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2007 J. Phys.: Condens. Matter 19 205108

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Low-temperature supercooled phase of α -cyclodextrin:4-methylpyridine:water mixture

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Received 10 October 2006

Published 25 April 2007

Online at stacks.iop.org/JPhysCM/19/205108

Abstract

A mixture made of α -cyclodextrin, 4-methylpyridine and water was recently reported to undergo an inverse melting/freezing phenomenon. The physical origin of this counterintuitive process is still a debated issue; nevertheless, the interplay of structural and dynamic features seems a key point in solving the apparent thermodynamic paradox. We investigated the dynamics of this mixture in a wide range of temperature, concentration and wavevector by time-resolved transient grating spectroscopy. We found that in the lower temperature region of the phase diagram the mixture shows clear evidence of a viscoelastic effect and a slowing-down phenomenon. These dynamic features suggest the presence of a glass transition at low temperature.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The unexpected physical phenomenon of reentrant phase transitions is present in several materials of different nature [1]. For example, it has been observed in a polymer as a crystal–amorphous transition on cooling [2], in liquid crystals as a reverse nematic–smectic transition [3], in several liquid mixtures as a coexistence closed-loop in temperature/concentration phase diagram [1], or in protein folding as a cold denaturation process [4]. The phenomenon has been named differently depending on the type of the physical property that shows reentrance. In particular, when a pure compound shows a crystal–liquid transition on cooling (or, vice versa, a liquid–crystal transition on heating) under isobaric conditions, the name *inverse melting* (*freezing*) has often been used. The thermodynamic interpretation of inverse melting processes was already predicted by Tammann [5], but they are still a debated issue [6, 7].

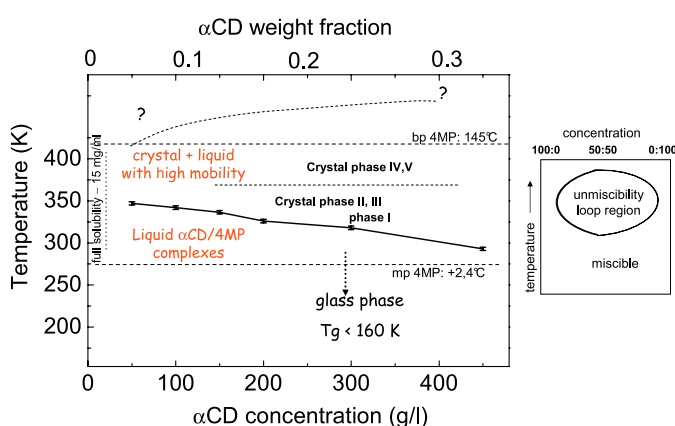


Figure 1. Phase diagram of the α CD:4MP:H₂O mixture, and some of the structural and dynamical properties. In the right-hand part a sketch of a typical immiscibility-loop phase diagram is given.

Here we focus our attention on the reentrant phase transition presented by a mixture composed of α -cyclodextrin (α CD), 4-methyl pyridine (4MP) and water, that was recently reported to undergo an inverse melting/freezing phenomenon [8]. The inverse melting (/freezing) transition is exothermic (endothermic), in contrast to the usual behaviour [9]. Indeed this mixture shows a complex phase diagram that has been only partially investigated and addressed. An attempt at a temperature–concentration (α CD/4MP) phase diagram is drawn in figure 1, based on previous experimental investigations, including static and dynamics measurements.

The α CD:4MP:H₂O mixture shows a reversible liquid–solid transition line in a large range of α CD/4MP concentrations. On increasing the amount of water, this line shifts towards lower temperatures. The transition can easily be observed by visual inspection, and it has been verified by analysis with scanning calorimetry, x-ray diffraction and quasi-elastic neutron scattering [10].

These crystallographic studies show that the solid phase presents five different crystalline forms as a function of temperature. The lowest temperature crystal, I in figure 1, is metastable and spontaneously transforms into the second one, II. All others, III–V, are stable and reversible with large hysteresis. All are hexagonal, and they can be distinguished into two groups. I, II and III have a vertical axis of about 45 Å, meaning that 3 α CD molecules pile in the vertical direction. The successive IV and V phases have a vertical axis reduced by a factor 3, and are described as horizontal sheets of α CD linked by water and/or solvent molecules. The stable crystals are estimated to contain about 6 ± 2 molecules of solvent per α CD, without any dependence on mixture concentrations of the generating liquid phase. Hence a partial phase separation takes place over the liquid–solid line, producing a coexistence of the crystal and liquid phases, as is confirmed by the presence of a liquid-like background underneath the Bragg peaks. The two coexisting phases are both composed by α CD and 4MP molecules with a relative percentage modulated by the concentration of α CD. For low α CD concentration, (lower than 200 in figure 1), the coexisting phases acquire the aspect of a viscous turbid liquid.

Diffusion coefficients of the different phases have been measured at the microscopic level using quasi-elastic neutron scattering [11]. The quasi-elastic signal in the liquid phase shows evidence of interactions between the 4MP and the α CD. The spectrum, typical of a long-range translational dynamics in the pure solvent, becomes characteristic of a confined translation or rotational motion when the α CD content is increased. Analysis of intensities leads to the conclusion that clusters of α CD–4MP (α CD and its solvation shell of 4MP) are formed in the liquid phase, made of about 4 ± 2 solvent molecules per α CD.

This scenario clearly reminds us of the reentrance of miscibility observed in various liquid mixtures [1] (e.g. guaiacol–glycerol–water and 3-methylpyridine–water–heavy water) that produce the typical closed loop in the temperature/concentration diagram, as drawn in the right-hand part of figure 1. In our mixture, only the lower part of the contour loop has been observed up to now, the upper part probably being hidden by the evaporation of the solvent. According to this point of view, the role of water can be rationalized. In fact, the presence of a closed loop is directly connected with the strength of hydrogen bonds between molecules [12]: the increase of strength produces a reduction of the loop gap. We found that the addition of water in this mixture lowers the liquid–solid transition temperature, while partial deuteration of α CD and water raises it. These observations suggest that the water decreases the strength of the hydrogen bonds.

In this context, we investigated the mixture dynamics in the low-temperature region of the phase diagram, i.e. below the melting point of 4MP (275 K). We found that this mixture can be easily supercooled and hence we have undertaken a systematic study of this low-temperature phase. Indeed, the presence of glass transitions in a binary mixture of sugar–water type has previously been reported [13], but only very few dynamic investigations of this kind of mixtures have been worked out. In this paper, we report a time-resolved spectroscopic investigation of the acoustic, thermal and structural dynamic processes from 290 to 160 K.

2. Material and methods

2.1. Sample preparation

α CD and 4MP were purchased from Alfa Aesar. The 4MP was distilled to remove any impurity and dried over a molecular sieve, and the hydrated α CD was dried under vacuum. Because of the very high hygroscopicity of both compounds, the water content is not fully controlled. At room temperature, the liquid phase of the mixture at relatively low concentration, 0–300 g l⁻¹, can be obtained with a variable water content. In contrast, at higher concentration level, >400 g l⁻¹, the liquid mixture is stable only with a very low level of water, as water induces the instantaneous formation of the solid phase. The temperature-dependent measurements were performed with a concentration α CD/4MP = 300 g l⁻¹ added to 15 g l⁻¹ of water, leading to a total (including crystallization water from the α CD) of about nine water molecules per α CD. The concentration-dependent measurements correspond to a sample with added water, 15 g l⁻¹, up to concentration of α CD/4MP = 300 g l⁻¹ and a dried sample for higher concentrations. Moreover, it was observed that the measured dynamics at room temperature (sound propagation and thermal relaxation) were not affected by the water content.

The pure solvent has a melting temperature of 275 K, and it can be supercooled down to 230 K. The addition of α CD prevents crystallization, and the mixture can be easily supercooled down to 160 K (we did not investigate lower temperatures) with relatively slow cooling rate (typically 10 K min⁻¹). This metastable phase does not crystallize and it can exist for a long period. It is optically homogeneous, isotropic and transparent.

Upon heating, starting from 160 K, the sample remains supercooled up to 230 K, when it suddenly turns into a white solid. If we further heat the sample a melting occurs around 270 K; afterwards it remains in the liquid phase until the inverse freezing transition takes place at 318 K, as previously discussed.

2.2. Transient grating measurements

Heterodyne-detected transient grating (HD-TG) spectroscopy has been used extensively and successfully for probing the dynamics of supercooled liquids of different nature [14, 15].

This time-resolved spectroscopic tool is able to probe a very broad time window, typically from 10^{-9} to 10^{-3} s, covering with a single experiment a dynamic range hardly explored by other methods. The technique is applied far from electronic or vibrational resonance of both of sample components, and the probed wavelength is much larger than the intermolecular characteristic distances. Therefore, an average of the density fluctuations is measured and one does not distinguish between the different components of the system.

The HD-TG set-up used in the present study is described elsewhere [14]. Briefly, the transient grating is induced on the sample by two interfering 20 ps laser pulses, produced by a mode-locked ND:YAG laser at 1064 nm. The probe is a continuous laser beam, obtained by an intra-cavity doubled ND:YAG laser (532 nm). It is diffracted by the induced grating and it provides the signal to be monitored. It was checked that no thermal lensing or power effects were present.

The excitation laser pulses create a density grating through absorption and electrostriction effects. In liquids characterized by a low viscosity, the thermal grating, induced by absorption, builds up the density grating in a very short timescale, typically 10^{-12} s. This produces an immediate rise of the HD-TG signal that decays afterwards with a relaxation constant related to the thermal diffusivity. The creation of the density grating might be delayed if the sample viscosity is high enough; this rising intensity is referred to as a structural component and it is a characteristic of the *structural relaxation phenomenon*, taking place in supercooled liquids and glasses. Overlapping these relaxations, one observes longitudinal acoustic oscillations launched by the density grating. Their frequency is $\omega = cq$, where c is the longitudinal sound velocity and q is the wavevector defined by the experimental geometry [14].

The analysis of the HD-TG signal was treated using the simplest solutions of the generalized hydrodynamic equations introduced by Yang *et al* [16], and also reanalysed by Torre *et al* in [14]. This hydrodynamic model describes the HD-TG response function and signal as

$$R(t) = Ae^{-\Gamma t} \cos(\omega t) + Be^{-\Gamma t} \sin(\omega t) + Ce^{-\Gamma_T t} + De^{-(t/\tau_\alpha)^\beta} \quad (1)$$

where Γ is the sound damping rate, ω is the sound frequency, Γ_T the thermal damping rate, and τ_α and β the structural relaxation time and stretching factor, respectively. The fit of HD-TG data enables the extraction of several parameters related to the acoustic propagation (sound velocity, $c = \omega/q$, and damping rate, Γ), thermal diffusivity ($\chi = \Gamma_T/q^2$) and structural phenomenon (relaxation time, τ_α , and stretching factor, β).

3. Results

3.1. Temperature dependence

On cooling the 300 g l⁻¹ mixture we obtained the supercooled phase. Since the supercooling phenomenon is very often the precursor of a glass transition, we measured the HD-TG signal as a function of temperature towards the possible glass transition. In figure 2 we show the HD-TG signal measured with $q = 1 \mu\text{m}^{-1}$.

At high temperatures, from 290 down to about 230 K, the data show a damped acoustic oscillation followed by an exponential decay. On lowering the temperature, the sound damping increases, reaching its maximum at ≈ 230 K. This is a viscoelastic phenomenon typical of glass-formers [14]. In fact, when the structural relaxation timescale becomes comparable to the period of the sound oscillations, i.e. when $(\omega\tau_\alpha) \approx 1$, a strong coupling takes place between these two dynamic processes, substantially increasing the sound damping effect.

At lower temperatures, the structural relaxation time becomes longer and the acoustic propagation starts to be decoupled from the structural phenomenon, so the damping rate

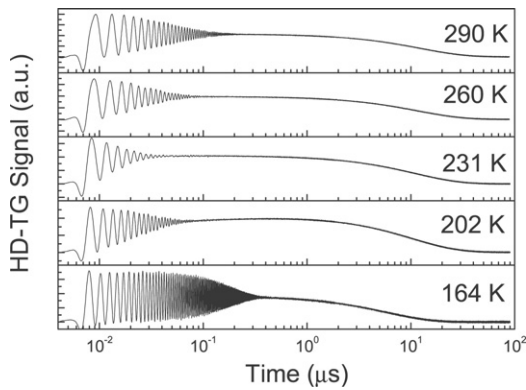


Figure 2. HD-TG signal from a α CD:4MP:H₂O mixture with a concentration of α CD/4MP = 300 g l⁻¹ measured at $q = 1 \mu\text{m}^{-1}$. Only five temperatures, out of 17 measured, are reported.

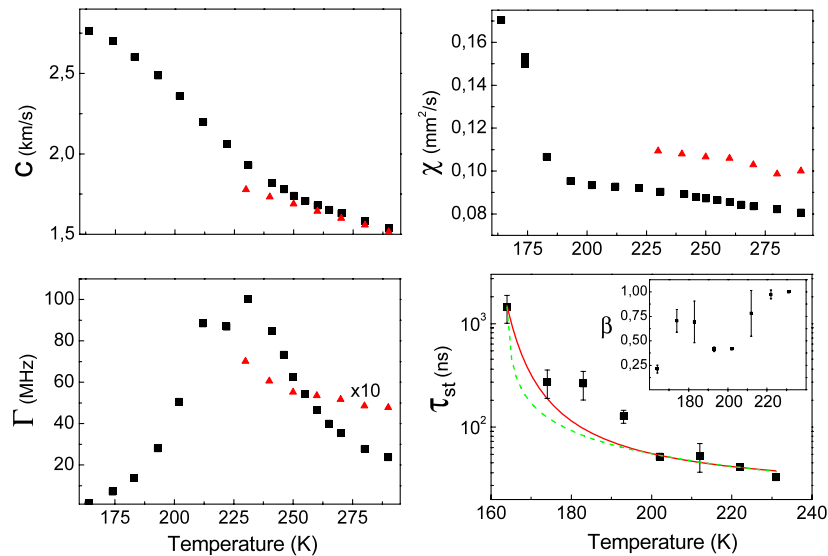


Figure 3. Temperature dependence of the dynamic parameters of the supercooled phase measured by HD-TG experiments: sound velocity and damping rate (left), thermal diffusivity (right top) and structural relaxation times (right bottom). Fit of structural relaxation times according to the VFT law (solid line) and power law (dashed line). For comparison, the parameters of the pure solvent are also reported as triangles.

decreases. Furthermore, the structural component appears directly in the HD-TG data as a rising intensity; see the 202 K data in figure 2. For these temperatures the fitting procedure enables a safe measure of structural times. In the data at the lowest measured temperature, 164 K, the structural rearrangement is very slow and the sound propagation is only weakly damped; in contrast, a coupling phenomenon between the structural dynamics and thermal diffusion starts [17].

The measured dynamic parameters, extracted from the fits, are plotted in figure 3. The velocity and damping rate of sound wave propagation (left panels on figure 3) show a typical dispersion phenomenon in the temperature dependence, indicating the temperature range where the structural dynamics couple to the sound wave propagation. The thermal diffusivity (right-top panel of figure 3) exhibits a weak temperature dependence up to about 190 K that increases substantially towards the low-temperature range. This peculiar effect has

been already identified in previous work [14, 17] and it arises from the coupling between the structural relaxation and the thermal diffusivity, when their timescales come closer. Alternative hydrodynamic models have been proposed to take this coupling properly into account [17, 18], but their use in the fitting of the present data is beyond the scope of the present paper.

In order to identify and characterize the supercooled and glass phases of this mixture, the temperature dependence of the structural phenomenon is the most relevant information measured in the present work. As we discussed, the structural component in the signal becomes easily measurable for temperatures lower than 230 K. The temperature dependence of its relaxation time between 230 and 164 K is plotted in figure 3. Clearly, a slowing-down phenomenon is present in the structural dynamics that suggests a possible glass transition. At 164 K, τ_α is $\approx 1 \mu\text{s}$, showing that a structural arrest has not been reached, and it could take place at lower temperatures. In order to extrapolate the T_g value we fitted the data with two simple scaling laws, typical for a glass transition [19]. The behaviour can be either fitted with a Vogel–Tammann–Fulcher (VTF) function:

$$\tau_\alpha \propto \exp\left(\frac{B}{T - T_\infty}\right) \quad (2)$$

with $B \approx 45$ and $T_\infty \approx 153$ K, or using the mode-coupling power law:

$$\tau_\alpha \propto (T - T_c)^{-\gamma} \quad (3)$$

with $\gamma \approx 0.6$ and $T_c \approx 160$ K. Normally these two scaling laws find very different values of the divergence temperature: typically $T_\infty \ll T_g$ and $T_c \gg T_g$. For the present results, given the limited temperature range investigated and the errors affecting the measurements, the two fits substantially agree to a divergence temperature of about 155 K. This can be taken as a first estimate of the glass transition temperature.

For comparison, measurements on the pure 4MP have been carried until crystallization occurred, i.e. from 290 to 225 K, covering 45 K below the 4MP melting point. The results of the fits are reported in figure 3 as triangles. No structural intensity arises down to 230 K, and the sound velocity varies linearly with temperature in the investigated range. The only sign of a possible viscoelastic effect is noticed in the damping of the sound wave, starting to increase from 250 K. With regards to pure αCD , it is expected to undergo a glass transition above room temperature, like that observed in other sugar matrices. However, an extensive study on diverse sugar compounds [20] could not detect any sign of a glass transition in αCD . This emphasizes the different nature of dynamics from the pure 4 MP and the mixture.

3.2. αCD concentration dependence

We investigated the dependence of the mixture dynamics on the $\alpha\text{CD}/4\text{MP}$ concentration. We measured the HD-TG signal at a fixed temperature, 300 K, and wavevector, $q = 1 \mu\text{m}^{-1}$, varying the concentration from 0 to 736 g l^{-1} . In figure 4 we report the physical parameters extracted from the data using the fitting procedure. At this temperature, the structural relaxation times can be extracted only from the HD-TG data corresponding to the samples with the two higher concentrations. In both the 600 g l^{-1} and 736 g l^{-1} mixtures we found $\tau_\alpha \approx 40$ ns with a $\beta \approx 0.6$.

As is clearly shown in the figure, the addition of αCD to the 4MP solvent strongly modifies the viscoelastic properties of the mixture. The sound velocity increases substantially with the sugar concentration, suggesting a stiffening of the mixture towards a solid-like dynamic behaviour. Also the sound damping rate increases with the concentration. These two features recall the first part of dispersion effect, from 300 to 225 K, shown by the mixture in the temperature dependence; see the left-hand panels of figure 3. In other words, on increasing

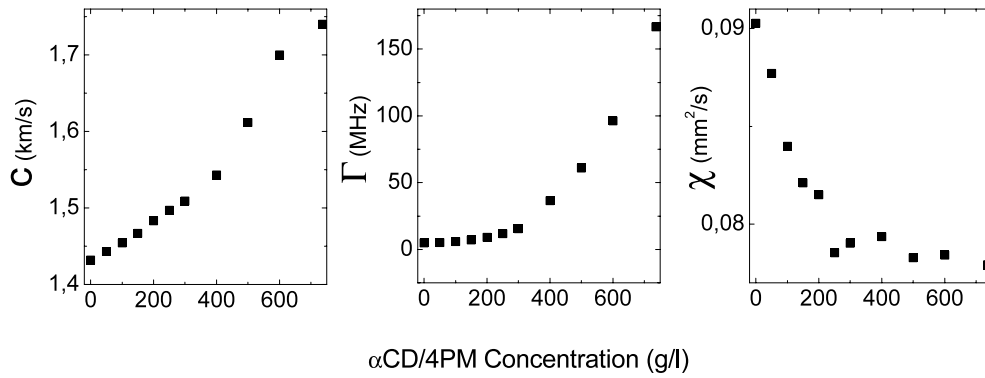


Figure 4. Dependence of the sound velocity, damping rate and thermal diffusivity on the α CD/4MP concentration.

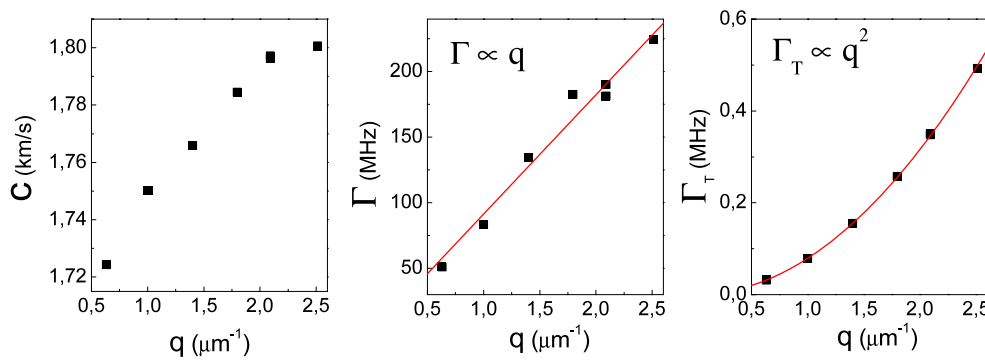


Figure 5. The q -dependence of the sound velocity, sound damping rate and thermal diffusivity in a 600 g l^{-1} mixture.

the α CD concentration, the structural dynamics slow down and the mixture viscosity grows, producing a viscoelastic acoustic response. The thermal diffusivity shows a moderate decrease with the α CD concentration.

3.3. q -dependence

We investigated the dependence of the mixture dynamics on the experimental q -wavevector. The TG set-up enables us to produce a transient grating characterized by six different wavevectors: $q = 0.63, 1, 1.4, 1.8, 2.1$ and $2.5 \mu\text{m}^{-1}$. We measured the HD-TG signal at 300 K in a mixture with a concentration of 600 g l^{-1} within the q -range reported.

A high concentration was chosen in order also to measure the structural relaxation of the q -dependence. This component follows a stretched exponential decay with $\tau_\alpha \approx 40 \text{ ns}$, not having any noticeable q -dependence.

The physical parameters obtained from the best-fit procedure are reported in figure 5. The sound velocity exhibits a small dispersion effect in the q -vector. The sound damping rate shows an almost linear dependence: the best fit gives $\Gamma \propto q$. Both these q -dependences do not agree with a simple hydrodynamic model, but they are consistent with the presence of a viscoelastic phenomenon. In fact, as previously discussed, when the timescale of the structural dynamics becomes comparable to the period of oscillation of the acoustic wave, it takes place a coupling

effect between the structural mode and the sound propagation. The thermal diffusivity follows the classical behaviour, with $\Gamma_T \propto q^2$.

4. Conclusion and perspectives

The present work aimed at exploring the dynamic behaviour of an α CD:4MP:H₂O mixture in the low-temperature region of the phase diagram by means of optical spectroscopy. We measured the mixture dynamics as a function of temperature, concentration and wavevector. The 300 g l⁻¹ mixture can be supercooled and its dynamics, towards low temperatures, shows a clear viscoelastic effect and a slowing-down phenomenon in the structural relaxation, suggesting a likely glass transition at 155 K. The measurements with varying concentration indicate a strong dependence of the viscoelastic properties on the α CD concentration. The addition of α CD to the solvent causes a strong increase of the viscosity that conversely shifts the timescale of the structural relaxation. This suggests that also the glass transition temperature is shifted towards higher temperatures. Also the q -dependence confirms the viscoelastic nature of the dynamic phenomenon observed. Further measurements, including x-ray diffraction, differential calorimetry and viscosity, are in progress on mixtures characterized by high concentration of α CD.

Acknowledgments

We would like to thank M R Johnson and H P Trommsdorff for fruitful discussions, and R Angelini, S DePanfilis and G Ruocco for comparing and discussing results on the mixture. We also thank R Eramo for the assistance with the Molder program. This work was supported by the EC grant No. RII3-CT-2003-506350, by CRS-INFM-Soft Matter (CNR) and MIUR-COFIN-2005 grant No. 2005023141-003.

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