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The effect of water and guest hydrophobicity on the complexation of oligomers with solid α-cyclodextrin

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Abstract

α-Cyclodextrin (α-CD), a cyclic oligosaccharide, can form inclusion complexes (ICs) with polymer molecules in which α-CD molecules stack in the columnar crystal to form a molecular tube. Physical mixtures of α-CD powder and oligomeric liquids such as poly(ethylene glycol) (PEG) have been shown to spontaneously form an IC, which is accompanied by a solid-state α-CD phase transformation from the cage to the columnar crystal structure. In this paper, the phase transformation is tracked with wide-angle X-ray diffraction as a function of temperature, atmospheric water vapor content and the type of guest molecule. A first-order kinetic model is used to describe the kinetics of complexation. The time required to completely complex PEG200 (200 g/mol) at low water activities is greater than 300 h, whereas only a few hours are necessary at high water activities. Solid-state complexation of α-CD with a hydrophobic guest molecule (hexatriacontane, HTC), is also reported here for the first time. Slower complexation kinetics are observed for α-CD with HTC compared to PEG600 (600 g/mol).

Keywords: α-Cyclodextrin; Inclusion complex; Phase transformation

1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides capable of forming inclusion complexes (ICs) with small molecules and macromolecules due to their hollow, truncated cone structure. CDs are most commonly composed of 6, 7, or 8 glucopyranose units, which correspond to α-, β-, and γ-CD, respectively. These molecules have a hydrophilic surface and a hydrophobic cavity in which various guest molecules can reside. CDs can exist in two general classes of crystal structures called cage and columnar [1]. In the cage structure (Fig. 1a), the CD cavities are not aligned but can still complex with small molecules such as methanol [2] and water [3]. In the columnar crystal (Fig. 1b), CDs stack on top of each other to form long cylindrical columns in which various chain-like guest molecules can be complexed [4–7].

Polymer/CD ICs are typically made by mixing CD solutions with solutions of low or high molecular weight polymers [4,5]. However, polymer/CD ICs have recently been made with CD in the undissolved state. Rusa et al. [8] suspended solid cage and columnar γ-CD particles in deuterated acetone solutions of poly(*N*-acylethylenimine) (PNAI). Using solution ^{1}H NMR spectroscopy, a reduction in proton peaks of the polymer molecules was observed over time as the polymer came out of solution and formed an IC with the γ-CD in the particles. A simultaneous build-up of water peaks in acetone was observed as a result of expulsion of water initially included inside the γ-CD cavities. They observed that PNAI with a higher molecular weight complexed to a greater degree than PNAI with lower molecular weight, though both were included with very similar kinetics. Particles of γ-CD in the cage structure must undergo a solid-state phase transformation to the columnar structure upon formation of the IC. Faster

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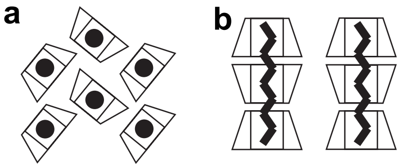

Fig. 1. Schematic representation of the packing of CD ICs within their crystal lattices: cage (a) and head-to-head columnar (b) structure.

complexation kinetics were observed when the suspended particles contained columnar γ-CD, since no solid-state phase transformation was necessary in that case.

Peet et al. [9] were able to obtain ICs of PEG and CD without any solvent. Liquid PEG having molecular weights of 200 or 400 g/mol was physically mixed with cage α-CD in a 2:1 ratio based on PEG repeat units per CD. During the complexation process α-CD transforms from the cage crystal to the columnar crystal to accommodate the PEG molecules. This conversion allowed X-ray diffractometry to be used to measure the complexation kinetics of PEG in α-CD. Similar work was reported by Harada et al. [10] which also showed that no change in α-CD particle morphology occured upon complexation.

Although Peet et al. [9] probed the temperature and molecular weight dependence of the PEG/α-CD phase transformation kinetics, they did not study the effect of water in the CD crystal. Water (i.e. relative humidity) is expected to be important in the complexation kinetics since it is a good solvent for both α-CD and PEG. In this paper, we report the effect of atmospheric water vapor on the PEG/α-CD complexation process. Parallel experiments were also carried out on hexatriacontane (HTC)/α-CD mixtures to understand the effect of guest hydrophobicity on complexation.

2. Experimental

2.1. Materials

The α-CD was purchased from Cerestar in powder form. HTC, PEG200 (200 g/mol) and PEG600 (600 g/mol) were purchased from Aldrich and used without further purification. PEGs and α-CD were vacuum-dried overnight at 50 °C to remove any absorbed water before use. Water was deionized with a Millipore Milli-DI system.

2.1.1. Wide-angle X-ray diffraction (WAXD)

WAXD measurements were performed using a Siemens type-F X-ray diffractometer with a Ni-filtered Cu-Kα radiation source ($\lambda = 1.54$ Å). The supplied voltage and current were 30 kV and 20 mA, respectively. The diffraction intensities were measured at every 0.1° from $2\theta = 10–25°$ at a rate of ($2\theta = 3°$)/min. The WAXD scans were obtained at room temperature, whereas the complexation experiments were conducted at 30 or 90 °C. To minimize the time spent outside of the humidity- and temperature-controlled environment, diffractograms were collected from $2\theta = 10–25°$, which includes all the peaks of interest. This yields a 5-min scan time which is very short compared to the time necessary for the complexation to finish (several hours at least).

Time-dependent experiments designed to track the phase transformation of α-CD were conducted at 30 °C with PEG200 and PEG600 mixed with α-CD in a 3:1 molar ratio (3 repeat units/α-CD molecule) and stored at various water activities (a). Samples were prepared by gently mixing liquid oligomer and solid CD in a mortar and pestle for approximately 1 min. A WAXD pattern was collected for this initial mixture which is defined as the start of the experiment ($t = 0$ h). The constant humidity chambers consisted of jars containing either pure deionized water ($a = 1$), dessicant ($a = 0$), or a saturated aqueous salt solution ($0 < a < 1$). The samples were removed from the humidity chambers at various times during the experiment and placed in the diffractometer to collect diffractograms as a function of time. The characteristic peaks for cage α-CD are centered at $2\theta = 12.0$ and 21.7°, which correspond, respectively, to the (031) and (331) planes with $d = 7.4$ and 4.1 Å [3]. Columnar α-CD has characteristic peaks at $2\theta = 13.0$ and 20.0°, which correspond to the (110) and (120) planes with $d = 6.8$ and 4.4 Å [6]. None of these d-spacings correspond in a simple way to the dimensions of an α-CD molecule. It should be mentioned that the peak assignments for the columnar structure are based on the analysis of an IC formed between α-CD and LiI_3/I_2 [6]. Although these peaks are commonly observed for other columnar α-CD ICs, a complete crystal structure determination has not been performed for the ICs studied in this paper since it is difficult to prepare large single crystals of the ICs. Thus, the same indexing assignments may not apply here.

For the HTC samples, α-CD and HTC powders were placed in a mortar and heated to 90 °C to ensure complete melting of HTC ($T_{melt} = 75$ °C). The components were then mixed in the hot mortar with a pestle also heated to 90 °C for approximately 1 min. A WAXD pattern was collected for this initial mixture which is defined as the start of the experiment ($t = 0$ h). The HTC/α-CD mixtures were removed from the humidity chambers at various times during the experiment and placed in the diffractometer to collect diffractograms as a function of time. To compare the results for HTC to PEG at the same temperature, similar experiments were conducted at 90 °C for PEG600/α-CD mixtures.

3. Results

Fig. 2 shows time-dependent X-ray diffraction patterns of a 3:1 (mol PEG repeat units/mol α-CD) mixture of PEG200 and α-CD which was complexed at a water activity of 1.0 and 30 °C. This ratio is 50 mol% in excess of the stoichiometric ratio [10] of 2:1 PEG repeat units per α-CD and corresponds to 13.6 wt% PEG. α-CD cage peaks are eliminated within 20 h while a gradual build-up of the columnar structure peak at $2\theta = 20°$ occurs. This provides clear evidence of a transformation from cage-to-columnar structure. The only mechanism by which cage α-CD converts to the columnar structure is through complexation/inclusion of PEG chains with/into α-CD cavities.

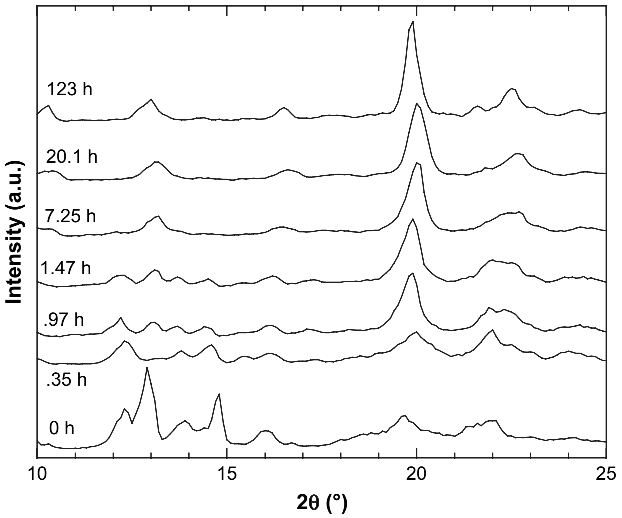

Fig. 2. Time-dependent diffractometer scans for a 3:1 mixture of PEG200 repeat units to α-CD complexed at $a = 1.0$ and 30 °C.

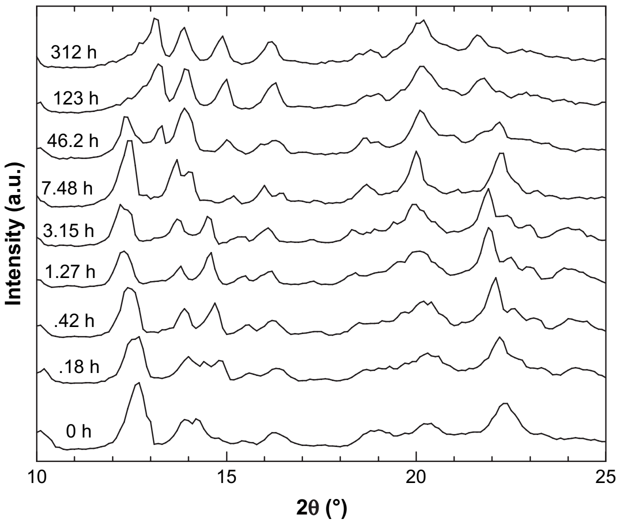

Fig. 4. Time-dependent diffractometer scans for a 3:1 mixture of PEG200 repeat units to α-CD complexed at $a = 0$ and 30 °C.

Mixtures of PEG200 and α-CD in a 3:1 molar ratio were also studied at activities of 0.8, 0.5, 0.1 and 0. WAXD patterns for the samples complexed at $a = 0.5$ and 0 are shown in Figs. 3 and 4, respectively. Conversion of cage to columnar α-CD is complete after approximately 23 h at $a = 0.5$ as indicated by the lack of change in peak intensities in Fig. 3 after this time. However, reflections for the cage structure persist for longer times at activities less than 0.8. This is illustrated in Fig. 4 which clearly shows that cage peaks remain after 45 h at $a = 0$ and 30 °C. Thus, a reduction in water activity slows the rate at which PEG complexes with α-CD and reduces the degree of conversion as well.

To quantify the rate of guest complexation, the integrated intensity of the columnar peak centered at $2\theta = 20°$ was used to identify the amount of IC present. Fig. 5 is a plot of the normalized integrated intensity of this columnar peak as a function of time at 30 °C for various samples. The presence of other small peaks that overlap with the $2\theta = 20°$ peak in some WAXD patterns may be partially responsible for the scatter in this data.

A first-order kinetic model has been used previously [9] to represent cage-to-columnar phase transformation data as shown in Fig. 5, and the same approach has been taken here. The rate of change of the peak intensity at $2\theta = 20°$ is assumed to be proportional to the amount of cage structure remaining in the sample. This is expressed as

$$\frac{\mathrm{d}I}{\mathrm{d}t} = k(I_\infty - I) \tag{1}$$

where I is the area of the peak at $2\theta = 20°$, I_∞ is the peak area at longer times, k is the rate constant and t is time. The solution to Eq. (1) is

$$I = I_\infty\left(1 - \mathrm{e}^{-kt}\right) \tag{2}$$

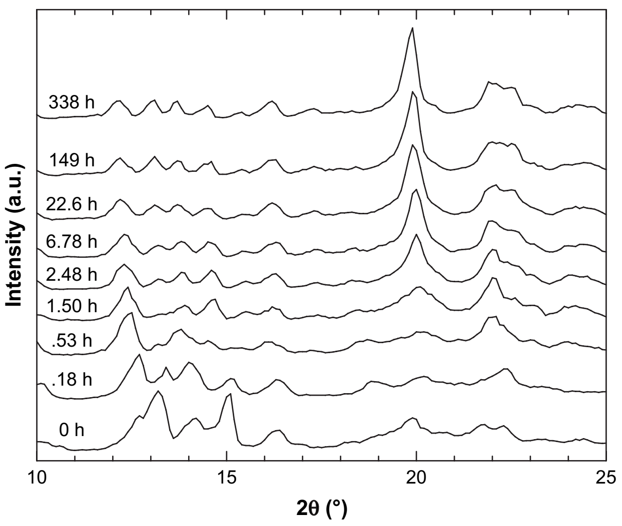

Fig. 3. Time-dependent diffractometer scans for a 3:1 mixture of PEG200 repeat units to α-CD complexed at $a = 0.5$ and 30 °C.

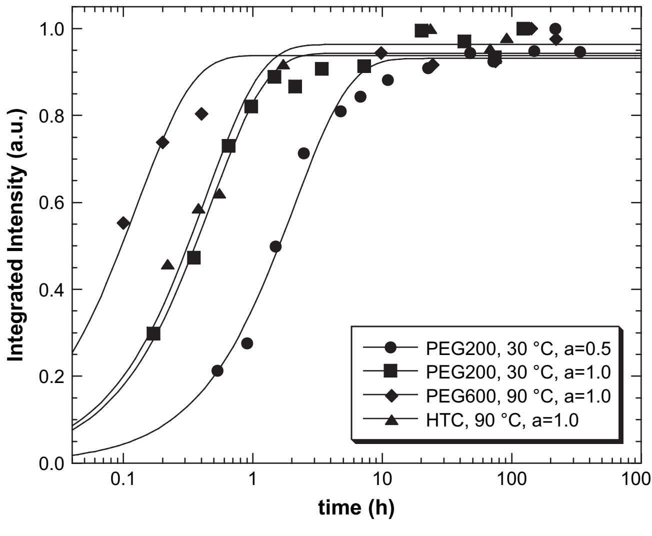

Fig. 5. Dependence of the normalized integrated X-ray intensities for the $2\theta = 20°$ columnar structure peak with time for several samples during complexation. The lines are fits of the first-order kinetic model to the data.

The solid lines in Fig. 5 represent fits to Eq. (2). This model assumes that the transformation occurs in one phase and is homogeneous. This is clearly not the case for these samples, so other kinetic models which account for the heterogeneous nature of the transformation were considered. Scanning electron micrographs (Fig. 6) show that many of the cage α-CD particles are lenticular in shape, thus the contracting cylinder rate law was tested which relates the surface area of the reaction front to the volume of unreacted material in each particle [11]. This model yields an expression in which I has a quadratic dependence on t. However, this model does not produce a plateau in I vs. t plots as observed experimentally (Fig. 5) and the quality of the fit to the data is not as good as the first-order model. Similarly poor results were obtained for the contracting sphere rate law [11]. Thus, we again adopt the first-order model here to represent the data and provide a convenient way to compare the complexation kinetics among the various samples. The parameters derived from the first-order fits are listed in Table 1.

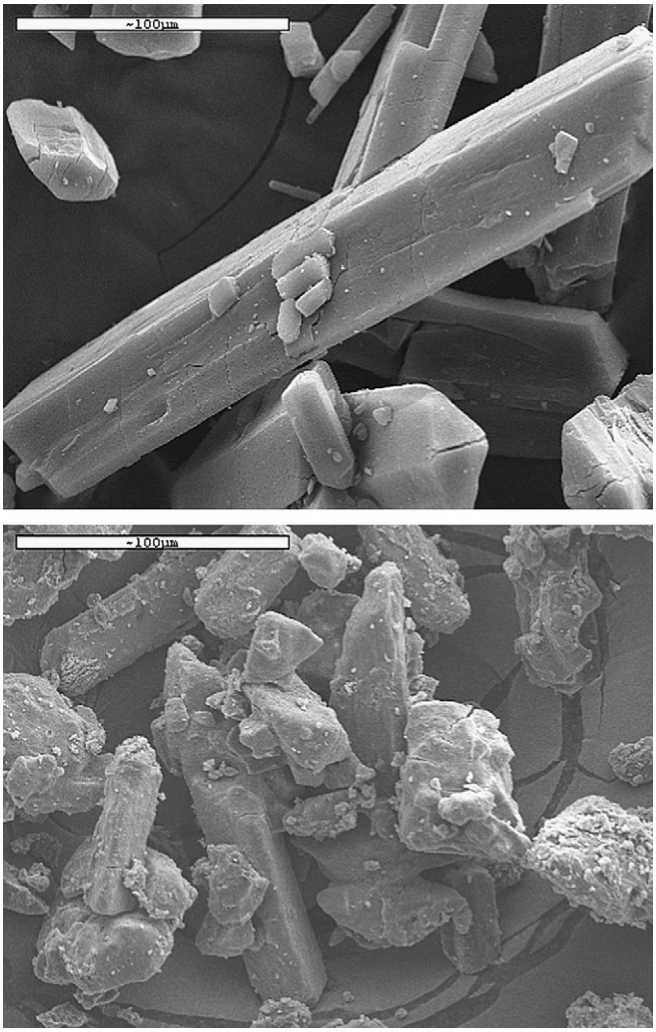

Fig. 6. Scanning electron micrographs at 500× for (a) as-received cage α-CD and (b) a 3:1 mixture of PEG200 repeat units to α-CD after complete complexation at 25 °C.

Table 1
Parameters for the first-order kinetic model

Guest molecule	Composition	Temperature (°C)	Water activity	k (h^{-1})	I_∞
PEG200	3:1[a]	30	0.5	0.48 ± 0.04[c]	0.93 ± 0.02[c]
PEG200	3:1	30	0.8	2.35 ± 0.21	0.96 ± 0.02
PEG200	3:1	30	1.0	2.11 ± 0.15	0.94 ± 0.01
PEG600	3:1	30	1.0	1.18 ± 0.17	0.93 ± 0.03
PEG600	3:1	90	1.0	7.88 ± 0.98	0.94 ± 0.02
PEG600	3:1	90	0.7	5.22 ± 0.81	0.96 ± 0.03
HTC	1:3.8[b]	90	1.0	2.33 ± 0.24	0.96 ± 0.03
HTC	1:3.8	90	0.7	2.76 ± 0.44	0.95 ± 0.03
HTC	1.9:1	90	1.0	3.77 ± 0.61	0.95 ± 0.03

[a] PEG repeat units/α-CD molar ratio.
[b] HTC molecules/α-CD molar ratio.
[c] Uncertainties in the parameters from the curve-fitting process.

It is clear from Table 1 that the rate of complexation as represented by k generally increases with decreasing molecular weight and with increasing water activity. The rate of transformation for PEG200 is almost twice the transformation rate of PEG600 in α-CD at $a = 1.0$ and 30 °C. The reduction in conversion rate with increasing guest molecular weight was observed by our group previously [9]. As the guest molecular weight increases, its diffusivity decreases and the probability of a chain end finding an α-CD cavity also decreases due to a reduction in the number of chain ends per unit mass of guest.

The effect of atmospheric water on complexation behavior is dramatic. In fact, the complexation rates at $a = 0$ and $a = 0.1$ are so low that formation of PEG200/α-CD IC does not reach completion after more than 300 h, whereas complete conversion is reached in a few hours at high water activities. The conversion rate at $a = 0.5$ is the lowest (Table 1) with $k = 0.48\ \text{h}^{-1}$. These low complexation rates are likely connected to the reduced degree of conversion at low water activities. The conversion rate for PEG200 at 30 °C reaches a limiting value at $a = 0.8$ within the parameter uncertainties shown in Table 1. This shows that the maximum effect of water on the complexation rate is reached at a water activity less than 1.0. Cage α-CD exists as a stable hexahydrate at 30 °C with two water molecules residing within each CD cavity and four water molecules outside [3]. This means that the water inside α-CD cavities must also be desorbed to allow inclusion of the guest molecules as the columnar crystal forms. As water activity increases, the driving force for desorption of the water in the α-CD cavities is reduced, which may explain the limiting effect of water on the transformation rate at activities above 0.8.

X-ray diffractograms for the complexation of a 3:1 mixture of PEG600 and α-CD at 90 °C are shown in Fig. 7. Increasing temperature not only increases the thermal energy of the molecules but also increases the maximum vapor pressure of water to 526 torr compared to 31.8 torr at 30 °C. At $a = 1$ and 90 °C, the PEG600/α-CD IC forms in less than 1 h and is completely converted, similar to PEG200/α-CD IC formation at $a = 1.0$ and 30 °C shown in Fig. 2. The absence of cage α-CD peaks in Fig. 7 is clear evidence that complexation is complete. A

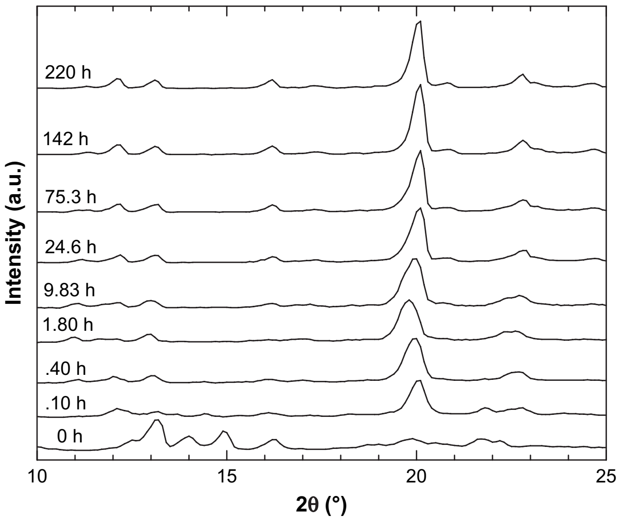

Fig. 7. Time-dependent diffractometer scans for a 3:1 mixture of PEG600 repeat units to α-CD complexed at $a = 1.0$ and 90 °C.

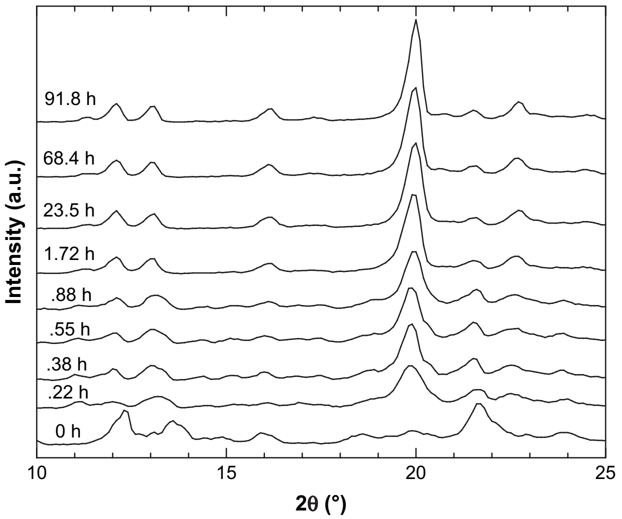

Fig. 8. Time-dependent diffractometer scans for a 1:3.8 mixture of HTC molecules to α-CD molecules complexed at $a = 1.0$ and 90 °C.

slight reduction in complexation rate is observed for PEG600/α-CD mixtures when the activity is reduced to 0.7 at 90 °C (Table 1).

Although the rate of complexation of α-CD with PEG200 is very low at low water activities, complexation occurs nonetheless as shown in Fig. 4. This is likely due to the ability of hydroxyl-terminated PEG to disrupt the hydrogen bonding network in the α-CD crystals as the PEG molecules diffuse into the α-CD particles. To test this hypothesis, similar studies were conducted with a hydrophobic guest molecule which has no inherent ability to hydrogen bond with α-CD molecules in the cage crystals.

HTC was chosen as the hydrophobic guest molecule because its conformation and all-trans end-to-end distance is similar to that of PEG600. Fully extended HTC is approximately 46 Å long while fully extended PEG600 is approximately 49 Å in length. Although the sizes of HTC and PEG600 are similar, the flexibility of PEG600 is higher because PEG600 has a higher conformational entropy than HTC [12]. This is reflected in their melting temperatures: 25 and 75 °C for PEG600 and HTC, respectively. To facilitate comparison, complexation of both HTC and PEG with α-CD was studied at 90 °C for water activities of 0.7 and 1.0. It should also be mentioned that as PEG600 chains move from their melt into the ∼5 Å channels of columnar α-CD, they not only lose more conformational entropy than HTC chains, but the energy of the included all-trans extended PEG600 conformation is higher than that for the HTC chains. From the sole perspective of the differences in their conformational characteristics, it must be concluded that PEG600 chains should be more difficult to confine in α-CD channels than HTC chains.

Composition for the HTC/α-CD samples is stated as a molar ratio of HTC molecules per α-CD molecules rather than using a repeat unit basis as for PEG. Fig. 8 shows the time-dependent X-ray diffractograms for a 1:3.8 molar ratio of HTC/α-CD complexed at $a = 1.0$ and 90 °C. This composition represents a 50 mol% excess of HTC, based on the HTC/α-CD molar ratio of 1:5.8 for complete coverage of the HTC molecule. This is the same mol% excess used for preparation of the 3:1 PEG/α-CD ICs. The peak at $2\theta = 21.6°$ is due to diffraction by uncomplexed HTC crystals. As in the case of PEG600/α-CD mixtures at 30 °C, a clear build-up of the peak at $2\theta = 20°$ occurs with time, indicating the formation of an HTC/α-CD IC at $a = 1.0$. To our knowledge, this is the first reported evidence of solid-state complexation of a hydrophobic oligomeric guest molecule with α-CD.

The effect of water in the HTC/α-CD IC system is profound, as no complexation occurs when the atmosphere is completely dry (data not shown). However, no change in the complexation rate occurs (within the parameter uncertainties in Table 1) when the water activity is reduced from 1.0 to 0.7. In Fig. 8, the persistence of the peak at 12°, normally associated with the cage structure, would suggest that complete conversion to the columnar structure does not occur at 90 °C. However, Li et al. [13] show that other oligoethylene/α-CD ICs exhibit a peak at $2\theta = 12°$, most likely due to the presence of oligoethylene molecules since columnar α-CD with no guest does not diffract at $2\theta = 12°$ [14]. Further evidence that this peak belongs to HTC/α-CD IC and not cage α-CD can be seen in the diffraction patterns at $t = 0$ and 0.22 h in Fig. 8. At $t = 0$, the 12° peak is due to cage α-CD. This peak disappears at $t = 0.22$ h and then reappears at longer times as the HTC/α-CD complexation proceeds. The growth of the 12° peak parallels the growth of the 20° peak associated with the columnar IC structure, thus at later times the 12° peak must also be associated with the columnar IC structure.

The rate of complexation is more than three times lower for HTC than for PEG600 (Table 1). This could be due to the higher mobility of PEG600 relative to HTC. Another possibility is that the inherent ability of PEG600 to hydrogen bond with α-CD helps to disrupt the intermolecular hydrogen bond network in the cage α-CD crystals. Both factors would serve to increase the complexation rate of PEG600 relative to HTC.

An additional experiment was performed to further probe the interactions of HTC with α-CD. A 1.9:1 molar ratio of HTC to α-CD was complexed at $a = 1.0$ and 90 °C. This constitutes a molar excess of HTC which is 1000% above the stoichiometric ratio of 1:5.8. Although the complexation rate constant shown in Table 1 is higher for this composition, the rate constant does not scale linearly with HTC concentration. This observation was made previously by our group [9] in which an increase in concentration of PEG200 resulted in a negligible increase in complexation rate with cage α-CD at 20 °C. The complexation rate would likely increase up to the point where α-CD particle surfaces are completely covered with guest molecules. Beyond this concentration, the extra guest molecules do not come in contact with α-CD particles and thus cannot contribute to the phase transformation. Based on the measured complexation rates for the HTC/α-CD IC, the α-CD particle surfaces probably become saturated with HTC molecules between the compositions of 1:0.5 and 1:3.8 HTC/α-CD.

4. Discussion

The mechanism of the phase transformation from cage to columnar αCD induced by formation of oligomer/α-CD ICs must involve the following steps, which may be sequential or cooperative: (1) disruption of the intermolecular hydrogen bonds in the α-CD cage structure, lending mobility to individual α-CD molecules; (2) desorption of the water molecules contained within the α-CD cavities; (3) threading of the oligomer into α-CD molecules and (4) recrystallization of the threaded α-CD into the columnar structure. The individual effects of relative humidity, guest hydrophobicity and temperature on these steps are now considered. Increasing humidity would be expected to accelerate step 1 but may retard steps 2 and 4. For recrystallization to occur (step 4), CD—CD hydrogen bonds must be re-established and the presence of excess water molecules may interfere with this process. However, the data in Table 1 show that the rate of the phase transformation increases with increasing humidity, thus the effect of humidity on step 1 must dominate. In addition, prior work from our group has shown that the driving force for water absorption by both PEG/α-CD and HTC/α-CD ICs is primarily enthalpic and is due to hydrogen bonding between the absorbed water and the hydroxyl groups on the CD molecules [15].

More hydrophobic guest molecules would be expected to retard step 1, however, hydrophobic molecules might also be expected to thread more rapidly into the hydrophobic α-CD cavity, increasing the rate of step 3. Data collected at the same temperature and water activity for the similar-sized oligomers PEG600 and HTC show that the transformation rate is lower for the more hydrophobic HTC guest (Table 1). Therefore, the effect of guest hydrophobicity on step 1 must again dominate. This receives further conformation from the fact that the conformational characteristics of HTC favor its threading (step 3) compared with PEG600, yet the latter is included more rapidly. Finally, increasing temperature would be expected to increase the rates of all steps in the mechanism, which is confirmed by the PEG data at 30 and 90 °C in Table 1. This analysis suggests that the key rate-controlling step in the phase transformation is disruption of intermolecular hydrogen bonds in the cage α-CD crystal lattice (step 1), and is facilitated by high water activities, elevated temperatures or hydrophilic guest molecules.

The phase transformation requires the presence of a complexing guest molecule that favors formation of a CD IC having the columnar structure. No transformation takes place upon exposure of the α-CD cage crystals to high humidities alone [16], and previous results from our laboratory have shown that the α-CD columnar structure with no guest present is unstable and reverts to the cage structure at high humidities [17]. This implies that the oligomer first threads individual α-CD molecules, followed by recrystallization of α-CD into the columnar structure, rather than formation of empty stacks of α-CD molecules which recrystallize into the columnar structure and are later threaded by the guest molecule. If threading does occur before recrystallization, then the intermediate state must be a transient amorphous structure at the interface between the columnar and cage crystal domains. No X-ray reflections other than those due to the cage and columnar structures would therefore be expected during the phase transformation, and none were observed.

It is possible to prepare α-CD in the columnar structure with no guest molecule present (other than the water of hydration) by rapid precipitation from chloroform solution [14]. It would be interesting to measure the complexation kinetics of PEG and HTC with pre-existing columnar α-CD and compare that data with the results obtained here. However, it would not be possible to use X-ray diffraction to follow the phase transformation, since the starting and ending crystal structures are the same. A further complication is the instability of the 'empty' columnar structure at high water activities [17]. As mentioned in Section 1, a similar study was carried out by Rusa, et al. [8] in which solid particles of cage or columnar γ-CD were suspended in deuterated acetone solutions containing dissolved PNAI. The complexation kinetics were faster for the columnar γ-CD particles than for the cage γ-CD particles, since no solid-state phase transformation occurs for the columnar γ-CD particles. This supports the conclusion reached above that threading of the guest molecule into the CD cavities is not the rate-controlling step in the phase transformation mechanism. Preliminary NMR experiments of this kind have been carried out with α-CD and PEG (MW = 200 and 400 g/mol) and these yielded the same result. Such NMR experiments have not been attempted with HTC.

5. Conclusions

Neat oligomeric liquids PEG and HTC form an IC with solid α-CD powder initially having the cage crystal structure. This results in a solid-state phase transformation to columnar α-CD, which can be tracked by WAXD to measure the complexation kinetics. The atmospheric water vapor content has a profound effect on the complexation kinetics. As water activity increases, the degree and rate of complexation both increase. A key step in the phase transformation appears to be breaking of intermolecular hydrogen bonds in the α-CD cage crystal lattice, which gives the α-CD molecules enough mobility to thread the oligomeric guest. At low water activities, an insufficient amount of water is present to break these hydrogen bonds and the rate of transformation is low (for PEG) or zero (for HTC). At higher activities, the complexation rate is faster, but may be limited by the reduced driving force for desorption of water molecules residing inside the α-CD cavities. It has been demonstrated that at high water activities, a hydrophobic guest molecule (HTC) is capable of complexing with solid α-CD and inducing the cage-to-columnar phase transformation. The rate of HTC complexation is slower than PEG, weakly dependent on HTC concentration, and highly dependent upon water activity.

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