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Relaxation kinetics of metastable caffeine: a time resolved dielectric investigation

A. A. DECROIX, L. CARPENTIER and M. DESCAMPS*
LDSMM (UMR CNRS 8024) and ERT 1066 « matériaux thérapeutiques »

Université Lille1 59655 Villeneuve d'Ascq cedex (France)

*Corresponding author. Email: marc.descamps@univ-lille1.fr

Using time resolved dielectric relaxation spectroscopy we have studied the kinetics of the first order phase transformation of caffeine from its high temperature rotational solid form to the room temperature phase. The results indicate that the kinetics can be fitted by a highly stretched exponential law. Kinetics thus differ from that of a “typical” nucleation and growth process. This unusual non-sigmoidal evolution can be understood as being dominated by slow nucleation in grains with a dispersion of their size ranging below the characteristic dimension of the nucleation and growth process. The relaxation times of polarization are characterized by an activation energy closely correlated with that of the nucleation process.

Keywords: Phase transition, Dielectric relaxation, Polymorphism, Size Effect

AMS Subject Classification: 77.22.Gm; 81.30.-t

1 Motivation and experimental strategy

Caffeine ($C_8H_{10}N_4O_2$) is a trimethylated purine which is widely used in agrochemistry and in pharmacy. In spite of a relative molecular simplicity, the solid state properties of caffeine remain largely enigmatic partly due to molecular disorder and notorious thermodynamic instabilities. Anhydrous crystalline caffeine is known to occur in two polymorphic phases (called I and II) which constitute an enantiotropic system [1]. Phase II converts into phase I upon heating on an unusually wide temperature range (400K – 440K) and melts at 508K. Phase I can be easily undercooled and maintained at low temperature in a very slowly relaxing metastable state. At room temperature the complete I→II transformation takes weeks or months [2]. Kinetics become significantly faster around 363K. Recent X-ray, dielectric relaxation and TSDC studies [3, 4, 5] have revealed that undercooled hexagonal phase I is characterized by a rotational dynamic disorder of the molecular dipoles. There is some suspicion that phase II is also dynamically disordered. The dynamic in undercooled form I is very slow, with a relaxation time around 1s at room temperature; the exceptional slowness of the molecular motions is probably one of the limiting factors of the phase's transformations kinetics. The system is very

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3 attractive for two fundamental reasons : (1) phase I is expected to undergo a glass like transition in the
4 crystalline state at temperatures not far below room temperature (“glassy crystal state”), and (2) it is
5 exceptional for a non diffusive system with a non conserved order parameter to show so slow relaxation
6 dynamics of metastable states.
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10 In this paper we discuss the results of a dielectric relaxation experiment on quantitative time-resolved studies
11 of the volume fractions of isothermally converting metastable disordered phase I. The caffeine molecule has a
12 sizeable permanent dipole moment ($\mu_D=3.70$ Debye). Large difference between the dielectric constants in
13 form II and in the highly disordered phase I is used to probe the kinetics. Dielectric spectroscopy further
14 allows to simultaneously provide characteristic molecular relaxation times at the various temperatures where
15 kinetics are followed. From this we may explore possible correlations existing between the time scales of the
16 kinetics and that of the slow molecular relaxations. We may also directly check the existence or not of a
17 molecular relaxation in phase II. In order to locate more precisely the transition point, the study was preceded
18 by a calorimetric investigation of the very blurred II \rightarrow I transition using varying temperature scan rate. The I
19 \rightarrow II transformation has been investigated with the dielectric technique [frequency domain 0.1 to 10^5 Hz] after
20 a quench from high temperature to three temperatures located in the domain where the transformation is the
21 fastest. The corresponding isothermal paths - from metastable to stable states - are indicated by arrows in the
22 sketch of the Gibbs diagram (Figure 1.a) which depicts the enantiotropic polymorphism of crystalline
23 caffeine. All experiments are made difficult because caffeine rapidly sublimates above 390K.
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37 **2 Materials and Methods**

38 Caffeine was purchased from Agros Organic in the form II and was purified by sublimation at 493K and 10^{-3}
39 torr onto a cold finger (at 285K). Pure form II was obtained by maintaining purified caffeine in an oven at
40 363K during several months. Pure form I was obtained by heating purified caffeine above the II \rightarrow I transition
41 temperature. For several experiments commercial caffeine (form II) was used as received.
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46 Thermal analysis was performed with a TA Instruments Q10 differential scanning calorimeter. Temperature
47 and enthalpy readings were calibrated using indium. The samples (typically 5mg) were sealed in aluminium
48 hermetic pans to prevent caffeine from sublimation. The pans were weighted before and after each experiment
49 to ensure that they were correctly sealed. Figure 1.b shows the II \rightarrow I transition observed by DSC. Commercial
50 caffeine (form II) was heated at different rates (0.1 and 5 K.min $^{-1}$ respectively called 1 and 2). This series of
51 experiments underlines the first order nature of the transition ($\Delta H=19.7$ J.g $^{-1}$) and the unusual width of the
52 peak (at 5K.min $^{-1}$, the transition peak lies between 408K and 438K). The peak becomes sharper as the heating
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rate decreases. The kinetic origin of this sharpening is an intrinsic feature of the orientational melting transition. These experiments show that caffeine can largely overheat and slowly relaxes to the high temperature phase. This is a surprising but interesting feature for a compound which undergoes rotational melting

The dielectric measurements were performed with the analyser DEA 2970 of TA instruments. The dielectric cell consists in two ceramic parallel plate sensors, with gold circular electrodes. Samples of caffeine are used in a form of a disk (25 mm of diameter and 2 mm of thickness) prepared by compressing 1.3g of caffeine under a pressing force of 50 kN.

3 Dielectric investigation of the I→II phase transition

Dielectric relaxation of phase II has been measured on a sample previously equilibrated several months at 363K. Full equilibration has been checked by X-ray diffraction analysis. Our measurements confirm the suspicion of a phase II dynamically disordered. The most probable relaxation time in phase II is very close to that of phase I at the same temperature. However the dielectric strength $\Delta\epsilon$ is four time smaller.

The change in dielectric strength is used in the present experiments to observe the volume fraction of the phases in the course of relaxation from one phase to the other. Prior each kinetic investigation, the system was prepared in a 100% metastable state by quenching the high temperature state I. The experiments were performed at three different temperatures: 333K, 343K and 363K, in the range where relaxation is expected to be in the fastest. Typical evolution of the loss factor during an annealing at 363K is shown in figure 2. The loss factor decreases significantly as a function of time. At this temperature the typical value of the loss factor of phase II is reached in about 170 h. Figure 3 shows the evolution of the transformed fraction $X(t)$ calculated from the time evolution of $\Delta\epsilon(t)$ at the investigated temperature. $X(t)$ can be well fitted with a stretched exponential:

$$X(t) = 1 - \exp[-(t/\tau)^n] \quad (1)$$

The value of the exponent is close to 0.5 at each temperature. Usually the nucleation and growth process which describes the kinetics of first order transitions shows sigmoidal variations with time frequently fitted by the Avrami law [6] $X(t) = 1 - e^{-f(t)}$ with $f(0)=0$ and $f(\infty) = \infty$. The function $f(t)$ is given by an integral involving the nucleation rate $N(t)$ and the domain growth rate $G(t)$. For the special case of homogeneous nucleation and a linear growth law of the linear dimension ($G(t) = V.t$, where V is constant), one obtains a power law $f(t) \propto t^p$ with $p=4$ for a constant nucleation rate N [6,7]. The exponent value n found in the present experiment is much lower than any expected value corresponding to a nucleation and growth law. It must

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3 however be remembered that the Avrami law is only expected in the limit of high enough values of the grain
4 size in which the transformation occurs [7]. Precisely, it applies for grain size dimension $L \gg \xi$, where the
5 natural length scale of the transformation $\xi = (V/N)^{1/d+1}$ (d: space dimension of the growth process).
6 Sigmoidal Avrami law becomes questionable when the transformation occurs in constrained geometry [7]. In
7 the extreme limit of a sample which is infinitely subdivided in cells so small that they are quite immediately
8 converted once nucleated, the transformed fraction $X(t)$ coincides with the nucleation fraction. For a
9 collection of cells which have the same linear size L , $X(t)$ is determined from:

$$dX/dt = (1-X) L^d N \rightarrow X(t) = 1 - \exp(-t/\tau) \quad (2)$$

10 In this limit, the kinetics characteristic time $\tau = (NL^d)^{-1}$ is only controlled by nucleation and becomes highly
11 dependant of the size. That is not the case for the relaxation time of the Avrami law $\tau_A = (NV^d)^{-1/d+1}$. A
12 stretched exponential law, such as that found in our experiments, is thus expected for a transformation
13 occurring in cells with a dispersion of grains size and for a temperature range where these sizes range below
14 ξ .

15 Since a unique exponent describes the power law kinetics we can deduce the temperature evolution of their
16 characteristic times. The most probable times of the dielectric relaxation functions are also directly obtained
17 from $\varepsilon''(\omega)$ maximum. Figure 4 represents the Arrhenius diagram of temperature evolutions for both
18 characteristic times. Despite seven decades difference in the characteristic times, the activation energies of the
19 phase transformation and polarization relaxation times are similar. Classical nucleation theory [8] gives the
20 following expression for the steady state nucleation rate:

$$N = N_0 \exp(-\Delta G^*/T) \exp(-E/T) \quad (3)$$

21 Where ΔG^* is the energy required to form a critical size nucleus ($\Delta G^* \sim (T_{tr} - T)^{-2}$). E is the activation energy
22 for molecule to "cross" the interface between the initial matrix and the new phase. It is the competing
23 combination of terms involved in the expression of N which is expected to determine the value and
24 temperature evolution of τ if the kinetics are described by relation (2). In the present case molecular rotation is
25 expected to be the involved basic dynamical process. E is thus expected to be comparable with the activation
26 energy of the dielectric relaxation. The similitude demonstrated by figure 4 strengthens the hypothesis that
27 nucleation is the driving mechanism of the first order kinetics. Since E is the limiting factor of the process, the
28 temperature range investigated is situated on the low temperature side of the nucleation rate maximum. X-ray
29 experiments further show that no evolution in the broadening of the Bragg peaks is observed during the
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3 transformation. This observation indicates that each grain is converted with the result that the average
4 crystallite size, which is reflected in the peak width is not modified.
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10 **4 Conclusion**

11 The main conclusions which may be drawn from our results are:

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14 (i) The relaxation kinetics can be described by a stretched exponential law and exhibits scaling behaviour.
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16 (ii) The activation energies of the kinetics and the dielectric relaxation process are closely similar.
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18 (iii) The transformation is expected to be driven by nucleation with a maximum rate situated at higher
19 temperature. In the investigated temperature range, the grain sizes of phase I in which transformation to phase
20 II proceeds are lower than the characteristic size of the nucleation and growth process ($\xi = (V/N)^{1/d+1}$). As a
21 result kinetics are only controlled by nucleation. Contrary to the usual sigmoidal Avrami law, the rate is
22 strongly dependent on the grain size. Consequently a dispersion of grains size explains the time stretching of
23 the evolutions.
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28 The slowness of the reverse transformation $II \rightarrow I$ above T_{tr} remains to be investigated and clarified.
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52 **Figure Caption**

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55 Figure 1

56 a : Schematic Gibbs diagram of the two enantiotropically related solid phases of anhydrous caffeine

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58 b : DSC thermograms recorded at a 0.1 K.min^{-1} (curve 1) and at a 5 K.min^{-1} (curve 2) scanning rate on commercial caffeine.
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Figure 2

Evolution during aging at 363K (stability domain of phase II) of the imaginary part of the dielectric susceptibility of phase I. Solid lines are the results of a fit on the Havriliak-Negami expression.

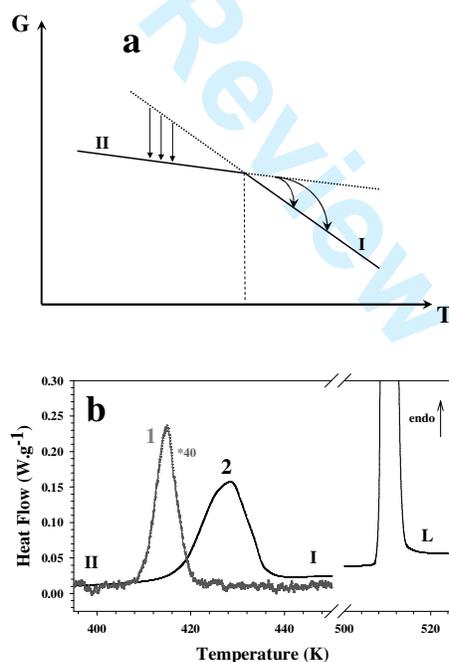
Figure 3

Time evolution of the transformed fraction characterizing the transition of anhydrous caffeine I \rightarrow II, determined from the decreasing of the dielectric strength during aging at $T=363\text{K}$, $T=343\text{K}$ and $T=333\text{K}$.

Figure 4

Temperature dependence of relaxation times as obtained from processes in phases I (full squares) and II (full triangles) and the characteristic times obtained by refinement by a stretched exponential for the three isothermal I into II transition (open circles). The insert represents the loss factor in phase I at 333K, 343K and 363K.

Figure 1



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Figure 2

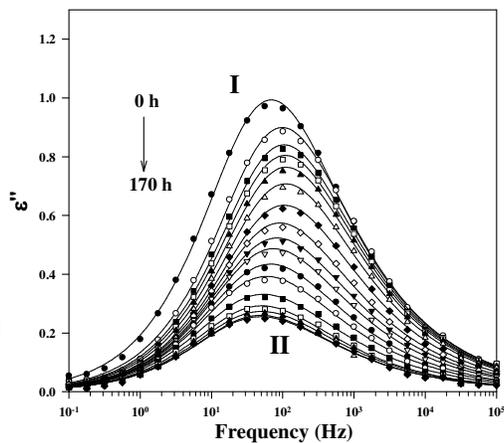


Figure 3

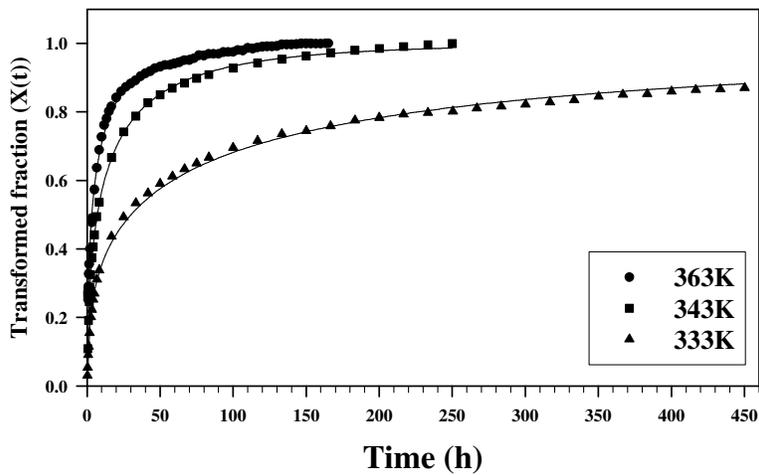


Figure 4

