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Dipole relaxation and proton transport in polycrystalline γ -cyclodextrin hydrate: A dielectric spectroscopy study

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ABSTRACT

The polycrystalline γ -cyclodextrin hydrate (γ -CD·12.2H₂O) has been investigated via dielectric spectroscopy over a frequency range of 0-100 kHz and the temperature ranges of 108.0-298.5 K (cooling) and 109.0-433.0 K (heating). At T < 250.0 K, the electrical properties of the sample accept a great contribution from the flip-flop proton orientational disorder and a much lesser one from the positional fluctuations of the water molecules. Moreover, a strong synergy is observed between the stability of the γ -CD molecules and the dynamic disorder of the infinite flip-flop chains. This type of disorder disappears upon cooling ($T_{trans} = 186.7$ K) and reappears upon heating ($T_{\text{trans}} = 194.5$ K). At T>250.0 K, the dielectric permittivity ε' and loss ε'' increase abruptly due to the proton dc-conductance of y-CD·12.2H₂O which has been interpreted in terms of a theoretical model (Pnevmatikos, 1988) being consistent with the generation of ionic defects and their combination with the dipole reorientations in a collective motion of soliton-type. The influence of the simultaneous dehydration process on this charge transport mechanism relies on the very sensitive balance between the diffusive motion of water molecules (exchange between symmetry related positions) and their removal from the crystal lattice. The Arrhenius semiconductive behavior of the ac-conductivity in the ranges of 257.1–313.2 K ($E_a = 0.42 \text{ eV}$) and 331.2–385.1 K ($E_a = 0.39$ eV) implies the dominance of water diffusion which conserves the structural integrity of the endless hydrogen-bonded chains and the proton transfer along them. The limited decrease of the acconductivity from 313.2 to 331.2 K along with its rapid decrease above 385.1 K, indicates that the removal of the water molecules rules out their diffusive motion. The Cole–Cole diagrams (ε'' vs. ε') make clear that during the heating process the grain boundary polarization gradually becomes more significant than the grain interior one. In the range of 348.0-385.1 K, the constrictive grain boundary resistances are totally eliminated allowing the extensive proton transport through the grains of the polycrystalline specimen.

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1. Introduction

Cyclodextrins (CDs) are doughnut-shaped macrocyclic maltooligosaccharides that consist of D-glucose units which exhibit ${}^{4}C_{1}$ chair conformation and are interconnected via $\alpha(1,4)$ linkages [1]. Their central cavity is hydrophobic as a result of the existing C(3)H, C(5)H hydrogen atoms and the ether-like O(4), O(5) oxygen atoms, whereas their periphery is hydrophilic due to the primary (O(6)H) and secondary (O(2)H, O(3)H) hydroxyl groups that are located in their narrow and wide rim, respectively. The smallest members of the family which are composed of six (α -CD), seven (β -CD), and eight (γ -CD) D-glucose units can act as hosts to a series of suitably-sized inorganic and organic guest components in solution as well as in solid state. Because of their fascinating ability to form a vast variety of stable inclusion complexes, cyclodextrins present numerous practical applications not only in industry [2–4] (pharmaceutics, foodstuffs, cosmetics etc.) but also in the intriguing fields of environmental protection [5], diagnostics [6], catalysis [7], chromatography [8] and supramolecular chemistry in general.

Interestingly enough, apart from the enormously large number of cyclodextrin inclusion complexes that have shown unique properties of potential usefulness, the non-complexed cyclodextrins which are crystallized from pure water have also proven to be of great significance. More explicitly, the single crystal X-ray and neutron diffraction analyses of α -CD [9–11], β -CD [12–14] and γ -CD [15–18] hydrates have revealed that some of the co-crystallized water molecules occupy positions in the CD cavities while the rest are located in the interstices between the neighboring CD-molecules. As a consequence, high density hydrogenbonding networks are produced and their extent has been found to increase in the order α -CD< β -CD< γ -CD due to the increment of both the number of CD hydroxyls and the degree of hydration per CD molecule in the same order. Nevertheless, it is worth mentioning that in most cases these complicated structural schemes do not constitute highly ordered arrangements but exhibit a considerable degree of disorder. This behavior stems from the fact that the involved H₂O

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molecules and – OH groups display various energy contents reflecting differences in the corresponding local environments. Therefore, it becomes apparent that the crystalline CD hydrates, besides being regarded as "frozen molecular conformations" of the CD flexible structures in aqueous solutions [13,19], further comprise reliable models for a profound understanding of the proton fluctuations in the proximity of many biomacromolecules relating to human life (e.g. proteins and DNA) [20,21].

Being complementary to the fundamental crystallographic techniques, dielectric spectroscopy emerges as a powerful tool for an indepth study of the dipolar rotational motions and orientational correlations in the crystalline lattice of CD hydrates. The dielectric measurements of β -CD hydrate by other researchers [22] as well as of α -CD and β -CD hydrates by our group [23,24] have detected all the phase transitions that are associated with changes in the dynamic properties of the water molecules and the CD hydroxyl groups. More thoroughly, the isothermal (fixed temperature) and isochronal (fixed frequency) experimental data of α -CD and β -CD hydrates have revealed the following issues: (i) at temperatures lower than ~230.0 K, the former system displays no order-disorder transition of the existing hydrogen bonds and consequently no important variation of its dielectric permittivity (ε') and loss (ε''); (ii) on the contrary, the latter system exhibits considerable order-disorder phenomena below ~230.0 K being consistent with concerted proton reorientations that make a great contribution to the relevant dielectric properties; (iii) both the dielectric permittivity (ε') and loss (ε'') of these two systems increase rapidly above ~230.0 K due to the rise of the dc-conductivity which involves extensive proton transfer. Moreover, it should be emphasized that our recent dielectric investigations (in combination with FT-Raman and thermal analysis methods) on a series of hydrated metal-polyiodide inclusion complexes of α -CD and β -CD have also proven to be very rewarding [25–32]. To the best of our knowledge, the present work comprises the first dielectric relaxation study of γ -CD hydrate in the solid state. Our main aim is to shed light on the dipole relaxation and ionic conduction mechanisms of this intriguing system which exhibits a much more complicated H-bonding network than those of α -CD and β-CD hydrates.

2. Experimental

2.1. Synthesis and characterization

 γ -CD was purchased from Sigma-Aldrich (purity>99.0). For the preparation of the corresponding hydrate, 4.8 g of γ -CD was added into 20 mL of distilled water at room temperature and the solution was gradually heated to ~70 °C under continuous stirring (full dissolution) [15,18]. Afterwards, the beaker (50 mL) containing the saturated solution was covered with a Teflon cap and it was immersed in a Dewar flask (500 mL) filled with hot water (~70 °C). After three days (slow cooling), γ -CD hydrate crystals had grown displaying uniform composition. These were isolated by filtration and dried in air.

Simultaneous thermogravimetry (TGA) and differential thermal analyses (DTA) of the obtained crystals were conducted using a METTLER TOLEDO STAR SYSTEM. The sample (30.75 mg) was placed in an open aluminum pan and both the variation of its weight and the relevant endothermic transitions were recorded during heating from 25 to 500 °C with a heating rate of 5 °C min⁻¹.

For the X-ray powder diffraction (XRPD) method, a few grams of γ -CD hydrate were finely hand-pulverized aiming at reducing the greater volume fraction of certain crystal orientations (texture) in the powdered sample. The experimental XRPD pattern was obtained with a Siemens D 5000 diffractometer using CuKa1,Ka2 radiation ($\lambda = 1.54059$ Å, 1.54439 Å) at 40 kV, 30 mA and a graphite crystal monochromator. The diffraction data were collected at room temperature covering the 2 θ range of 5–40° with a constant step of 0.015° and a dwell time of 5 s/step.

2.2. Dielectric relaxation spectroscopy (DRS)

For the dielectric spectroscopy experiment a pressed pellet of powdered sample (593.0 mg), 20 mm in diameter with thickness 1.08 mm was prepared with a pressure pump (Riken Powder model P-1B) at room temperature. Two platinum foil electrodes were pressed at the same time with the sample. The pellet was then loaded into a temperature-controlled chamber, between two brass rods accompanied by a compression spring. The electrical measurements were taken using a low-frequency (0-100 kHz) dynamical signal analyzer (DSA-Hewlett-Packard 3561A) at the temperature ranges of 108.0–298.5 K (cooling) and 109.0-433.0 K (heating). In order to avoid possible "shock-freezing" of the reoriented dipoles [14], the cooling process was accomplished via the very slow flow of liquid nitrogen, whereas concerning the rate of the heating process it was controlled via the use of a reliable electrical resistance heater. The obtained data can be transferred to a PC through an HP 82335 Interface Bus (IEEE-488), where they can be stored and analyzed by a software program (2plt-1996). The complex permittivity ε^* , impedance Z^* , conductivity σ^* along with the phase shift φ and the respective Argand diagrams (ε'' versus ε' and Z'' versus Z') can be calculated and plotted as a function of both temperature and applied frequency. An analytical description of the process is given in previous articles [23,25].

3. Results and discussion

The TGA and DTA curves of the γ -CD hydrate from ambient temperature to 500 °C (heating rate: 5 °C min⁻¹) are shown in Fig. 1. The two step weight loss of 14.40% over the temperature range of ~28-140 °C (inset in Fig. 1) implies a two step dehydration process being consistent with ~12.2 co-crystallized water molecules per y-CD molecule (general composition γ -CD \cdot 12.2H₂O). The degree of hydration found in our work is lower than the four different degrees of hydration which have been reported to date for solid γ -CD hydrate (γ-CD·13.3H₂O, γ-CD·14.1H₂O, γ-CD·15.7H₂O, and γ-CD·17H₂O, respectively) relying on the data obtained from detailed crystallographic investigations [15-18]. These variations in water content conform to an uncertainty concerning the exact hydration number of the "fully" hydrated γ -CD paralleling the case of β -CD hydrate [33–36]. More specifically, as regards β -CD hydrate (monoclinic $P2_1$) two nearly identical clathrates have been determined by means of X-ray and neutron diffraction techniques which are described as β -CD \cdot 12H₂O [12] and β -CD · 11H₂O [13,14], respectively. The discrepancy of one water



Fig. 1. Simultaneous thermogravimetry (TGA) and differential thermal analyses (DTA) of γ -CD·12.2H₂O from 25 to 500 °C (heating rate: 5 °C min⁻¹). The inset clearly shows that the progressive dehydration (28–140 °C) involves two steps being associated with the loss of 7.41% (2.28 mg) and 6.99% (2.15 mg) of the total sample weight (30.75 mg), respectively.

molecule per β -CD has been ascribed to the different statistical distribution of the disordered water molecules mainly in the corresponding host cavities, reflecting inaccuracies in structural analyses and strong influence of both crystallization conditions and history of the crystals [13]. In relation to the latter factor the single crystal X-ray diffraction studies of β -CD hydrate crystals (not in contact with mother liquor) at a range of ambient humidities (between 15% and 78%) have revealed a gradual decrement of the unit cell volume with decreasing humidity due to the continuous loss of water molecules which is associated with a fast diffusion process through the lattice [33,36]. The specific crystal packing arrangement has been found to remain intact in the "normal" humidity range and to collapse irreversibly below 15% humidity (heterogeneity in the sample), whereas the dehydration has proven to affect to a greater extent the intra-cavity water molecules than the inter-cavity ones. These conclusions have been further vindicated via solid state NMR experiments [34,35].

According to the aforementioned issues, the fact that in the current research the water content of the crystalline γ -CD hydrate is lower than those described in the relevant literature [15–18] can now be explained. More explicitly, in all four structure determinations that have been conducted so far for γ -CD hydrate (monoclinic $P2_1$) the crystals were sealed in thin glass capillaries along with a trace of mother liquor aiming at preventing dehydration [15–18]. Such a treatment makes sense having in mind the case of β -CD hydrate where the insertion of partially dehydrated crystals (exposed to atmosphere-"dry" material) into the saturated solvent resulted in their complete re-hydration ("fully" hydrated material) [33,36]. In view of this, the crystallographically demonstrated differences in the degrees of hydration of the "fully" hydrated γ -CD materials [15–18] seem to exclusively emerge from variations on the employed method of crystal growth and some inaccuracies in structural analyses. In the present study, the isolation of the synthesized γ -CD hydrate crystals from the mother liquor through filtration as well as their exposure to air (drying process) clearly indicates that they have suffered dehydration to a certain extent something that justifies their comparatively low hydration state. However, despite the partial dehydration observed, the crystal structure of the sample has retained its main characteristics. This becomes evident from the experimental X-ray powder diffraction pattern of γ -CD \cdot 12.2H₂O at ambient temperature (Fig. 2) which exhibits well-distinguishable Bragg reflections at positions (2θ angles) identical to those of the reflections in the theoretical pattern of γ -CD·14.1H₂O calculated from the corresponding single crystal data by Bettinetti et al. [37]. The relative reflection intensities in the current pattern differ from the corresponding ones in the simulated one [37] as a result of: i) the variance in the relevant hydration states which indicates that the cocrystallized water dipoles of these systems are neither expected to



Fig. 2. X-ray powder diffraction pattern of γ -CD · 12.2H₂O at ambient temperature.

display equivalent lattice positions/occupancies nor exactly the same H-bonding schemes, and ii) an inevitable though little contribution of preferred orientation effects (texture).

The conserved crystal packing arrangement (monoclinic $P2_1$) is in agreement with a herringbone motif of γ -CD molecules (Fig. 3) which in contrast to the respective motif of β -CD hydrate [12–14] leads to the formation of intermolecular interstitial narrow channels along the crystallographic *b*-axis [15–18]. These channels are further connected with the γ -CD cavities (on their narrow O(6) ends) and appear to play a fundamental role in the long range mobility of the water molecules during dehydration. As regards the latter process, the present thermal analysis measurement (Fig. 1) reveals that it consists of two welldefined steps with temperature rise. The first step involves a weight loss of 7.41% (~6.2 H₂O) in the range of ~28-67 $^{\circ}$ C, whereas the second step involves a weight loss of 6.99% (~6 H₂O) in the range of ~67–140 °C. These results cannot be interpreted in terms of a separate removal of intra-cavity and inter-cavity water in the first and second steps, respectively [34] since the dehydration of CD hydrates has proven to be assisted by both the enclosed H₂O molecules and the interstitial ones (albeit not to the same extent) [33,36]. What can be stated here is that the first step corresponds to the loss of the H₂O molecules with a higher energy content than that of the H₂O molecules whose loss is responsible for the second step. Furthermore, it has been experimentally shown that between the "fully" hydrated and dehydrated forms of γ -CD there is an intermediate form described as γ -CD·7H₂O [34,37,38]. The X-ray powder diffraction pattern of this form is characterized by the disappearance or attenuation of certain reflections that exist in the pattern of the "fully" hydrated form (Fig. 2) and the appearance of new reflections clearly suggesting a different crystal structure [37,38]. In our work, a very similar intermediate form arises (γ -CD·6H₂O) when the first step of dehydration becomes completed (Fig. 1) supporting important changes in phase relating to heterogeneity effects. At higher temperatures, the total loss of the water content occurs resulting in the substantial disruption of the stacking order of γ -CD molecules and the highly decreased crystallinity of the sample (amorphous state) [34,38]. The enormous weight loss above 274 °C (Fig. 1) is attributed to the decomposition of γ -CD molecules [37].



Fig. 3. The crystal packing arrangement of γ -CD molecules in γ -CD·12.2H₂O viewed along the crystallographic *a*-axis and based on the X-ray and neutron diffraction studies of the γ -CD·17H₂O [15], γ -CD·14.1H₂O [17], and γ -CD·15.7D₂O [18] single crystals. The gray curved line highlights the narrow intermolecular interstitial channel along the *b*-axis.

The phenomena described above are further elucidated via the employment of dielectric relaxation spectroscopy (DRS) which enables valuable insights into the dipole relaxation and ionic conduction mechanisms that are related to the phase transitions within polycrystalline γ -CD hydrate. The experimental data obtained were analyzed in terms of the complex permittivity ε^* , the phase shift φ (or phase angle) and the complex conductivity σ^* . Complex permittivity ε^* is defined as follows [39–41]:

$$\varepsilon^*(f) = \varepsilon'(f) - j\varepsilon''(f), \tag{1}$$

where the real part ε' defines the capacitance of the sample, the imaginary part ε'' (loss factor) expresses the energy dissipation per cycle, *f* is the frequency of the applied electric field and $j = \sqrt{-1}$. Generally, the imaginary ε'' versus real ε' plots (named Cole–Cole or Argand plots) are used for the interpretation of all the relaxation processes that take place in the systems under investigation. In the rare case of a single relaxation time τ , a perfect semicircle is formed (Debye relaxation) whose center is localized on the real axis. The complex permittivity of a Debye-type ideal material is described by the expression [42]:

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + j\omega\tau},\tag{2}$$

where ε_s is the static permittivity, ε_{∞} the permittivity at high frequencies, and $\omega = 2\pi f$ the angular frequency. When there is a distribution of relaxation times, a semicircular arc appears (Cole–Cole relaxation) having its center lying below the real axis. In that case, the complex permittivity can be described by the Cole–Cole formalism [42,43]:

$$\varepsilon^*(\omega) = \varepsilon_{\omega} + \frac{\varepsilon_s - \varepsilon_{\omega}}{1 + (j\omega\tau)^{1-\alpha}},\tag{3}$$

where α represents a measure of the distribution of relaxation times. Concerning the phase difference φ (also known as phase shift or phase angle) between the applied voltage $V^*(t)$ and the resulting current $I^*(t)$ it is given by the relation [42]:

$$\phi = \tan^{-1} \left(\frac{\varepsilon''(f)}{\varepsilon'(f)} \right),\tag{4}$$

while the complex conductivity σ^* is represented by the following expression [40]:

$$\sigma^*(f) = \sigma'(f) + j\sigma''(f), \tag{5}$$

being related to the complex permittivity ε^* as [40,41]:

$$\sigma^*(f) = j\omega\varepsilon_0\varepsilon^*(f),\tag{6}$$

where ε_o is the dielectric permittivity of free space (8.854 · 10⁻¹² F/m). Furthermore, it has been often reported that the bulk ac-conductivity σ of a disordered solid can be expressed as the sum of two independent terms [44]:

$$\sigma(\omega) = \sigma_{dc} + \sigma'(\omega), \tag{7}$$

where σ_{dc} is the dc-conductivity and $\sigma'(\omega) = \omega \varepsilon''(\omega) \varepsilon_o$ the frequency dependent conductivity which is related to localized hopping motions in the sample.

At low frequencies ($\omega\tau \ll 1$) there is negligible phase lag between the applied field and molecular orientation indicating that the orienting torque in the crystal lattice is not effectively hindered by the existing frictional forces [45]. For this reason, the temperature dependencies of the real (ε') and imaginary (ε'') parts of the dielectric constant over the range of 108.0–298.5 K (slow cooling) are investigated at the fixed



Fig. 4. Temperature dependence of the real part ε' of the dielectric constant of γ -CD·12.2H₂O during the cooling process at a fixed frequency of 300 Hz.

frequency of 300 Hz (Figs. 4 and 5) in order to achieve a better overall understanding concerning the underlying relaxation processes. As the temperature is gradually lowered, the real part ε' exhibits a rapid decrease up to 252.5 K followed by an extended sigmoid curve with an inflection point $\varepsilon' = 6.28$ at T = 186.7 K. The imaginary part ε'' abruptly drops up to 252.5 K further displaying a well-distinguishable bellshaped curve with peak value $\varepsilon''_{max} = 0.74$ at T = 186.7 K. The sigmoid and bell-shaped curves in $\varepsilon'(T)$ and $\varepsilon''(T)$ variations, respectively, are characteristic of a dipolar reorientation process, whereas the highly increased values of both ε' and ε'' above 252.5 K are indicative of the dcconductance of γ -CD \cdot 12.2H₂O [22]. The interconnection between these two mechanisms becomes evident from the frequency variation of ε' and ε'' at selected temperatures during the cooling process (Figs. 6 and 7). At ambient temperature (298.5 K) the real part ε' presents a very low value at 10⁵Hz which seems to result from very rapid polarization processes in the crystals. As the frequency decreases, ε' increases in a sigmoid fashion displaying a well-defined plateau in the range of ~ 10^3 – 10^4 Hz and an enormous rise below 10^3 Hz. During cooling from 298.5 to 108.0 K, the high frequency value of ε' essentially remains invariant, the height of the sigmoid curve continuously decreases whereas the observed rise in the low frequency range becomes highly attenuated at 270.7 K and disappears at lower temperatures. It is worth noting, that at 179.5 and 200.4 K the upper plateau of the sigmoid curve exhibits an inclination being consistent with a slight increment of ε'



Fig. 5. Temperature dependence of the imaginary part ε'' of the dielectric constant of γ -CD·12.2H₂O during the cooling process at a fixed frequency of 300 Hz.



Fig. 6. Frequency dependence of the real part ε' of the dielectric constant of γ -CD·12.2H₂O at seven different temperatures during the cooling process.

towards 10^2 Hz. The frequency variation of the imaginary part ε'' at 298.5 K, displays a broad dielectric loss peak at high frequencies and an abrupt increase at low frequencies. This behavior resembles that of a series of polycrystalline hydrated proteins whose dielectric studies have revealed two types of dielectric dispersion. The high frequency loss peak, designated as α -dispersion, has been associated with charge carriers that hop between localized sites [45–48], whereas the low frequency rise, designated as Ω -dispersion, has been assigned to space charge polarization emerging from accumulation or electrochemical generation of protons at the sample/electrode interfaces [48,49]. From 298.5 to 108.0 K, what becomes obvious is the total disappearance of the Ω -dispersion along with the gradual attenuation of the α -dispersion that is further accompanied by small shifts to lower frequencies in the range of 108.0–200.4 K.

It is well known that α -dispersion is centered at the characteristic frequency f_{max} which is related to the most probable relaxation time τ as [45]:

$$\tau = \frac{1}{\omega} = \frac{1}{2\pi f_{\text{max}}}.$$
(8)

The position shifts of the α -dispersion in Fig. 7 imply variations of the relaxation time as a function of temperature. Aiming at gaining additional information on the hydrogen bond dynamics in γ -CD hydrate we have calculated the relaxation time for each temperature value in the



Fig. 7. Frequency dependence of the imaginary part ε'' of the dielectric constant of γ -CD·12.2H₂O at seven different temperatures during the cooling process.



Fig. 8. Temperature dependence of the most probable relaxation time τ of γ -CD·12.2H₂O during the cooling process.

range of 108.0–298.5 K (Fig. 8) using Eq. (8). The corresponding f_{max} values have been determined by fitting the local maximum of the loss peaks over a short frequency range. The absolute values of τ vary between 6.1 μ s and 7.7 μ s in contrast to the case of β -CD hydrate in our previous investigation [23] where the values of τ were found to vary between 8.0 µs and 11.5 µs. This difference indicates that the water network presents a higher degree of disorder in γ -CD hydrate than in β -CD hydrate something that has already been proven by the detailed deuterium NMR study of both materials [50]. This work has further demonstrated reorientational rates that are comparable to those obtained from our dielectric data. The increase of the relaxation time auin the range of 186.7-247.3 K conforms to an ordering effect as the temperature is lowered. However, from 186.7 to 148.8 K au continuously decreases revealing an increase of the lattice disorder. This peculiar behavior makes sense taking into consideration that proteins as lysozyme and collagen have been surprisingly found to display an increase of the relaxation time with increasing temperature indicating a negative activation enthalpy [51,52]. The activation entropy has been also determined to be negative suggesting that the activation process involves breaking of a hydrogen bond between the protein and a water molecule followed by the formation of more stable hydrogen bonds between the reorienting water molecule and its neighbors. Inversely in the current research, the decrease of τ upon cooling may result from the perturbation of strong hydrogen-bonding interactions and the subsequent formation of weaker ones due to temperature induced changes in the specific structural characteristics of the existing hydrogen bond geometries.

Comparison of the γ -CD hydrate crystal structure at 295.0 K [17] with the one at 110.0 K [18] provides the basis for a profound interpretation of the dielectric properties described above. On one hand, the X-ray diffraction study of γ -CD \cdot 14.1H₂O at 295.0 K by Harata [17] has shown that all glucose units are well-ordered whereas 7.1 water molecules are located in the γ -CD cavity being distributed over 14 positions and 7 water molecules are located outside the γ -CD cavity being distributed over 9 positions, 5 of which are fully occupied. On the other hand, the detailed neutron diffraction analysis of γ -CD · 15.7D₂O at 110.0 K by Ding et al. [18] has demonstrated that 1 glucose unit (G8) is somewhat disordered as a whole, while 8.8 water molecules are hosted in the γ -CD cavity being disordered and distributed over 17 positions. The rest 6.9 water molecules are located in 8 interstitial sites, 5 of which are fully occupied. In Fig. 9 we display a representation of the asymmetric unit in the crystal structure of γ -CD·15.7D₂O based on the relevant crystallographic investigation [18] where the water sites outside the γ -CD cavity have been labeled W1–W7 and the water sites inside the γ -CD cavity have been labeled



Fig. 9. Representation of the asymmetric unit of γ -CD·15.7D₂O based on the relevant single crystal neutron diffraction study at 110.0 K carried out by Ding et al. [18]. The researchers have labeled the water sites (here depicted as gray spheres) outside the γ -CD cavity W1–W7 and those inside the γ -CD cavity W8–W18. The symbols A and B are indicative of alternative lattice positions.

W8-W18 (A and B comprise alternative positions). Ding et al. have further managed to carry out a valid correlation between the low temperature water sites in their work and the ambient temperature water sites reported in Harata's contribution [17]. More specifically, they have verified that 6 interstitial water sites (W1–W5, and W7) and 10 intra-cavity water sites (W8, W9A, W10A, W11A, W12, W13B, W14, W16, W17A, and W18) of γ -CD \cdot 15.7D₂O at 110.0 K exhibit identical lattice positions and similar occupancy factors (with prominent differences in very few cases) with certain water sites of γ -CD·14.1H₂O at 295.0 K. Furthermore, they have maintained that due to the severe disorder of the water molecules in the γ -CD cavity only 5 D atom positions could be unambiguously assigned. These findings make clear that as the temperature is lowered no substantial ordering of the water molecules takes place in contrast to β -CD·11D₂O [14] and β -CD·ethanol·8D₂O [53] materials, both of which presented a complete ordering of their co-crystallized water molecules upon cooling to 120.0 and 15.0 K, respectively. However, despite the fact that the water molecules of γ -CD \cdot 15.7D₂O do not order during the cooling process the unit cell volume surprisingly undergoes a very large shrinkage of 3.5% [18] which is comparable to the respective cell volume shrinkages that have been observed for β -CD·11D₂O (2.8%) and β -CD·ethanol·8D₂O (3.5%) due to solvent-ordering effects. We strongly believe that the most plausible rationalization of this discrepancy is the significant attenuation of extensive proton transport mechanisms that seem to dominate the lattice dynamics of γ -CD hydrate and become evident from our dielectric measurements.

The gradual decrease of ε' in an extended sigmoid fashion from 252.5 to 108.0 K (Fig. 4) as well as the relaxation peak of ε'' over the same temperature range (Fig. 5) is ascribed to the disorder–order transition ($T_{\text{trans}} = 186.7$ K) of the existing flip-flop hydrogen bonds to those of normal type according to the following scheme:

Flip-flop hydrogen bonds have been originally detected in the single crystal of β -CD·11H₂O at 293.0 K by means of high resolution neutron

diffraction analysis conducted by Betzel et al. [13]. Interestingly enough, this work has revealed that out of the 53 H-bonds per asymmetric unit, 35 are of normal type $(O-H\cdots O-H)$ whereas, 18 comprise an average over two alternative states $(0-H\cdots 0) \leftrightarrow (0\cdots H-0)$. For the latter bond type, the term "flip-flop" has been introduced by the researchers since the involved H atoms are dynamically disordered changing positions (rather by rotation) from one state to the other in a concerted mode whereas, the oxygen atoms act as "fixed centers". The two H atom sites are energetically nearly equivalent (entropically favored) presenting similar occupational parameters (~0.5) and $H \cdots H$ separation in the range of 0.86–1.15 Å. These hydrogen bonds have been found to form complicated motifs that include circular arrangements and infinite chains running through the whole crystal. Their dynamic nature has been verified by the detailed neutron diffraction study of β -CD \cdot 11D₂O at 120.0 K [14] which apart from the ordering of the water network it has further proven that, 14 out of the 18 flip-flop H-bonds are transformed into normal ones. The remaining flip-flop bonds constitute a fourmembered ring which is positioned at the junction of several homodromic rings and infinite chains highlighting an energetic advantage at 120.0 K over an entropy advantage at ambient temperature. Not only have these sound results been consistent with preliminary calorimetric measurements of β -CD \cdot 11H₂O [54], but they have also been validated from molecular dynamics simulations of this crystalline system at 293.0 and 120.0 K [55,56]. In the present case, the disorder-order transition of the flip-flop bonds appears to be exclusively responsible for the enormous attenuation of the α -dispersion in Fig. 7 showing that the orientational disorder of H atoms affects the dielectric behavior of γ -CD hydrate to a much greater extent than the positional disorder of water molecules (which is retained upon cooling). Pathmanathan et al. have reached the same conclusion as regards the dielectric properties of solid β -CD hydrate [22]. The progressive ordering of flip-flop hydrogen bonds takes place over a wide temperature range as it is demonstrated by the gradual increase of the relaxation time τ from 247.3 to 186.7 K (Fig. 8). The transition temperature (T_{trans}) of 186.7 K implies that below this value all (or the greatest percent) of dynamically disordered H atoms have been transformed into well-ordered ones. Moreover, it should be noted that according to the quasielastic neutron scattering study of β -CD·11H₂O, the rates of both the rotational jumps and positional fluctuations in the crystal lattice range between 10^{10} and 10^{11} s⁻¹ [57]. The fact that in the current research the respective rates range between 10^5 and 10^6 s⁻¹ (correlating well with NMR experiments [50]) may be attributed to a coupling of fast local motions to slower collective ones [58].

The decrease of τ from 186.7 to 148.8 K is consistent with the formation of flexible structural schemes that seem to succeed the disorder-order transition of the flip-flop bonds. Such a consideration is further supported by some temperature-induced differences that have been traced in the conformation of γ -CD molecules and the associated hydrogen-bonding interactions. The X-ray structural analysis of γ -CD·14.1H₂O at 295.0 K [17] has shown that the γ -CD molecules display the shape of a nearly regular octagon consisting of well-ordered glucose units that adopt the ${}^{4}C_{1}$ chair conformation. The C(6) – O(6) bonds of glucoses 1, 5 and 8 are also well-ordered ((+) gauche orientation), the C(6) - O(6) bond of glucose 6 is twofold disordered ((+) gauche/(-) gauche), whereas no intramolecular hydrogenbonding exists between the O(2)H hydroxyl of glucose 7 and the O(3) H hydroxyl of glucose 8. Moreover, most of the γ -CD hydroxyl groups are hydrogen bonded to interstitial water molecules. On the contrary, the neutron diffraction study of γ -CD \cdot 15.7D₂O at 110.0 K [18] has revealed that the γ -CD molecules do not constitute rigid octagons. This is because glucose 1 is distorted highly deviating from the ideal chair conformation and presenting a threefold disordered C(6) - O(6) bond ((+) gauche major orientation) while glucose 8 is somewhat disordered as a whole requiring diffraction data of higher resolution for the accurate determination of the relevant atomic positions. Additionally,

the C(6) - O(6) bonds of glucoses 5 and 6 are well-ordered ((+) gauche and (-) gauche, respectively), the O(3)D hydroxyl of glucose 8 donates a hydrogen bond to the O(2)D hydroxyl of glucose 7, whereas the γ -CD hydroxyl groups interact not only with interstitial water molecules but with 11 out of the 17 intra-cavity water sites as well. These findings suggest a strong synergy between the flip-flop hydrogen-bonding network in the crystal lattice and the stability of the γ -CD macrocycles. When the disorder-order transition of the former is completed, the latter ones progressively adopt a conformation of higher energy being consistent with the gradual attenuation of certain hydrogen bond geometries. This phenomenon is expected to be assisted by changes in the diffusive motion of some disordered water molecules with temperature indicating that the resulting partially occupied sites exhibit weaker coordination schemes. At this point, we avoid any further discussion since the hydrogen-bonding networks of CD hydrates comprise too complicated structures (usually numerous three-center or even four-center H-bonds are present [14,18,53,59]) to be interpreted in detail. However, it is obvious that the transition of flip-flop hydrogen bonds to those of normal type is followed by an increase in the disorder of particular dipolar moieties. The sequence of these two effects is also confirmed by the frequency variation of ε' at selected temperatures during cooling (Fig. 6). More specifically, the small increment of ε' towards 10^2 Hz (inclination of the upper plateau) at 200.4 K (slightly above $T_{\text{trans}} = 186.7$ K) as well as at 179.5 K (slightly below $T_{\rm trans} = 186.7$ K) conforms with the existence of disordered dipoles of reduced energy that stay better aligned with the applied electric field at low frequencies. At 200.4 K, the reorientational motions of H atoms (flip-flops) have significantly slowed down justifying such a behavior. Similarly at 179.5 K, the perturbation of strong hydrogen-bonding interactions and the formation of weaker ones have already begun and the electric field affects the orientation of the involved dipoles to an important extent until they possess a higher degree of disorder at lower temperatures. This becomes evident at 140.2 and 108.0 K where the inclination of the upper plateau of the ε' (log*f*) sigmoid curve has totally disappeared. Furthermore, we clarify that the γ -CD hydrate does not seem to retain any flip-flop arrangements upon cooling contradicting the behavior of β -CD hydrate. The dielectric study of the latter system by Pathmanathan et al. [22] has not only detected a loss peak of ε'' at 209.8 K which has been ascribed to the disorder-order transition of the flip-flop bonds but also a second loss peak at 109.0 K which has been correlated with the frozen-in disorder of proton motions in the remaining four-membered flip-flop ring [14]. Similar results have been obtained from our recent dielectric investigation of the α -cyclodextrin polyiodide inclusion complex (α -CD)₂·Sr_{0.5}·I₅·17H₂O where the main loss peak of ε'' at 173.7 K (flip-flop transition) has been found to be accompanied by a second one at 128.8 K [32]. In the present case, even though the disorder of water molecules is conserved during cooling, no loss peak of ε'' is observed in the range of 108.0–140.0 K (Fig. 5) and this fact indicates the absence of any local flip-flop networks along with the dominance of proton orientational disorder over the water positional disorder concerning the macroscopic polarizability of the sample.

For a deep insight into the dc-conductance properties of γ -CD·12.2H₂O we rely on the proton mobility mechanisms that have been suggested for the polarization and conduction of ice crystals [60–68]. The hexagonal ice structure (I_h) comprises a well-defined hydrogen-bonding network that follows the Bernal–Fowler rules [69]. Violation of these rules leads to the spontaneous formation of Bjerrum and ionic defects. The Bjerrum defects (orientational defects) result from the rotation of successive water molecules in such a way that one doubly occupied bond (O–H···H–O, D-defect) and one vacant bond (O···O, L-defect) are generated. As regards ionic defects, these originate from the proton jump between two neighboring water molecules and the formation of one hydroxyl ion (OH[–], I[–] defect) and one hydronium ion (H₃O⁺, I⁺ defect). Pnevmatikos [70] as well as Tsironis and

Pnevmatikos [71] have proposed a reliable atomic model that describes simultaneously the Bjerrum and ionic defect generation and propagation in guasi one-dimensional hydrogen-bonded systems using soliton properties. More specifically, the rotation of a proton from a certain O-O bond to the vicinal one and the hopping of a proton from one equilibrium position of the hydrogen bond to the other are combined in a collective motion that can be interpreted in terms of soliton-like dynamics. Under the influence of a dc-electric field even though the defects with positive effective charge (D, I⁺) and negative effective charge (L, I⁻) propagate to opposite directions the propagation of protons in both cases takes place in the same direction. The success of this model lies in the detailed explanation of the non-transient proton conductivity in one-dimensional hydrogen-bonded systems. Interestingly, Nylund et al. [72] have suggested that the aforementioned model can be also used for the elucidation of proton conduction in twodimensional hydrogen-bonded systems such as CD hydrates. This can be better understood having in mind that despite the fact that the high symmetry constraints that exist in ice and ice clathrates are not traced in β - and γ -CD hydrates [13], the proton orientational disorder of the former materials [60,73] strongly resembles the flip-flop disorder that has been observed for the latter ones. Accordingly, Pathmanathan et al. [22] have shown that the activation energy relating to the disorderorder transition of the existing flip-flop bonds in β -CD \cdot 11H₂O is in good agreement with the activation energies of Bjerrum-defects in ice clathrates and glassy water [74,75]. Moreover, the dielectric relaxation study of ice [63] has demonstrated the characteristic Debye correlation time of $\sim 10^{-5}$ s at 263 K which has been further confirmed via NMR measurements [76] and is directly comparable to the relaxation time values reported in the current research. In view of these aspects, the polarization/conductivity mechanisms in ice and y-CD · 12.2H₂O appear to be very similar and consequently the high values of the $\varepsilon'(T)$, $\varepsilon''(T)$ variations above 252.5 K (Figs. 4 and 5) and the Ω -dispersion of the ε'' (log f) variation at low frequencies (Fig. 7) arise from the continuous proton transport along the infinite flip-flop chains that run through the whole crystal lattice. This process is consistent with the combination of ionic and orientational defects to a collective motion of soliton type. Below ~252.5 K the ionic defects diminish and the orientational ones seem to dominate the lattice dynamics up to the point where the disorder-order transition of the flip-flop bonds to those of normal type becomes completed.

While the phase transitions of γ -CD·12.2H₂O as the temperature is lowered are of considerable interest, the disorder properties that appear upon heating are equally appealing. This is because the respective dielectric data apart from vindicating the origin and reversibility of the already detected dynamic phenomena during the cooling process also address the influence of the progressive dehydration on the underlying charge transport mechanisms; this particular issue has been neglected so far in the dielectric studies of α - and β -CD hydrates [22–24]. From 109.0 to 254.3 K, the real part ε' increases in an extended sigmoid fashion with inflection point $\varepsilon' =$ 6.43 at T = 194.5 K (Fig. 10) whereas the imaginary part ε'' displays a well-distinguishable bell-shaped curve with peak value $\varepsilon''_{max} = 0.74$ at T = 194.5 K (Fig. 11). These experimental features are related to the order–disorder transition of some normal hydrogen bonds to those of flip-flop type according to the following scheme:

0—H…0—H	\rightarrow	0—H…H—O	(10)
(normal H – bonds)		(flip - flop H - bonds).	(10)

The transition temperature ($T_{\text{trans}} = 194.5$ K) is slightly higher than the corresponding one found for the inverse disorder–order transition of the flip-flop bonds ($T_{\text{trans}} = 186.7$ K) implying a limited thermal hysteresis effect [25,77]. Above ~254.3 K, the dc-conductivity of γ -CD·12.2H₂O is activated and both ε' and ε'' gradually adopt very high values that have no significance in the conventional dielectric sense [78]. For this reason, we focus on the temperature dependencies



Fig. 10. Temperature dependence of the real part ε' of the dielectric constant of γ -CD-12.2H₂O during the heating process at a fixed frequency of 300 Hz.

of the phase shift φ (Fig. 12) and the ac-conductivity σ (Fig. 13) over the whole range of 109.0–433.0 K. The topical minimum of the $\varphi(T)$ variation at T=194.5 K (φ_{\min} =83.2°) along with the bell-shaped curve (a) of the ln $\sigma(1/T)$ variation is attributed to the order–disorder transition of some normal hydrogen bonds to flip-flop ones. From 257.1 to 313.2 K, the phase shift drops rapidly to 67.4° whereas, the ac-conductivity exhibits the linear part (b) obeying the following Arrhenius expression [79–81]:

$$\sigma = \sigma_{\rm o} \exp\left[-\frac{E_a}{kT}\right],\tag{11}$$

where activation energy $E_a = 0.42 \text{ eV}$, σ_o the pre-exponential factor, k the Boltzmann's constant and T the absolute temperature. This semiconductive behavior results from the generation of ionic defects and their coupling with the reoriented protons to a collective motion of soliton type along the endless hydrogen-bonded chains of the crystals. However, in the narrow range of 313.2–331.2 K, both the small increment of the phase shift to the value of 69.1° and the deviation of the ac-conductivity from the Arrhenius law, reflect the perturbation of the aforementioned proton transport mechanism. This can be explained in terms of the simultaneous dehydration which despite the fact that it begins at ~301.0 K according to the thermal analysis data (Fig. 1) its influence on the underlying proton mobility effects seems to become strong between 313.2 and 331.2 K. From 331.2 to 385.1 K, the phase



Fig. 11. Temperature dependence of the imaginary part ε'' of the dielectric constant of γ -CD-12.2H₂O during the heating process at a fixed frequency of 300 Hz.



Fig. 12. Temperature dependence of the phase shift ϕ of γ -CD·12.2H₂O during the heating process at a fixed frequency of 300 Hz.

shift presents a remarkable decrease to the value of 27.8° while the acconductivity displays the linear part (c) with activation energy $E_a = 0.39$ eV. These experimental features clearly indicate that the protonic conductivity of γ -CD·12.2H₂O is further amplified. In the range of 385.1–404.5 K, the phase shift and the ac-conductivity show an enormously abrupt increase and decrease, respectively, since the continuous removal of the water molecules from the crystal lattice comprises the predominant mechanism leading to the rupture of the extended hydrogen-bonding networks and the consequent elimination of proton conduction. The slight decrease of φ above 404.5 is mainly ascribed to the remaining γ -CD hydroxyl groups (the decomposition of γ -CD macrocycles occurs at T>547.0 K according to Fig. 1) which possess high thermal energy and are expected to undergo very rapid proton transfer processes.

The conditions under which the dehydration and proton transport become interconnected can be fully comprehended by careful inspection of the specific dynamic characteristics of crystalline CD hydrates. More explicitly, the single crystal X-ray diffraction study of β -CD hydrate at a wide range of ambient humidities (15–78%) by Steiner and Koellner [36] has revealed that during the dehydration process the water molecules rapidly diffuse through the lattice although there are no permanent continuous channels. Molecular dynamics simulations by Koehler et al. [55,56] have proven that the vibrational motions of the C and O atoms of β -CD macrocycles result in the transient formation of narrow diffusion paths which allow the fast diffusion of water molecules. Additionally, Steiner et al. [82] have carried out the



Fig. 13. Temperature dependence of the ac-conductivity σ (ln σ vs. 1/*T*) of γ -CD-12.2H₂O during the heating process at a fixed frequency of 300 Hz.

assessment of H_2O/D_2O and $H_2^{16}O/H_2^{18}O$ exchange effects in crystalline β-CD hydrate by means of Raman spectroscopy and mass spectrometry, respectively. In both experiments, the relevant exchange processes have been found to be complete exhibiting comparable rates and implying a permanent internal transfer of protons and of intact water molecules. As the authors report this means that a particular water molecule "experiences" many H-(or D)-transfer processes as it "travels" between adjacent asymmetric units. In relation to this, the in-depth solid state NMR investigations of β -CD hydrate by Ripmeester [35] as well as of β - and γ -CD hydrates by Usha and Wittebort [50] have proven that water diffuses through the crystal lattice by exchanging among symmetry related crystallographic positions. Therefore, in our case it appears to be explicit that by the initiation of the dehydration process (~301.0 K) the concomitant diffusional jumps of the water molecules between adjacent asymmetric units are highly correlated. This dynamic averaging which involves both the intra- and inter-cavity water molecules [32,50] is expected to be much more favored in the γ -CD hydrate than in the β -CD one since the herringbone motif of γ -CD molecules (Fig. 3) includes intermolecular interstitial channels (these are absent in the structure of β -CD hydrate [12–14]) that are directly connected with the γ -CD cavities. In the light of this, the endless hydrogen-bonded chains of the crystal lattice seem to undergo structural transitions (rapid water exchange) which leave them as whole entities unchanged retaining the already described proton transport mechanism along them. Such a consideration presupposes that the time of transit of the water molecules is much shorter than the time of their residence in the respective chain positions [50]. As it becomes apparent, the water diffusion does not contribute directly to the increment of the ac-conductivity as the phenomenon its self but rather indirectly by conserving the structure and proton mobility effects of the infinite hydrogen-bonded chains that run the crystals. In view of this, the calculated activation energy $E_a = 0.42$ eV of the linear part (b) in the $\ln\sigma(1/T)$ variation (Fig. 13) does not correspond exclusively to the diffusion of orientational and ionic proton defects [83,84] but further incorporates the energy required for the associated water diffusional jumps. The deviation of the ac-conductivity from the Arrhenius semiconductive behavior in the range of 313.2-331.2 K makes clear that the influence of the dehydration on the dielectric properties of γ -CD \cdot 12.2H₂O relies on the very sensitive balance between the diffusive motion of water molecules and their removal from the crystal lattice. In the above temperature range, the latter process dominates the former one causing discontinuities along the chain lengths and attenuation of the proton conduction. It is believed that the greatest percent of the crystal water which is expelled at this stage belongs to the intra-cavity spaces where there is larger freedom of the water molecules (higher energy) in comparison to the interstitial channels [17,18,85]. The linear part (c) of the ac-conductivity above 331.2 K indicates that the water diffusion becomes the predominant mechanism again. The calculated activation energy $E_a = 0.39$ eV apart from being related to the transfer of protons and water molecules also accepts a large contribution from the energy required for the following transformation [25–32]:

$$(H_2O)_{tightly bound} \rightarrow (H_2O)_{easily movable},$$
(12)

which most of the interstitial water molecules undergo. At room temperature, the majority of the water molecules which reside in the interstices of the crystal lattice are neatly coordinated with fully occupied positions (tightly bound state) [17]. During heating they become disordered (easily movable state) exhibiting extensive diffusional jumps between adjacent asymmetric units. This phenomenon restores the structural integrity of the hydrogen-bonded chains giving new rise in the ac-conductivity (linear part (c)) up to 385.1 K. At higher temperatures, the removal of the water molecules from the sample completely rules out their diffusive motion resulting in the rapid drop of the ac-conductivity.

The variation of the most probable relaxation time τ as a function of temperature is shown in Fig. 14. Each value has been estimated from the maximum of the respective ε'' (logf) loss peak using Eq. (8). In the range of 109.0–306.5 K, the relaxation time varies between 6.1 and 7.7 µs presenting an increase from 148.2 to 197.8 K due to the breaking of weak hydrogen bonds and the formation of more stable ones [51,52] as well as a decrease from 197.8 to 254.3 K which is ascribed to the order-disorder transition of some normal hydrogen bonds to flip-flop ones. Above 306.5 K, τ increases rapidly to the value of 8.5 µs at 331.2 K as a result of the dehydration process which has already begun at ~301.0 K (Fig. 1) and progressively perturbs the concerted dipole reorientation along the endless hydrogen-bonded chains. Moreover, we believe that the increase of au may also be assisted by the conformational rearrangements of the γ -CD macrocycles which succeed the removal of the intra-cavity water molecules [34]. At T>331.2 K, the values of the relaxation time could not be validly determined since the corresponding ε'' (logf) loss peaks became disfigured due to the extensive lattice disorder. Thus, we turn our attention to the Cole–Cole diagrams (ε'' vs. ε') [42] which provide access to qualitative information on the dielectric relaxation properties of γ -CD · 12.2H₂O even at very high temperatures (Fig. 15a–d).

The depressed semicircle at 109.0 K (Fig. 15a) is consistent with a distribution of relaxation times further indicating that the complex permittivity ε^* can be described by the Cole–Cole formalism (Eq. (3)). This semicircle corresponds to the polarization mechanism in the bulk grain interior and its small missing part at high frequencies emerges from the frequency limitation of the equipment used here, which can measure only up to 10^{5} Hz. In the wide range of 109.0–181.5 K, the diameter of the semicircle displays a limited increase implying that the degree of lattice disorder increases to a small extent. This is because the thermal energy gain of the positionally disordered water molecules upon heating is effectively counterbalanced by the disruption of less favorable hydrogen bond geometries and the formation of more favorable ones similarly to the case of solid hydrated proteins such as lysozyme and collagen [51,52]. As this process takes place, the disorder of the involved dipoles progressively diminishes and consequently they can stay better aligned with the applied field at low frequencies. This explains not only the appearance of the linear spike in the low frequency region of the ε'' vs. ε' semicircle at the temperatures of 139.8, 160.6, and 181.5 K but also the inclination of the upper plateau of the corresponding ε' (log f) sigmoids in the inset of Fig. 15a. From 181.5 to 222.7 K, the diameter of the semicircle increases more rapidly due to the orderdisorder transition of some normal hydrogen bonds which begins at $T_{\text{trans}} = 194.5 \text{ K}$ and gradually induces an extensive degree of flip-flop disorder in the crystal lattice. Initially (slightly above T_{trans}), the energy of the reoriented protons is relatively low and therefore their alignment



Fig. 14. Temperature dependence of the most probable relaxation time τ of γ -CD·12.2H₂O during the heating process.



Fig. 15. Cole–Cole diagram (ε" vs. ε') of γ-CD·12.2H₂O: a) at six different temperatures during heating from 109.0 to 222.7 K with the inset depicting the corresponding ε' (log*f*) variation over the same range, b) at five different temperatures during heating from 242.0 to 322.0 K, c) at four different temperatures during heating from 331.2 to 385.1 K, and d) at three different temperatures during heating from 402.6 to 433.0 K.

with the applied field is evident from the low frequency spike of the semicircle at 201.5 K and the upper plateau inclination of the respective ε' (log f) sigmoid (inset in Fig. 15a). However, at 222.7 K the orientational disorder of protons has increased leading to the disappearance of both the aforementioned experimental features. In the range of 242.0–322.0 K (Fig. 15b), apart from the semicircle relating to the grain interior contribution a second semicircle is generated (~263.2 K) at low frequencies which is also depressed and becomes well-distinguishable at higher temperatures. This semicircle is assigned to the dc-conductance of protons which pile-up at the grain boundaries of the sample giving rise to a relaxation mechanism under the applied electric field (Maxwell-Wagner) [86,87]. This phenomenon is directly related to the Ω -dispersion of the ε'' (log *f*) variation (Fig. 7) that has been detected during the slow cooling of the crystals. As the temperature is raised to 322.0 K, the ratio of the low frequency to the high frequency semicircle diameter continuously increases revealing that the grain boundary polarization appears to be more significant than the grain interior one upon heating. At 322.0 K, the low frequency semicircle is accompanied by a linear response which is almost vertical to the real axis and corresponds to the sample/electrode interface polarization. This behavior can be better understood taking into consideration the two-path model suggested by Lilley and Strutt [88] for the ion transport through the grain boundaries of polycrystalline specimens. According to this model, there are easy path connection points across the grain boundaries which require the same activation energy as the motion in the bulk and path connection points that require higher activation energy than the bulk. The appearance of the linear response at very low frequencies shows that a certain percent of protons passes through the former path connection points of the adjacent grain boundaries and is gradually accumulated on the sample/electrode interface. The transport of the rest protons across the sample is hindered by the latter path connection points retaining the grain boundary semicircle. In the range of 331.2–385.1 K (Fig. 15c), it is obvious that this semicircle progressively disappears whereas the linear response becomes more intense. These facts conform to the rapid elimination of the constrictive grain boundary resistances and the extensive diffusion of protons through the grains of γ -CD hydrate. Above 385.1 K, the removal of the water molecules from the crystal lattice dominates resulting in the decomposition of the endless hydrogen-bonded chains and the attenuation of the proton conduction. For this reason, from 402.6 to 433.0 K (Fig. 15d) the diameter of the grain interior semicircle decreases while the linear response vanishes. The total loss of the water content strongly perturbs the stacking order of the γ -CD molecules leading to an amorphous state [34,36]. The appearance of the low frequency arc in Fig. 15d may be attributed to the constraints imposed by the collapse of the crystalline structure on the local proton transfer mechanisms between the remaining γ -CD hydroxyl groups.

4. Concluding remarks

The polycrystalline γ -cyclodextrin hydrate (γ -CD·12.2H₂O) comprises a reliable model for the dipole relaxation and proton transport in many hydrated biological structures. At temperatures lower than ~250.0 K, the dielectric behavior of this system is affected to a great extent from the flip-flop proton orientational disorder and to a lesser extent from the positional fluctuations of the crystalline water molecules. The dynamic disorder of the infinite flip-flop chains gradually disappears upon cooling ($T_{\text{trans}} = 186.7 \text{ K}$) and reappears upon heating ($T_{\text{trans}} = 194.5 \text{ K}$) whereas, a strong synergy is observed between this type of disorder and the stability of the γ -CD molecules. At temperatures higher than ~250.0 K, both the dielectric permittivity ε' and loss ε'' rise abruptly due to the dc-conductance of the sample. The interpretation of this phenomenon has been based on a theoretical model which is consistent with the generation of ionic defects and their combination with the reoriented protons in a collective motion of soliton-type. This model correlates well with the frequency variation of the dielectric loss ε'' (α - and Ω -dispersion) in the present experimental work. As the temperature is raised, the effect of the progressive dehydration on the ac-conductivity σ relies on the very sensitive balance between the diffusive motion of water molecules and their removal from the crystal lattice. The former phenomenon involves rapid water exchange between symmetry related positions conserving the structure and proton mobility effects of the endless hydrogen-bonded chains. On the contrary, the latter phenomenon leads to the decomposition of the aforementioned chains and the important attenuation of proton conduction. In the ranges of 257.1-313.2 K and 331.2-385.1 K, the water diffusion dominates resulting in the continuous increment of the ac-conductivity which follows the Arrhenius law with activation energies 0.42 and 0.39 eV, respectively. The small decrease of σ from 313.2 to 331.2 K as well as its tremendous decrease above 385.1 K shows that the removal of the water molecules rules out their diffusive motion. Finally, the temperature-dependent Cole–Cole diagrams (ε'' vs. ε') apart from revealing a distribution of relaxation times for both the grain interior and grain boundary polarization mechanisms further support the coexistence of low and high activation energy path connection points for ion transport through the grain boundaries. Above 348.0 K, the grain boundaries become highly conductive leading to the free proton migration across the grains of the sample.

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References

- [1] J. Szejtli, Chem. Rev. 98 (1998) 1743.
- [2] C. Vaution, M. Hutin, F. Glomot, D. Duchêne, in: D. Duchêne (Ed.), Cyclodextrins and Their Industrial Uses, Editions de Santé, Paris, 1987, p. 299.
- [3] T. Loftsson, D. Duchêne, Int. J. Pharm. 329 (2007) 1
- [4] J. Szejtli, in: J.L. Atwood, J.E.D. Davies, D.D. MacNicol (Eds.), Inclusion Compounds, Vol. 3, Academic Press, London, 1984, p. 331.
- [5] J. Szejtli, Cyclodextrin Technology, Kluwer Academic Publisher, Dordrecht, 1988, p. 335.
- [6] J. Szejtli, Cyclodextrin Technology, Kluwer Academic Publisher, Dordrecht, 1988, p. 411.
- [7] Y. Wang, L. Mei, J. Biosci. Bioeng. 4 (2007) 345.
- [8] W.L. Hinze, Sep. Purif. Rev. 10 (1981) 159.
- [9] P.C. Manor, W. Saenger, J. Am. Chem. Soc. 96 (1974) 3630.
- [10] B. Klar, B.E. Hingerty, W. Saenger, Acta Crystallogr. Sect. B. B36 (1980) 1154.
- [11] K.K. Chacko, W. Saenger, J. Am. Chem. Soc. 103 (1981) 1708.
- [12] K. Lindner, W. Saenger, Carbohydr. Res. 99 (1982) 103.
- [13] Ch. Betzel, W. Saenger, B.E. Hingerty, G.M. Brown, J. Am. Chem. Soc. 106 (1984) 7545.
- [14] V. Zabel, W. Saenger, S.A. Mason, J. Am. Chem. Soc. 108 (1986) 3664.
- [15] J.M. MacLennan, J. Stezowski, Biochem. Biophys. Res. Commun. 92 (1980) 926.
- [16] K. Harata, Chem. Lett. (1984) 641.
- [17] K. Harata, Bull. Chem. Soc. Jpn. 60 (1987) 2763.
- [18] J. Ding, Th. Steiner, V. Zabel, B.E. Hingerty, S.A. Mason, W. Saenger, J. Am. Chem. Soc. 113 (1991) 8081.
- [19] J.E.H. Koehler, W. Saenger, W.F. van Gunsteren, Eur. Biophys. J. 15 (1987) 197.

- [20] G.A. Jeffrey, W. Saenger, Hydrogen Bonding in Biological Structures, Springer, Berlin, 1991.
- [21] M.G. Usha, R.J. Wittebort, J. Mol. Biol. 208 (1989) 669.
- [22] K. Pathmanathan, G.P. Johari, J.A. Ripmeester, J. Phys. Chem. 93 (1989) 7491.
- [23] J.C. Papaioannou, N.D. Papadimitropoulos, I. Mavridis, Mol. Phys. 97 (1999) 611.
- [24] J.C. Papaioannou, N.D. Papadimitropoulos, K. Viras, Mol. Phys. 99 (2001) 239.
- [25] V.G. Charalampopoulos, J.C. Papaioannou, Mol. Phys. 103 (2005) 2621.
- [26] V.G. Charalampopoulos, J.C. Papaioannou, H.S. Karayianni, Solid State Sci. 8 (2006) 97.
- [27] J.C. Papaioannou, V.G. Charalampopoulos, P. Xynogalas, K. Viras, J. Phys. Chem. Solids 67 (2006) 1379.
- [28] V.G. Charalampopoulos, J.C. Papaioannou, K.E. Tampouris, Solid State Ionics 178 (2007) 793.
- [29] V.G. Charalampopoulos, J.C. Papaioannou, Carbohydr. Res. 342 (2007) 2075.
 [30] V.G. Charalampopoulos, J.C. Papaioannou, G. Kakali, H.S. Karayianni, Carbohydr. Res. 343 (2008) 489
- [31] V.G. Charalampopoulos, J.C. Papaioannou, Solid State Ionics 179 (2008) 565.
- [32] V.G. Charalampopoulos, J.C. Papaioannou, K. Viras, H.S. Karayianni, G. Kakali, Supramol. Chem. 22 (2010) 499.
- [33] Th. Steiner, G. Koellner, S. Ali, D. Zakim, W. Saenger, Biochem. Biophys. Res. Commun. 188 (1992) 1060.
- [34] S.J. Heyes, N.J. Clayden, C.M. Dobson, Carbohydr. Res. 233 (1992) 1.
- [35] J.A. Ripmeester, Supramol. Chem. 2 (1993) 89.
- [36] Th. Steiner, G. Koellner, J. Am. Chem. Soc. 116 (1994) 5122.
- [37] G. Bettinetti, Cs. Novak, M. Sorrenti, J. Therm. Anal. Calorim. 68 (2002) 517.
- [38] Y. Nakai, K. Yamamoto, K. Terada, A. Kajiyama, I. Sasaki, Chem. Pharm. Bull. 34 (1986) 2178.
- [39] J. Liu, C.-G. Duan, W.-G. Yin, W.N. Mei, R.W. Smith, J.R. Hardy, Phys. Rev. B 70 (2004) 144106.
- [40] M.M. Ahmad, K. Yamada, T. Okuda, Solid State Commun. 123 (2002) 185.
- [41] J.R. Macdonald, Impedance Spectroscopy, Wiley, New York, 1987, p. 1.
- [42] K.S. Cole, R.H. Cole, J. Chem. Phys. 9 (1941) 341.
- [43] A.K. Jonscher, J. Mater. Sci. 13 (1978) 553.
- [44] A.K. Jonscher, M.S. Frost, Thin Solid Films 37 (1976) 267.
- [45] R. Pethig, Annu. Rev. Phys. Chem. 43 (1992) 177.
- [46] P.R.C. Gascoyne, R. Pethig, J. Chem. Soc., Faraday Trans. 77 (1981) 1733.
- [47] S. Bone, J. Eden, R. Pethig, Int. J. Quantum Chem. Quantum Biol. Symp. 8 (1981) 307.
- [48] H. Morgan, R. Pethig, Int. J. Quantum Chem. Quantum Biol. Symp. 11 (1984) 209.
- [49] H. Morgan, R. Pethig, J. Chem. Soc., Faraday Trans. 82 (1986) 143.
- [50] M.G. Usha, R.J. Wittebort, J. Am. Chem. Soc. 114 (1992) 1541.
- [51] S.C. Harvey, P. Hoekstra, J. Phys. Chem. 76 (1972) 2987.
- [52] J.R. Grigera, F. Vericat, K. Hallenga, H.J.C. Berendsen, Biopolymers 18 (1979) 35.
- [53] Th. Steiner, S.A. Mason, W. Saenger, J. Am. Chem. Soc. 112 (1990) 6184.
- [54] T. Fujiwara, M. Yamazaki, Y. Tomizu, R. Tokuoka, K. Tomita, T. Matsuo, H. Suga, W. Saenger, Nippon Kagaku Kaishi 2 (1983) 181.
- [55] J.E.H. Koehler, W. Saenger, W.F. van Gunsteren, Eur. Biophys. J. 15 (1987) 211.
- [56] J.E.H. Koehler, W. Saenger, W.F. van Gunsteren, Eur. Biophys. J. 16 (1988) 153.
- [57] Th. Steiner, W. Saenger, R.E. Lechner, Mol. Phys. 72 (1991) 1211.
- [58] W. Doster, S. Cusack, W. Petry, Nature 337 (1989) 754
- [59] C. Ceccarelli, G.A. Jeffrey, R. Taylor, J. Mol. Struct. 70 (1981) 255.
- [60] L. Pauling, J. Am. Chem. Soc. 57 (1935) 2680.
- [61] N. Bjerrum, Science 115 (1952) 385.
- [62] R.P. Auty, R.H. Cole, J. Chem. Phys. 20 (1952) 1309.
- [63] H. Gränicher, C. Jaccard, P. Scherrer, A. Steinemann, Discuss. Faraday Soc. 23 (1957) 50.
- [64] H. Gränicher, Proc. R. Soc. London A. 247 (1958) 453.
- [65] R.K. Chan, D.W. Davidson, E. Whalley, J. Chem. Phys. 43 (1965) 2376.
- [66] A. von Hippel, D.B. Knoll, W.B. Westphal, J. Chem. Phys. 54 (1971) 134.
- [67] A. von Hippel, J. Chem. Phys. 54 (1971) 145.
- [68] G.P. Johari, J. Chem. Phys. 64 (1976) 3998.
- [69] J.D. Bernal, R.H. Fowler, J. Chem. Phys. 1 (1933) 515.
- [70] S. Pnevmatikos, Phys. Rev. Lett. 60 (1988) 1534.
- [71] G.P. Tsironis, S. Pnevmatikos, Phys. Rev. B 39 (1989) 7161.
- [72] E. Nylund, K. Lindenberg, G. Tsironis, J. Stat. Phys. 70 (1993) 163.
- [73] W.F. Kuhs, M.S. Lehmann, Nature 294 (1981) 432.
- [74] D.W. Davidson, in: F. Franks (Ed.), Water-A Comprehensive Treatise, Vol. 2, Plenum, New York, 1973, p. 115.
- [75] J.P. Johari, A. Hallbrucker, E. Mayer, Nature 330 (1987) 552.
- [76] R.J. Wittebort, M.G. Usha, D.J. Ruben, D.E. Wemmer, A. Pines, J. Am. Chem. Soc. 110 (1988) 5668.
- [77] J.C. Papaioannou, T.C. Ghikas, Mol. Phys. 101 (2003) 2601.
- [78] A.R. West, Solid State Chemistry and its Applications, Wiley, 1984, p. 534.
- [79] M.M. Ahmad, Solid State Ionics 177 (2006) 21.
- [80] S. Selvasekarapandian, R. Baskaran, M. Hema, Physica B 357 (2005) 412.
- [81] A. Dutta, T.P. Sinha, J. Phys. Chem. Solids 67 (2006) 1484.
 [82] Th. Steiner, A.M. Moreira da Silva, J.J.C. Teixeira-Dias, J. Müller, W. Saenger, Angew. Chem. Int. Ed. Engl. 34 (1995) 1452.
- [83] H. Gränicher, Physik Kondensierten Materie 1 (1963) 1.
- [84] C. Jaccard, Helv. Phys. Acta 32 (1959) 89.
- [85] G. Raffaini, F. Ganazzoli, Chem. Phys. 333 (2007) 128.
- [86] J.C. Maxwell, Electricity and Magnetism, Vol. 1, Oxford University Press, Oxford, England, 1873.
- [87] P.K. Larsen, R. Metselaar, Phys. Rev. B 8 (1973) 2016.
- [88] E. Lilley, J.E. Strutt, Phys. Status Solidi A. 54 (1979) 639.