal hysteresis during the cooling-heating cycle for all samples. (b) The frequency dependence of ϵ'' exhibits both α- and Ω-dispersions in the three complexes TRIDI16.4, TRIDI10.5 and TRIMO16.2. The TRIMO10.7 sample exhibits only α-dispersion.

The fact that only one-step was found in the ϵ' vs. T plots indicates that the water molecules cannot be divided into strongly bound molecules and easily movable molecules as was found for the systems β-CD and β-CD·4-t-butylbenzylalkohol (β-CD·TERB) [7] and (α-cyclodextrin)$_2$·$Cd_{0.5}$·I_5·$26H_2O$ [9]. The loss peak of the ϵ'' vs. T plot is attributed to the transition between ordered and

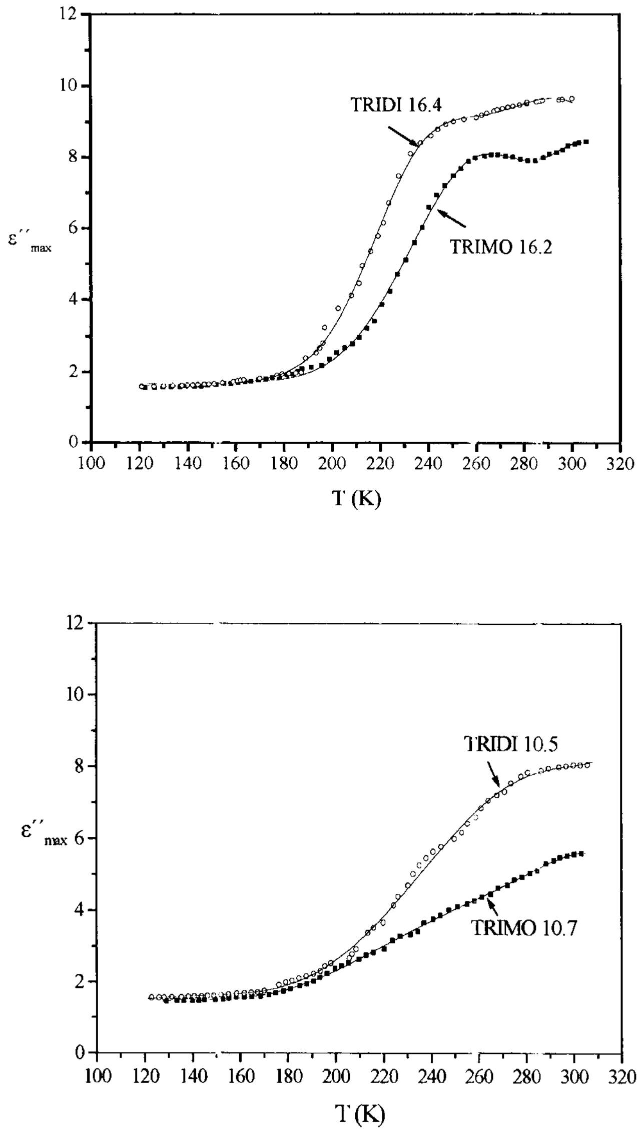

Figure 7. Temperature dependence of ϵ''_{max} of the complexes

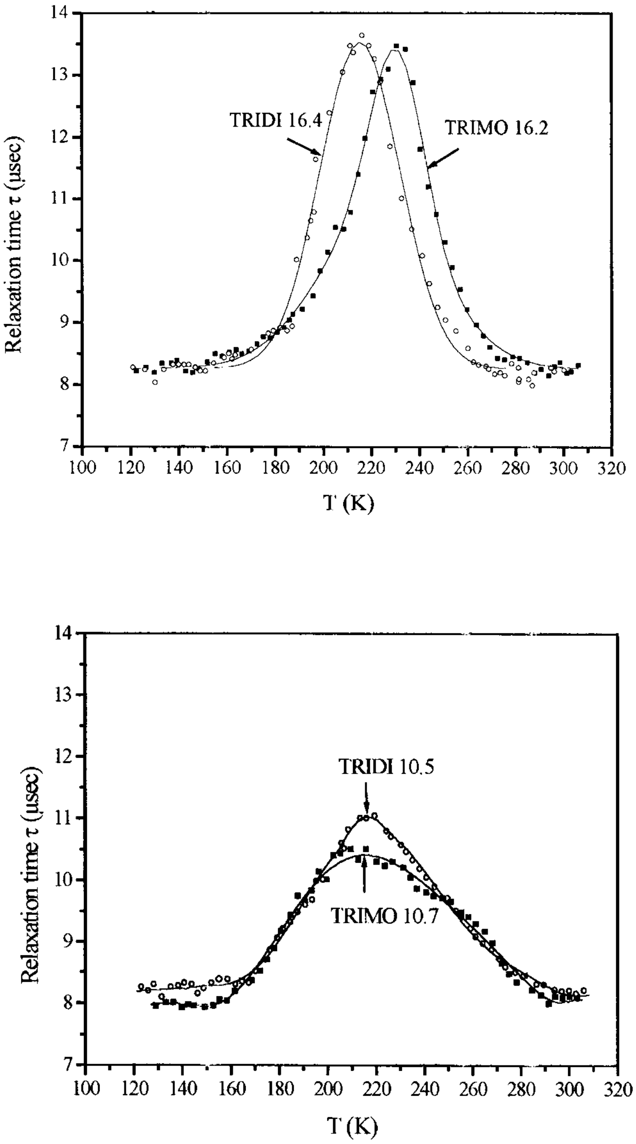

Figure 8. Temperature dependence of the relaxation time τ of the complexes.

disordered β-CD hydroxyl groups and water molecules. The transition temperature 202.7 K of TRIDI16.4 is smaller than the 214.5 K of TRIMO16.2. An explanation for this fact is the different H-bonding scheme in the primary faces of the β-CD dimers. In the TRIDI16.4 inclusion complex the existence of a higher number of H-bonds at the primary face both among the host hydroxyl groups and the guest carboxylic groups with water molecules facilitates the transformation process from order to disorder and it starts at a lower temperature. The primary hydroxyl groups in TRIMO16.2 are less exposed to water and the guest is completely isolated in the hydrophobic surrounding of the channels. For the partially dehydrated forms TRIMO10.7 and TRIDI10.5, Figure 2, the common peak temperature 202.7 K of the ϵ'' vs. T plot has the same value as that of the TRIDI16.4. This means that the order to disorder transformation process was unaffected by the dehydration process in the case of TRIDI10.5, whereas in the case of TRIMO10.7 it was unexpectedly facilitated since the transition temperature decreased from 214 K to 202.7 K, probably because the removal of water molecules from the primary face environment generates more disordered primary hydroxyls. The partial dehydration from the primary face of TRIMO10.7 might be the reason for the lack of Ω-dispersion exhibited by this sample only, a phenomenon probably due to ionic conductance.

The relaxation time τ varies with temperature, in a Λ-like curve, Figure 8, which suggests that the activation processes involve the breaking of hydrogen bonds and the formation of more stable hydrogen bonds, similar to the previous systems β-CD and β-CD/t-butylbenzylic alcohol (β-CD/TERB) [7]. The activation energies as calculated from the Arrhenius equation (4)

$$\tau = \tau_0 \exp(-E/RT) \tag{4}$$

by plotting ln τ against $1/T$ for the linear regions on either side of the transition temperature of β-CD·TRIMO and β-CD·TRIDI in both hydration forms are listed in Table I. The activation energies of TRIMO16.2 and TRIDI16.4 have absolute values close to 5 kJ/mol in the range 1.98–

Table 1. Activation energies and transition temperatures of the β-CD complexes β-CD·TRIMO and β-CD·TRIDI in two hydration forms

Sample	$T_{\text{transition}}$ (K)	$E(T < T_{\text{transition}})$ (kJ/mol)	$E(T > T_{\text{transition}})$ (kJ/mol)
TRIMO16.2	230	3.79	−7.31
TRIMO10.7	216	1.81	−1.85
TRIDI16.4	216	4.91	−6.29
TRIDI 10.5	216	1.68	−2.37

$3.82 k_B T_{\text{transition}}$ a value higher than the corresponding value of ~2.5 kJ/mol of β-CD and β-CD·TERB, indicating that the association among the molecules of the complexes of TRIMO16.2 and TRIDI16.4 is more stable. The activation energies of TRIMO10.7 and TRIDI10.5 are similar to those of β-CD and β-CD.TERB [7].

The thermal hysteresis observed in all systems examined is a result of the H-bond transformation discussed above. Therefore, it appears in a temperature range approximately from 170 K to 270 K, i.e., around the order–disorder transition temperature. The area enclosed by the two curves (cooling, heating), Figures 3 and 4, that is, the area of the hysteresis loop, is proportional to the energy dissipated within the material. The thermal hysteresis of this type makes these materials valuable as thermal absorbers in the appropriate temperature range.

Conclusions

The dielectric behavior of complexes TRIMO16.2, TRIMO10.7, TRIDI16.4 and TRIDI10.5 are described well by Debye-type relaxation (α-dispersion). All systems except TRIMO10.7 exhibit an additional Ω-dispersion at low frequencies ($f < 1000$ Hz) which is probably due to ionic conductance.

The fact that only one-step was found in the ϵ' vs. T plots indicates that the water molecules cannot be divided into strongly bound molecules or easily movable molecules as was found for the systems β-CD, β-CD.TERB [7] and (α-CD)$_2$·Cd$_{0.5}$·I5.26H$_2$O [9].

The transition temperature of TRIMO16.2 is 214.5 K, whereas that of TRIMO10.7, TRIDI16.4 and TRIDI10.5 is the same, viz. 202.7 K. This means that the order–disorder transformation process was unaffected by the dehydration process in the case of TRIDI10.5, whereas in the case of TRIMO10.7 it was unexpectedly facilitated, since the transition temperature decreased from 214.5 K to 202.7 K, probably because of a lower stabilization of primary hydroxyl groups.

The activation energies of TRIMO16.2 and TRIDI16.4 have absolute values of ~5 kJ/mol in the range 1.98-$3.82 k_B T_{\text{transition}}$ and are higher than the corresponding values of ~ 2 kJ/mol of β-CD and β-CD·TERB, indicating that the molecules of the complexes studied here associate more strongly. The activation energies of TRIMO10.7 and TRIDI10.5 are similar to those of β-CD and β-CD·TERB [7].

A thermal hysteresis appears, in both complexes and in both hydration forms, as a result of the order-disorder transformation.

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References

1. S. Makedonopoulou, I.M. Mavridis, K. Yannakopoulou, and J. Papaioannou: *J. Chem. Soc. Chem. Commun.* 2133 (1998).
2. S. Makedonopoulou, J. Papaioannou, I. Argyropoulou, and I. Mavridis: *J. Incl. Phenom. Macrocycl. Chem.* **36**, 191 (2000).
3. S. Makedonopoulou: *Structure Determination of Cyclodextrin Complexes with X-ray Diffraction*, Ph.D., University of Athens (1999).
4. S. Makedonopoulou, A. Tulinsky, and I.M. Mavridis: *Supramol. Chem.* **11**, 73 (1999).
5. D. Mentzafos, I.M. Mavridis, G. Lebas, and G. Tsoucaris: *Acta Crystallogr.* **B47**, 746 (1991).
6. S. Makedonopoulou and I.M. Mavridis: *Acta Crystallogr.* **B56**, 322 (2000).
7. J. Papaioannou, N. Papadimitropoylos, and I.M. Mavridis: *Mol. Phys.* **97**, 611 (1999)
8. J. Papaioannou, N. Papadimitropoylos, and K. Viras: *Mol. Phys.* **99**, 239 (2001).
9. T. Ghikas and J. Papaioannou: *Mol. Phys.* **100**, 673 (2002)
10. C. Betzel, W. Saenger, B.E. Hingerty, and G.M. Brown: *J. Am. Chem. Soc.* **106**, 7545 (1984).
11. V. Zabel, W. Saenger, and S.A. Mason: *J. Am. Chem. Soc.* **108**, 3664 (1986).
12. P. Debye: *Polar Molecules*, Chemical Catalog Company Inc., New York, pp. 77ff. (1929).
13. C.P. Smyth: *Dielectric Behavior and Structure*, New York , McGraw-Hill (1955).
14. K. Bhattacharyya, and B. Bagchi: *J. Phys. Chem. A* **104**, 10603 (2000)