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ELECTRICAL EFFECTS ACCOMPANYING THE PHASE TRANSITIONS IN ETHANOL CRYOCONDENSED THIN LAYERS

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The behaviour of the surface potential of ethanol layers deposited on a cooled substrate was studied. A spontaneous surface potential increase was detected for samples deposited at temperatures close to the well known phase transition (crystallization to crystal I phase) temperature. The activation energy for crystallization was estimated to be 20.7 ± 0.4 kJ/mol. In addition, thermally stimulated current (TSC) spectra were measured. It was suggested that the amorphous ethanol condensed below 125 K might exist in a glassy state and that the crystallization to crystal I phase runs from a glassy state via a crystal II phase.

Keywords: Condensate; Phase transition; Crystallization; Ethanol

INTRODUCTION

The ethanol is a commonly known substance which is used as a solvent medium in many experiments. Ethanol can form a glassy state very easily, and therefore it has been used as a glassy matrix as well. The glassy state can be achieved when the liquid is cooled fast enough to avoid nucleation into a crystal. The first studies of the glass transition phenomenon of ethanol were made more than 70 years ago (Gibson, Parks and Latimer, 1920). In 1977, using calorimetric and DTA methods Haida, Suga and Seki (1977) showed that ethanol is an example of a low molecular-weight compound exhibiting multiple glass-transition phenomena. The ethanol glassy liquid phase can be easily prepared by rapid (faster than 30 K/min) cooling of the liquid

down to below $T_g = 95$ K – glass transition temperature. By heating the ethanol glassy state from below 95 K one can prepare a new phase of ethanol – metastable crystal II. The Crystal II phase can also be produced by strictly controlled cooling of the liquid. During heating, the crystal II melts at $T = 127.5 \pm 0.5$ K, and during melting an irreversible transition into the crystal I phase occurs. The crystal I phase could also be grown from a supercooled liquid by annealing the sample at a temperature close to the melting point (~ 156 K). An X-ray study of ethanol crystal at 87 K prepared from liquid and annealed at ~ 156 K revealed a monoclinic unit cell with space group Pc, $a = 5.377$ Å, $b = 6.882$ Å, $c = 8.225$ Å, $\beta = 102.2^\circ$, $V = 298.6$ Å³ (Jönsson, 1975). The density of the crystal at $T = 87$ K was calculated to be 1.025 g cm⁻³.

Fast quenching of liquids is one of the most popular ways of preparing a glassy state. Another method to obtain non-crystalline solids showing glass transition phenomena is the condensation of molecules from a vapor state onto a cooled substrate. Glass transition phenomena were found for methanol (Sugisaki, Suga and Seki, 1968a) and water (Sugisaki *et al.*, 1968b) molecules deposited on a chilled substrate. The vapor condensation process can therefore be treated as the equivalent of extremely fast quenching. For a number of liquids, such as e.g. methanol, the glass transition temperature for deposited samples does not differ detectably from that prepared by fast quenching of a liquid. Thin films cryocondensed from polar molecules onto a deeply cooled substrate exhibit very interesting electrical effects, which do depend on the condensation temperature.

Since 1969, when charge generation phenomena during condensation of water molecules onto a cooled substrate were found (Elliot *et al.*, 1969), the electrical properties of thin layers cryocondensed from polar molecules have been widely investigated. It was shown by Kutzner (1972) and by Chrzanowski and Sujak (1981) that the value, as well as, the sign of the cryocondensate surface charge depends on the condensation temperature and the kind of molecules only. They observed periodic changes of the surface charge with condensation temperature.

Periodic changes of the surface potential were also observed for condensate layers created from dipole molecules on a substrate with a uni-directional temperature gradient (Chrzanowski and Sujak,

1983; Sobolewski and Sujak, 1989). The main reason for the surface potential (surface charge) generation at the condensate layer is the ordering of the orientation of polar molecules during condensation (Kutzner, 1972; Chrzanowski and Sujak, 1981; Onsager *et al.*, 1978). The orientation of polar molecules could be induced by resonance interaction between molecules and the substrate phonons (Kutzner, 1972) or between molecules and the electromagnetic radiation from the substrate (Chrzanowski and Sujak, 1981) or induced by asymmetric electric field lines around a condensing molecule (Onsager *et al.*, 1978).

The aim of this paper is a comparison of some electrical effects (in isothermal and nonisothermal conditions) observed for ethanol cryocondensed thin layers with literature phase diagrams of ethanol, especially in the vicinity of the crystal II–crystal I phase transition occurring at $T \sim 128$ K.

EXPERIMENTAL

The samples were created by condensation of a vapor phase of ethanol onto a cooled substrate. The p.a. 99.8% liquid ethanol was a source of vapors to be condensed.

Two kind of experiments were performed.

To obtain a thermally stimulated current (TSC) spectrum, the samples were condensed at $T \sim 80$ K onto a mica substrate with double-comb shape Au electrodes. Next the samples were heated and the current in the measuring cell was recorded by an electrometer.

To obtain isothermal crystallization kinetics for different crystallization temperatures at nearly the same time, condensation was carried out onto a stainless steel substrate showing a constant, unidirectional temperature gradient. The temperature distribution along the condensing substrate was linear.

The surface potential distribution along the whole length of cryocondensed layer was measured by the Kelvin method, using a vibrating electrode system. An electrode, 5 mm in diameter, was located 2 mm above the condensing substrate.

The cryocondensate layer thickness as well as the condensation rate were measured by an interference method. The details of the

apparatus and the method of measurements can be found elsewhere (Sobolewski and Sujak, 1989).

The condensation process was conducted under 10^{-2} Pa of vacuum pressure, while the pressure before and after condensation was equal to about 10^{-4} Pa.

The surface potential distribution of the ethanol cryocondensate layer created on the substrate with uni-directional temperature gradient obtained immediately after condensation (squares) and one hour later (triangles), for a layer $4.2 \mu\text{m}$ thick is shown in Fig. 1. As can be seen, the value, as well as the sign of the surface potential, for an ethanol cryocondensed thin layer depends on the condensation temperature.

A positive sign of the surface potential was observed for layer fragments condensed within 103–112 K ($x < 2.5$ cm) while the negative sign of the surface potential appeared within 112–135 K ($2.5 \text{ cm} < x < 9$ cm). Above 135 K ($x > 9$ cm) the surface potential of ethanol deposits was equal to zero. It is also clearly seen that the ethanol layer

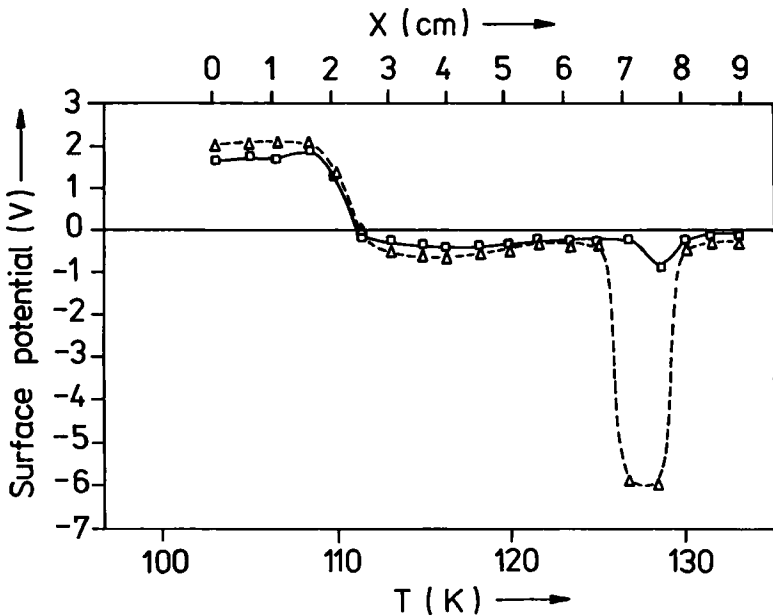


FIGURE 1 The surface potential distribution of ethanol thin layer condensed onto a substrate with uni-directional temperature gradient as measured just after condensation (squares) and one hour later (triangles) for $4.2 \mu\text{m}$ of layer thickness.

fragment formed at $T = 125\text{--}130\text{ K}$ shows a spontaneous increase of its surface potential with time. The highest value of the surface potential increase was reached at $T_m \sim 128\text{ K}$. The surface potential of other condensate fragments did not change significantly with time. The spontaneous increase of the surface potential with time, as measured at $T = 128\text{ K}$, for different condensate layer thicknesses, is presented in Fig. 2. Taking into consideration the results of calorimetric and DTA measurements of ethanol made by Haida *et al.* (1977) one can conclude that the spontaneous increase of the surface potential, as observed for an ethanol condensate fragment deposited between $125\text{--}130\text{ K}$, is related to irreversible crystallization to the crystal I phase. Our temperature $T_m = 128\text{ K}$ agrees very well with the melting temperature of the crystal II phase (crystallization to the crystal I phase) $T = 127.5 \pm 0.5\text{ K}$ (Haida *et al.*, 1977). Thus it seems that the curves presented in Fig. 2 do show crystallization kinetics. The kinetics of the crystallization process could be well described by the well known, phenomenological, Avrami equation (Avrami, 1939):

$$X(t) = 1 - \text{Exp}(-(K \times t)^n), \quad (1)$$

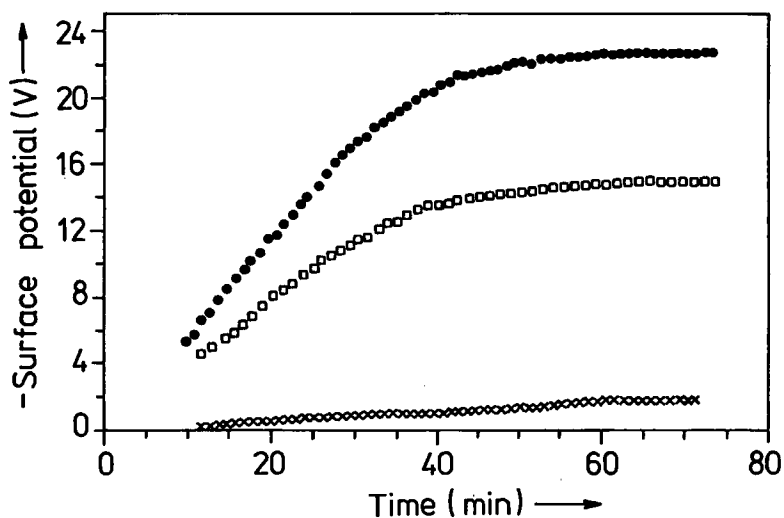


FIGURE 2 Spontaneous increase of the surface potential for ethanol condensate fragments created at vicinity of 128 K , for different layer thickness: $2.7\text{ }\mu\text{m}$ (crosses), $5.2\text{ }\mu\text{m}$ (squares) and $6.1\text{ }\mu\text{m}$ (points).

where X is a crystallized volume fraction, t – time, n – depends on the mechanism of growth and the dimensionality of the growing crystal, K is defined as the effective overall reaction rate, which is usually assigned to an Arrhenius temperature dependence:

$$K = K_0 \times \text{Exp}(-E/RT), \quad (2)$$

where E is the effective activation energy describing the overall crystallization process, K_0 is a constant.

Assuming that the crystallized fraction X is proportional to $U(t)/U_{\text{sat}}$, where $U(t)$ is the surface potential measured at time t , and U_{sat} represents the saturation potential obtained for a condensate fragment deposited at $T \sim 128$ K, one can obtain the $X(t)$ curves for different temperatures.

Figure 3 shows the family of $X(t)$ curves as measured at temperatures 126.8 K – a, 127.7 K – b, 128.6 K – c and 129.4 K – d respectively – all curves were normalized to the value of the saturation potential obtained for the fragment condensed at $T = 127.7$ K. The condensate layer thickness was equal to $7 \mu\text{m}$. The full line curves represent the best fits of the experimental data (points) by Eq. (1).

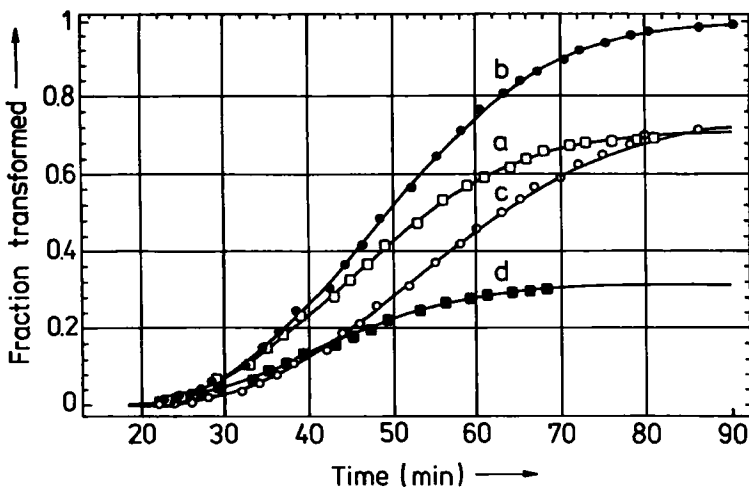


FIGURE 3 Normalized crystallization kinetics of ethanol crycondensate fragments deposited at temperatures: 126.8 K – a, 127.7 K – b, 128.6 K – c and 129.4 K – d respectively.

Taking into consideration Eq. (2), we obtain the effective activation energy as (20.7 ± 0.4) kJ/mol (average of 15 experiments). This value seems to be much too high compared with the literature value (Haida *et al.*, 1977) of the enthalpy difference between crystal I and crystal II phases (2.8 kJ/mol) obtained for phases created from the liquid state. Our value is rather closer to the activation enthalpy (22.8 kJ/mol) of relaxation phenomena around the glass transition region in a glassy liquid state. To explain our activation energy, one should assume that the thin ethanol layer condensed from the vapor phase onto a substrate within the range 125–130 K can exist in a glassy state (glassy liquid or glassy crystal II) and therefore the transformation observed in the vicinity of 128 K should run from a glassy state – via the crystal II phase – to the crystal I phase finally.

Because the TSC technique is very sensitive to phase transformations, we applied it to find out if the transformation at 125–130 K is really governed by two processes. Figure 4 shows a typical TSC spectrum, as observed for an ethanol cryocondensed layer created at $T \sim 80$ K. The heating rate was constant and equal to 1.5 K/min. A small polarizing voltage $U = 3$ V was applied to the measuring cell. In this case the cryocondensate layer thickness was equal to $11.5 \mu\text{m}$ (the same type of TSC spectrum was observed for thicknesses in the

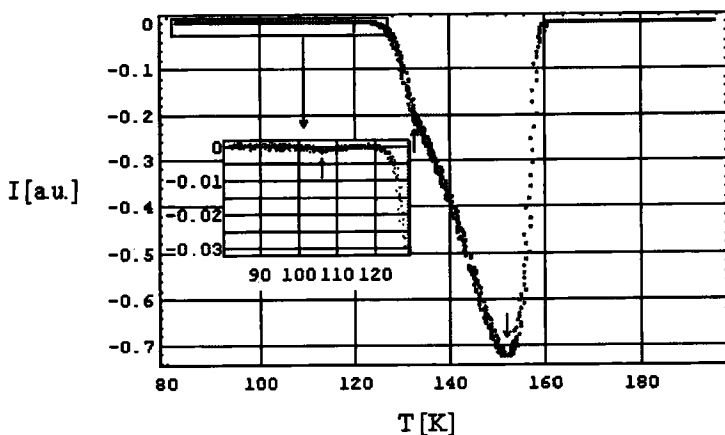


FIGURE 4 Typical TSC spectrum of $11.5 \mu\text{m}$ thick ethanol layer condensed at $T = 80$ K as measured within a double comb-shaped silver electrodes cell. $I_{\text{max}} = 72$ Na, heating rate 1.5 K/min, polarizing voltage = 3 V.

3–15 μm range). One can distinguish three peaks, marked by arrows, on the TSC spectrum: first appearing at $T \sim 105$ K, very small in comparison with others, second in the vicinity of 134 K, and a third above 150 K. The TSC current vanishes near 159 K – which nicely corresponds with the melting point of ethanol. The strong increase of TSC current observed at $T \sim 120$ K suggests that a crystalline phase – crystal II is starting to grow. At about 134 K the TSC curve changes its shape, which could be related to the appearance of a new crystalline phase – crystal I. Because the temperature of strong increase of the TSC current coincides with the temperature of the phase transition one can assume that the current intensity is proportional to the rate of the phase transition. On the basis of such an assumption the activation energy calculated from the TSC curve could be considered as an activation energy of the phase transition process. A semilogarithmic plot of the TSC current in an appropriate temperature range is presented in Fig. 5. It is seen that an exponential dependence between the TSC current and reciprocal temperature really exists. The estimated activation energy was $E_1 \sim 41$ kJ/mol for the low-temperature curve part and $E_2 \sim 10.9$ kJ/mol for the high-temperature part (obtained as average values from 12 experiments). The E_1 value may be compared with values of heat of adsorption for ultra-thin ethanol layers (exposure 3.3 L:1 L = 10^{-6} Torr s) measured by

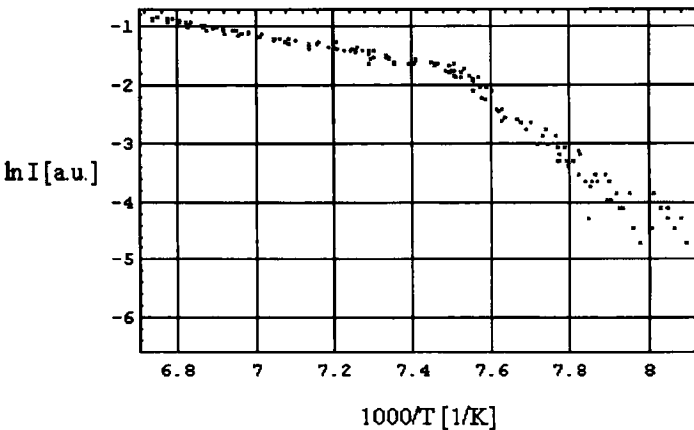


FIGURE 5 Semilogarithmic plot of TSC current versus reciprocal temperature for ethanol cryocondensed layer of 11.5 μm of thickness.

Thermal Desorption Spectroscopy (TDS), as presented by Wang, Ng, Lim, Lueng, Wu and Chen (1994). This was obtained for ethanol layers deposited at $T = 108$ K on a polycrystalline silver substrate and reveals four peaks at $T_m = 113$ K, 132 K, 134 K, 150 K. The heat of adsorption for these peaks were estimated to be 33.2 kJ/mol, 38.8 kJ/mol, 39.5 kJ/mol and 44.2 kJ/mol respectively. These values suggest rather weak bonding between substrate and molecules, and so the authors concluded that ethanol molecules adsorbed on a cooled, silver substrate might exhibit a certain degree of rotational freedom. These 4 peaks on the TDS spectrum might be due not only to ethanol molecules adsorbed on different crystal planes or different surface sites, as suggested by the authors, but (in accordance with our measurements) might be related to phase transformations occurring in appropriate temperature range, as well. The phase transformation process, in its initial stage should liberate ethanol molecules, and because of the weak bonding with the substrate, the molecules might be able to evaporate from the sample surface – as has been shown (Wang *et al.*, 1994) the evaporation is very strong at 132 K and 134 K.

A comparison of E_1 obtained from the TSC spectrum with overall activation energy for crystallization estimated for isothermal conditions, might lead to the conclusion that the ethanol layer condensed near 128 K is not unique in the initial structure – it may contain crystalline grains. This is similar to methanol (Sugisaki *et al.*, 1968a) and water condensates (Sugisaki *et al.*, 1968b), where the vitreous samples contain a small crystalline component. The existence of the crystalline component seems to be due to the warming of the sample surface during condensation, especially for high condensation rates.

The results presented above show that the spontaneous increase of the surface potential is generated by the crystallization process occurring at $T \sim 128$ K for an ethanol cryocondensed layer.

During the crystallization the molecular dipoles are ordered resulting in the observed current and the surface potential changes.

Acknowledgements

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