chemistry and structure

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Hydrogen-bond network breakage as a first step to isopropanol crystallisation

Here we present an experimental study of isopropanol crystallisation in real time by means of a novel experimental set-up combining simultaneously structural measurements with dynamical techniques. This set-up, developed at the ILL, consists of a sample cell that allows simultaneous measurements of neutron diffraction (ND) and dielectric spectroscopy (DS) [1]. By performing the simultaneous experiment, information can be obtained from both phases, amorphous and crystalline, and this can provide a complete description of the changes occurring during the crystallisation process. The use of this novel set-up allowed us to demonstrate that breakage of the hydrogen-bond network is a precursor step for the crystallisation of isopropanol [2].

Glass forming liquids are a class of materials that can be maintained out of equilibrium in the amorphous state, without crystallising. Below the equilibrium melting temperature, the supercooled liquid is thermodynamically unstable due to its higher free energy as compared to that of the crystal, and consequently above the glass transition temperature T_g, the supercooled liquid tends to reduce its free energy by undergoing a first order phase transition. By means of this transition, referred to as crystallisation, molecules self-assemble forming crystals. In order to obtain precise information about the changes occurring in a supercooled liquid during crystallisation, a real time experiment may be crucial since it allows us to monitor simultaneously and in real time both the crystal development and the dynamic changes occurring in the amorphous phase. Therefore, an improvement in the understanding of crystallisation in terms of inter-relation between crystalline and amorphous development can be obtained when diffraction experiments are simultaneously accompanied by dielectric spectroscopy.

Recently we have developed an experimental set-up which allows us to perform, for the first time, simultaneous measurements of time resolved neutron diffraction (ND) and dielectric spectroscopy (DS) [1]. A picture of the ND-DS sample holder is shown in figure 1. The liquid is placed in a container between two metallic electrodes and is subjected to an alternating electric field of angular frequency ω. Dielectric spectroscopy measures the complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ as a function of frequency, where ε' is the dielectric constant and ε'' is the dielectric loss, and is a very suitable method to study molecular dynamics in liquids above T_g. Simultaneous ND and DS experiments

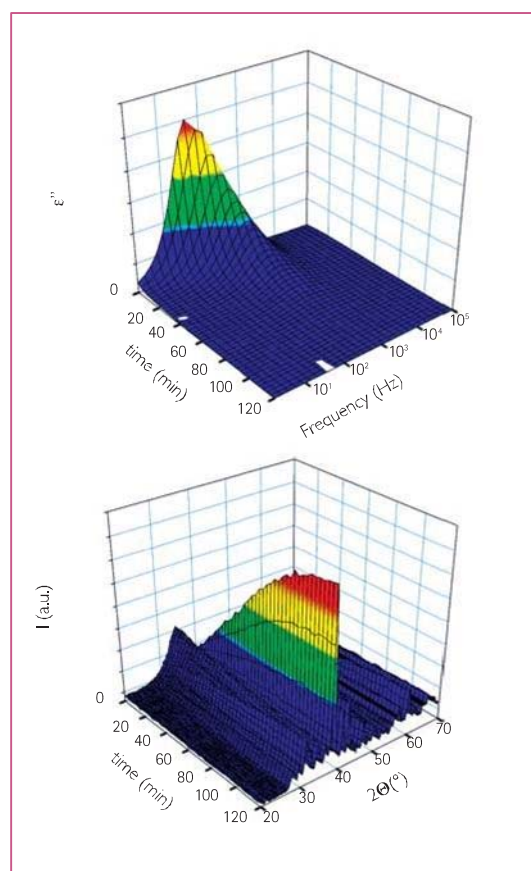**Figure 1:** Picture of the neutron diffraction — dielectric spectroscopy cell (ND-DS).

Figure 2: Simultaneous dielectric loss spectroscopy (DS) (top) and neutron diffraction (ND) (bottom) experiments as a function of time during an isothermal experiment (T = 139 K). The ND patterns were recorded with an acquisition time of 3 min.

were performed on the diffractometer D1B at a fixed wavelength of λ = 2.52 Å. Dehydrated deuterated isopropanol (2-propanol D8) was quenched in the glassy state at 75 K from room temperature. Crystallisation temperatures, T_c, were reached by heating the sample from 75 K up to T_c. Figure 2 presents ND-DS data during a crystallisation experiment at T_c = 139 K. The ND intensities are given as a function of the scattering angle 2Θ and the ε'' data from DS are presented as a function of frequency. The initial amorphous state is characterised by an amorphous halo in the ND diagram and by the primary relaxation process of isopropanol in the DS data. As time increases, the onset of crystallisation is denoted by the incipient appearance of Bragg peaks in the ND patterns and a decrease of the dielectric relaxation intensity.

The dielectric losses are described considering two relaxations: primary and secondary, being Cole-Davidson processes. The fraction of relaxing species can be estimated from the relaxation strength that corresponds to the area below each relaxation. Figure 3 shows the area ($\Delta\varepsilon$) below the primary and the secondary relaxation as a function of the crystallinity, estimated from the ND data at T_c = 139 K. Primary relaxation (figure 3, top) decreases dramatically in the first stages of crystallisation and shows a strong deviation from the two-phase model (phases that correspond to network and crystalline). This can be interpreted as due to the existence of an intermediate step between the situation in which the molecule is in the network and that in which it occupies a position in the crystal. On the other hand
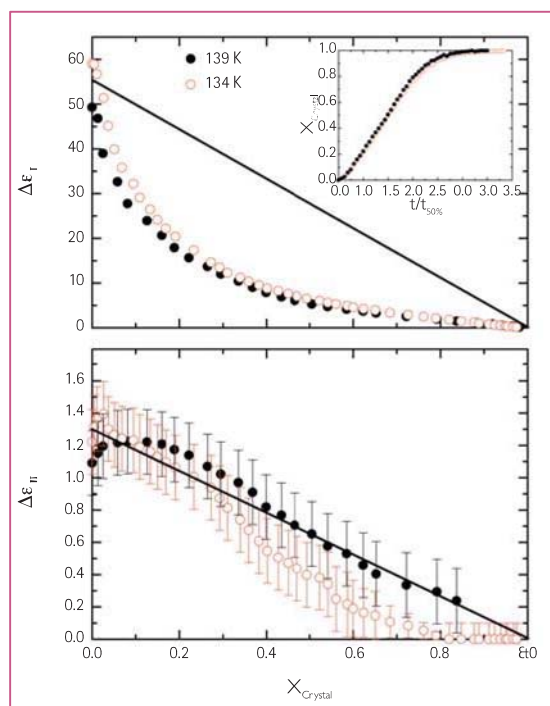

Figure 3: The relaxation strength of each process for the primary $\Delta\varepsilon_I$ (upper plot) and the secondary $\Delta\varepsilon_{II}$ (lower plot) relaxation processes as a function of crystallinity.

the dynamics of the hydrogen-bond network, represented by the mean average frequency of the relaxing species F_{max}^I, shows an increase in the initial crystallisation stages [2]. Both experiments and computer simulations, indicate that in hydrogen-bonded liquids the primary relaxation time is described by the wait-and-switch model [3-5]. First a molecule of the network switches its position to reorient itself, but it must wait until a favourable condition for reorientation exists in the network. The mean relaxation, time $\tau=1/(2\pi F_{max})$ is expected to depend inversely upon the number density of available hydrogen bonding sites [4]. Therefore, in our case, interpreting the decrease of $\Delta\varepsilon_I$ as due to a depletion of the hydrogen-bond network is consistent with a parallel increase of the available

hydrogen-bond sites as indicated by the increase of F_{max}^I. Secondary relaxation (figure 3, bottom) follows the two-phase model and the associated process appears as a consequence of the collective motions in the amorphous phase above T_g. Consequently, $\Delta\varepsilon_{II}$ is expected to decrease with increasing crystallinity as shown in figure 3 (bottom). Moreover, in this case the observed decrease is much closer to two-phase behaviour, indicating that the relaxing species, which are lost in the amorphous phase, are almost completely transferred to the crystalline phase.

In conclusion, the first simultaneous experiment allowed us to confirm that a breakage of the hydrogen-bond network occurs as a first step in the formation of crystals during the crystallisation of isopropanol.

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