

The Solid State Polymorphism and Dynamics of 2,3-Dimethylbutan-2-ol (2,3-DM-2-B)

E. JUSZYŃSKA*, M. MASSALSKA-ARODŹ, P.M. ZIELIŃSKI AND J. KRAWCZYK

The H. Niewodniczański Institute of Nuclear Physics, PAS, E. Radzikowskiego 152, 31-342 Kraków, Poland

(Received February 29, 2012; in final form July 21, 2012)

In the paper we present adiabatic calorimetry and dielectric spectroscopy results for 2,3-dimethylbutan-2-ol (2,3-DM-2-B), one of the isomers of neohexanol. For 2,3-DM-2-B we have detected the following phase transitions: C2 (249.8 K) \rightarrow C1 (262 K) \rightarrow Is. No glass phase was found. In both crystalline phases C2 and C1 three relaxation processes were detected. These processes are discussed in relation to the calorimetric studies.

PACS: 65.40.-b, 65.40.Ba, 66.30.hp, 77.22.Gm

1. Introduction

Plastic crystalline phases tend to occur in compounds with globular shape of molecules [1]. Their structure is of high symmetry with activated rotational degrees of freedom of molecules placed in centers of crystalline lattice. Due to the low value of enthalpy and entropy of fusion plastic phases are energetically close to the liquid phases [2]. Calorimetric studies [2–4] showed that plastic phase can be easily vitrified to glass with positional order of molecules, whose orientational disorder is frozen-in. Due to that for a plastic glass phase a much smaller jump in the heat capacity at T_g is observed than in case of heating a glass of isotropic liquid phase [5, 6].

Recently, we have studied four isomers of neohexanol (2,2-dimethylbutan-1-ol) to elucidate the influence of OH bonding on formation of plastic crystalline phase in these aliphatic alcohols (abbreviated here as DM-B) with globular molecules [7]. The molecules have several conformations.

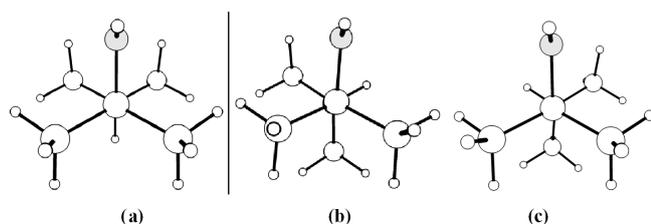


Fig. 1. Geometry of the lowest energy conformers of 2,3-DM-2-B for trans (a), gauche (–) (b), and gauche (+) (c) conformations.

In Fig. 1 the structures of three lowest energy conformers of 2,3-DM-2-B, $(\text{CH}_3)_2\text{CHC}(\text{CH}_3)_2\text{OH}$ (formed of trans and gauche (–) and gauche (+) molecular conformations), calculated on the B3LYP/6-311G** level

are displayed. They are characterized by C1 symmetry. In density functional theory (DFT) calculations the electronic energy of 1.36163×10^{-15} J was found for trans conformation and of 1.36195×10^{-15} J for gauche (–) and gauche (+) conformations. Various locations of the hydroxyl groups (and of the methyl ones) in the isomeric molecules result in different solid state polymorphism of the substances. Interestingly enough, differential scanning calorimetry (DSC) measurements have revealed that in fact only for two isomers, i.e., 2,2-dimethylbutan-1-ol, $(\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{OH})$, and 3,3-dimethylbutan-2-ol, $((\text{CH}_3)_3\text{CCH}(\text{OH})\text{CH}_3)$, plastic crystalline phases were identified [7]. It was not the case for 3,3-DM-1-B, $((\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{OH})$, of the strongest OH bonding between molecules, identified using infrared absorption spectroscopy [7], where isotropic liquid was easily supercooled and vitrified. Those results were later confirmed in the adiabatic calorimetry experiment [8]. In DSC observations of the fourth isomer, the 2,3-DM-2-B compound, where hydrogen bonding seems to be the weakest, the monotropic system of thermodynamic phases has been identified with two crystalline phases. They are not plastic crystals, as the entropy of melting (40.2 J/(mol K)) is higher than 21 J/mol value given by the Timmermans criterion [9]. Among four isomers of neohexanol only for 2,3-DM-2-B no tendency to vitrification was traced even on fast cooling of the sample. Similarly to DSC findings, in the inelastic incoherent neutron scattering experiment [10] for slowly and rapidly cooled samples crystal-like vibrational spectra have been identified at 20 K.

In the present paper we report the results of adiabatic calorimetry undertaken to check the phase situation of the 2,3-DM-2-B substance in a wide temperature range. Moreover, complex dynamics of molecules found by detailed dielectric relaxation spectroscopy measurements in both crystalline phases will be shown and discussed in respect of dynamics observed for other isomers.

* corresponding author; e-mail: Ewa.Juszyńska@ifj.edu.pl

2. Experimental

The substance of purity higher than 99% was purchased from the Aldrich Chemical Company and used without purification.

Heat capacity measurements of 2,3-DM-2-B have been performed by adiabatic calorimetry in the temperature range from 100 K to 300 K in various experimental runs. A laboratory made adiabatic calorimeter described elsewhere [11, 12] was used. The mass of the sample was 6.6007 g (0.0646 mol). Calorimetric studies were carried out using two methods of measurements. The first is the traditional one where the absolute values of the heat capacity of the substance in subsequent temperatures were measured during heating. The second method of measurement is a pseudo-DTA method, called the drift method [13]. It consists in determining evolution of rate of temperature changes $\Delta T/\Delta t$ (T vs. t) in response to the step by step heating of the sample with fixed portions of energies. These two methods were used simultaneously. In addition the drift method was used to measure changes of thermodynamical features occurring during cooling of the substance.

The dielectric measurements of the complex electric permittivity $\varepsilon^*(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu)$, i.e., of the absorption $\varepsilon''(\nu)$ and the dispersion of $\varepsilon'(\nu)$, have been made in the frequency range from 0.02 Hz to 10 MHz and in the temperature range from 123 K to 300 K during cooling and heating of the substance [14]. The sample was placed in the flat capacitor between the circular electrodes of 10 mm diameter. The distance between the electrodes was equal to 1.5 mm. The values of $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ were measured with an accuracy of 2% in the liquid and up to 5% in the solid phases. Dielectric relaxation measurements have been performed using Novocontrol Spectrometer. Temperature of the sample has been controlled using the Novocontrol Quatro system with a cryo-system [15]. The rate of changes of temperature varied from ± 5 K/min to ± 20 K/min.

3. Results

3.1. Polymorphism

A complex endothermic anomaly was detected by the calorimetric measurements of heat capacity $C_p(T)$ as shown in Fig. 2: a small maximum at $T_1 = 249.8$ K is ascribed to $C2 \rightarrow C1$ transition while a larger peak with maximum at $T_m = 261.8$ K is ascribed to melting of the crystal C1. One can suspect that on cooling not all of the phase C1 is transformed to phase C2. Thus, on heating a part of the sample, already in phase C1, does not contribute to the first transition responsible for the small anomaly. That hypothesis was supported by observation of a single anomaly at $T_c = 241$ K in cooling runs performed by drift method and by earlier DSC measurements (see Fig. 3).

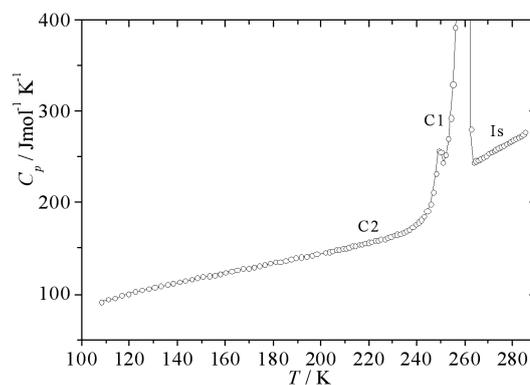


Fig. 2. Measured heat capacity of 2,3-dimethylbutan-2-ol. The data were obtained during heating run after the sample was initially cooled from room temperature to the liquid helium temperature with the average rate of 1 K min^{-1} .

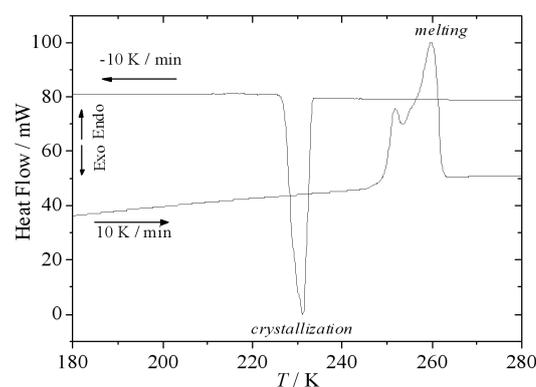


Fig. 3. DSC thermogram of 2,3-dimethylbutan-2-ol obtained on cooling and heating with the rate of 10 K min^{-1} .

3.2. Dynamics

The dielectric relaxation studies were performed in three runs, i.e., during slow cooling down to 120 K, then heating and subsequent cooling the sample.

Temperature dependence of the dielectric constant corresponds to the $C2 \rightarrow C1 \rightarrow \text{Is}$ phase sequence (see Fig. 4), the same as that observed in calorimetric studies. Surprisingly, in temperature range of both crystalline phases C1 and C2, dynamics of molecules was detected.

In Fig. 5 dielectric dispersion and absorption measured during the second cooling run at several temperatures are presented. Comparing the results of three runs one can say that absorption curves observed on cooling were slightly higher than those observed on heating and nearly 5 K supercooling of C1 was detected. No dielectric absorption was evidenced in liquid phase in the frequency range available. In both C1 and C2 crystalline phases the absorption curves of low intensity ($\varepsilon''_{\text{max}} \approx 0.01$) were observed corresponding to the Arrhenius type relaxation process denoted as (1). On lowering temperature the intensities of absorption curves grow till the $C1 \rightarrow C2$

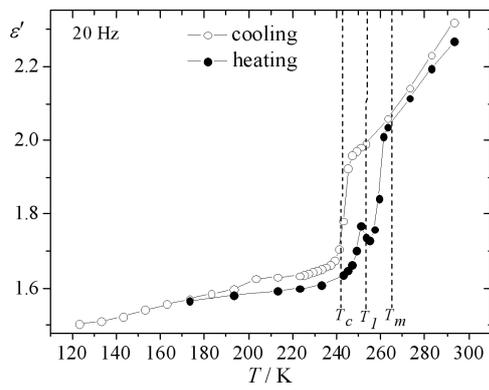


Fig. 4. The temperature dependence of $\epsilon'(\nu)$ for 2,3-dimethylbutan-2-ol, obtained at 20 Hz during cooling (\circ) and heating (\bullet) of the sample. The dashed lines indicate the phase transitions observed on heating (T_1 and T_m) and on cooling (T_c) by adiabatic calorimetry method.

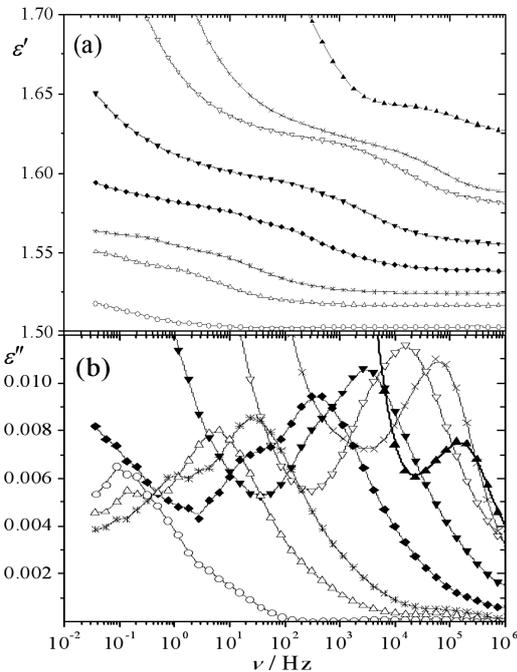


Fig. 5. Dielectric dispersion (a) and absorption (b) data for 2,3-dimethylbutan-2-ol observed during the second run of cooling in the temperature range from 245 K to 123 K. Symbols correspond to the following temperatures: 245 K (\blacktriangle), 233 K (\times), 213 K (∇), 193 K (\blacktriangledown), 173 K (\blacklozenge), 153 K ($*$), 143 K (Δ), 123 K (\circ).

transition. In phase C2 an extra slower process (2) was evidenced below 213 K, which seems to merge with the main process at higher temperatures. Intensities of both processes decrease with lowering temperature. Moreover, one can see that when the sample was cooled down below 173 K contribution of a faster very weak ($\epsilon''_{\max} \approx 0.005$) process (3) is visible. Taking into account calorimetric

data and due to very small intensity of dielectric absorptions, the processes (1) and (2) can be ascribed to conformational motions of trans and gauche conformers of 2,3-DM-2-B molecule (see Fig. 1). Process (3) seems to be related to the faster OH group rotations [16, 17].

4. Discussion

For 2,3-DM-2-B no trace of any glass transition was detected. The values of the enthalpy and entropy changes at the phase transitions are: $\Delta H = 0.19 \text{ kJ mol}^{-1}$ and $\Delta S = 0.7 \text{ J mol}^{-1} \text{ K}^{-1}$ for $C2 \rightarrow C1$ transition and $\Delta H = 7.19 \text{ kJ mol}^{-1}$ and $\Delta S = 27.4 \text{ J mol}^{-1} \text{ K}^{-1}$ for melting of phase C1. The large thermal effect at melting is the evidence of the activation of positional and orientational degrees of freedom of 2,3-DM-2-B molecules in this transition.

For description of the dielectric relaxations the Havriliak–Negami formula [18] was used

$$\epsilon^*(\omega) = \epsilon_\infty + \Delta\epsilon/[1 + (i\omega\tau)^{1-\alpha}]^\beta + A/\omega \quad (1)$$

with shape parameters $1 - \alpha$ and $\beta(1 - \alpha)$ ($0 < (1 - \alpha)$, $\beta(1 - \alpha) \leq 1$) corresponding to the distribution of the relaxation time τ . $\Delta\epsilon$ means dielectric increment. The last term describes the electric conductivity observed for high temperatures at low frequencies. For $\beta(1 - \alpha) = 1 - \alpha = 1$ the process is of the Debye type.

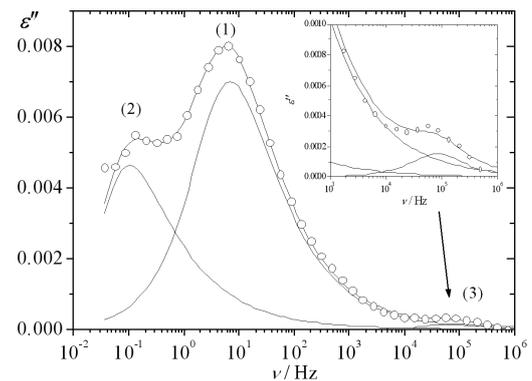


Fig. 6. Example of decomposition of the absorption curve (\circ) at 143 K into three processes (solid lines).

In Fig. 6 one can see an example of a contribution of three processes to the absorption observed at 143 K during the second cooling run. The values of the fitting parameters for processes observed are the following: $1 - \alpha \sim \beta(1 - \alpha) \approx 0.612$, $\Delta\epsilon = 0.023$ and $\tau = 0.038 \text{ s}$ for the process (1), $1 - \alpha \sim \beta(1 - \alpha) \approx 0.464$, $\Delta\epsilon = 0.01$ and $\tau = 2.766 \text{ s}$ for the process (2), and $1 - \alpha \sim \beta(1 - \alpha) \approx 0.995$, $\Delta\epsilon = 0.0003$ and $\tau = 1.895 \times 10^{-6} \text{ s}$ for the process (3). Estimated error of the fitted parameters does not exceed 10%. For processes (1) and (2) the deviations from the Debye shape relaxation are large.

Temperature dependence of the relaxation times obtained by fitting Eq. (1) to the results of three experimental runs is presented in Fig. 7. According to the

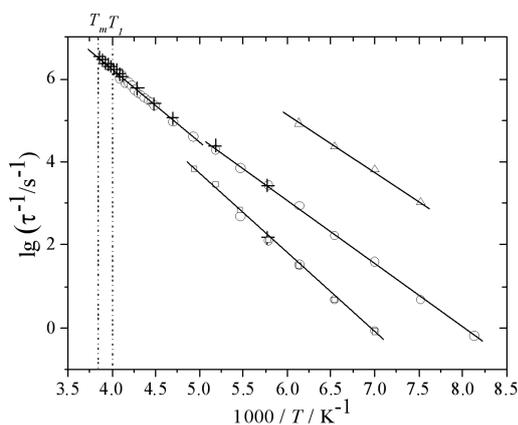


Fig. 7. The temperature dependence of the relaxation rate for three processes. Different symbols correspond to three experimental runs: \square cooling and $+$ for heating, \circ and Δ for second cooling.

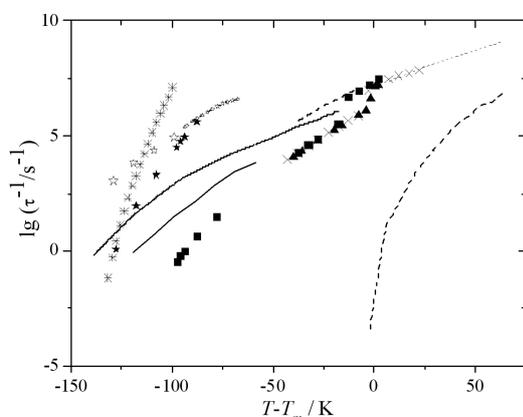


Fig. 8. The temperature dependence of the relaxation rate for processes observed in 2,3-DM-2-B (solid lines and $*$), 3,3-DM-1-B (dashed lines and $*$, [7]) and in 2,2-DM-1-B (\blacksquare , \blacktriangle , \times symbols and \star) where melting processes of two plastic crystalline phases were observed at $T_m = 235.7$ K (for 2,3-DM-2-B), and $T_m = 250.8$ K (for 3,3-DM-2-B) [19]. For 3,3-DM-2-B $*$ corresponds to β -process observed in low temperatures.

Arrhenius equation the energy barrier for the process (1) is 8.8 ± 0.1 kJ/(mol K) above 200 K and 7.1 ± 0.7 kJ/mol below, while for process (2) 10.9 ± 0.9 kJ/(mol K). For process (3) the energy barrier was estimated roughly to 2.8 ± 0.2 kJ/(mol K).

Figure 8 presents the temperature dependence of the reciprocal relaxation times $\lg(\tau^{-1}/s^{-1})$ vs. $T - T_m$ for processes observed in 2,3-DM-2-B and other three isomers [8, 19]. In liquid phase of 2,2-DM-1-B and 3,3-DM-1-B reorientations of whole molecules have the same rate (see squares and crosses, and dashed line, respectively). Effect of supercooling of isotropic phase was found for both substances. Moreover, in liquid of 3,3-DM-1-B, with the strongest OH bonding between molecules, the ultra

slow reptation process, typical for motions of polymer chain, was found [8], not observed for other isomers.

Rotation of whole molecules was not detected in the well ordered crystalline phases of 3,3-DM-1-B and of 2,2-DM-1-B (see lack of experimental points near $T - T_m$ of -50 K). Relaxation ascribed to such motions was detected in the plastic phases C, C1 and C2 of 2,2-DM-1-B (see crosses, triangles and squares). For crystalline phases of 2,3-DM-2-B the relaxations ascribed in this paper to conformational motions in trans and gauche conformers (see solid lines) occur in higher frequencies than relaxation connected with rotation of whole molecules in 2,2-DM-1-B. It is worth to note that for crystalline phases of 2,3-DM-2-B dielectric increments for relaxation (1) and (2) are two orders of magnitude smaller than those connected with motions of whole molecules in plastic phases of 2,2-DM-1-B [17].

Finally, one can see that relaxations connected with the fastest motions, ascribed to hydroxyl groups, have been observed for crystalline phases of all isomers (see stars). For 3,3-DM-2-B it is the only motion giving very weak well distinguished relaxation [20]. Temperature dependence of that intra molecular rotation is similar for 3,3-DM-1-B and 2,3-DM-2-B. For 3,3-DM-2-B and 2,2-DM-1-B the dependences are much stronger (see $*$ and filled stars in Fig. 8) and about 120 K below T_m the relaxation times are equal to about 10 s. Energy barriers for OH group rotations in crystalline phases of four isomers are the following: 14.21 ± 0.05 kJ/mol for 2,2-DM-1-B, 23 ± 0.2 kJ/(mol K) for 3,3-DM-1-B, 2.8 ± 0.2 kJ/(mol K) for 2,3-DM-2-B and 2.9 ± 0.2 kJ/(mol K) for 3,3-DM-2-B. One can see that for 1-butanols the energy barriers are much higher as motion of the OH groups is hindered by the higher bond strength than for other two isomers.

5. Summary

Comparing the results of $C_p(T)$ obtained by adiabatic calorimetry for four isomers of the neohexanol, i.e., for 2,3-DM-2-B, 3,3-DM-2-B, 2,2-DM-1-B and 3,3-DM-1-B compounds [7], one can see very different polymorphism of solid state. Among four isomers only 2,3-DM-2-B is not a glass former and it has a simple polymorphism with two crystalline phases. Basing on calorimetric results the C2 and C1 phases are stable ordered crystals. It is interesting that in dielectric relaxation experiment dynamics of molecules was detected in both phases: in phase C2 two weak Arrhenius type relaxation processes (1) and (2) of similar energy barriers were observed and ascribed to conformational motions of gauche and trans conformers of 2,3-DM-2-B molecules. In addition, a contribution of the faster very weak kHz-relaxation process (3) was traced at low temperatures of the crystal C2 phase and ascribed to OH group rotation. In the phase C1 it was possible to detect only one absorption curve — it seems that at higher temperatures both processes (1) and (2) merge. Structural studies should help to elucidate the ordering of molecules and the packing coefficient of them

in C1 and C2 phases regarded as the ordered crystals on basis of thermal effect measured at melting.

Acknowledgments

The authors would like to thank Prof. Antoni Kocot and Dr. Kamil Kamiński for their help in the dielectric measurements at the Silesian University.

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