Available online at www.sciencedirect.com
ScienceDirect
Physica B 403 (2008) 109–114
PHYSICA B
www.elsevier.com/locate/physb

Neutron scattering studies of solid-state polymorphism in dimethyl butanol glass formers

E. Juszyńska[a], M. Massalska-Arodź[a,*], I. Natkaniec[a,b], J. Krawczyk[a]

[a]*The H. Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Radzikowskiego 152, 31-342 Kraków, Poland*
[b]*Frank Laboratory of Neutron Physics, JINR, 141980 Dubna, Russia*

Received 23 February 2007; received in revised form 9 August 2007; accepted 10 August 2007

Abstract

Inelastic incoherent neutron scattering (IINS) and neutron powder diffraction (NPD) studies have been performed for two dimethyl 1-butanols and two dimethyl 2-butanols with CH_3 side molecular groups. Low-temperature vibrational density of states confirmed solid-state polymorphism detected by calorimetric methods, i.e., existence of crystalline and ODIC phases for all isomers, orientationally disordered glass for 2,2-DM 1-B and 3,3-DM 2-B, and glass of isotropic phase for 3,3-DM 1-B. Difference in vibrational density of states between glass and the ordered crystal has shown the so-called Boson peak. Influence of the OH group position in the molecules on their vibrational dynamics up to 50 meV is discussed.

PACS: 78.70.nx; 61.66.hq; 63.50.+x

Keywords: Neutron scattering; Vibrational dynamics; 3, 3-Dimethyl 2-butanol; 2, 3-Dimethyl 2-butanol; 3, 3-Dimethyl 1-butanol; 2, 2-Dimethyl 1-butanol; Boson peak

1. Introduction

Four isomers of dimethyl butanol of chemical formula $C_6H_{13}OH$ have nearly globular molecules thanks to CH_3 side groups. Earlier DTA [1,2], adiabatic calorimetry [3,4] and dielectric studies [1–3,5] for some isomers, and the systematic DSC studies [6] for all of them, i.e., 1-butanols: $CH_3CH_2C(CH_3)_2CH_2OH$ (2,2-DM-1B, called also neohexanol) and $(CH_3)_3CCH_2CH_2OH$ (3,3-DM-1B) and 2-butanols: $(CH_3)_3CCH(OH)CH_3$ (3,3-DM-2B) and $(CH_3)_2CHC(CH_3)_2OH$ (2,3-DM-2B) have shown diverse solid state polymorphism depending on location of CH_3 and OH groups in the molecules. In our IR studies [6] hydrogen bonds between molecules were found. Details of molecular shape influence strength of hydrogen bonds and vibrational intra-molecular dynamics. Phase transition sequences for all isomers are collected in Table 1. Solid phases studied in our neutron-scattering measurements at low temperature, i.e., crystalline phase C3, orientationally disordered crystal (ODIC) C2 and its glass GC2 in 2,2-DM 1-B; crystalline phase C1 and glass of liquid (LQG, called structural glass) in 3,3-DM 1-B; ODIC C4 and glass GC4 in 3,3-DM 2-B and crystalline phase C2 in 2,3-DM 2-B are indicated in bold.

Neutron scattering method is a very good experimental tool for studying the lattice and vibrational dynamics in the frequency range up to 50 meV. So far we have reported results of the inelastic incoherent neutron scattering (IINS) for two dimethyl 2-butanols only [8]. The main goal of the present studies is to extend the investigations to two 1-butanol compounds in order to get insight into the influence of the position of the OH and CH_3 molecular groups on density of vibrational states (DOS) in various low-temperature solid phases and on details of phase diagrams for four dimethyl butanols. Differences in the low-energy lattice vibrations spectra of a crystalline phase, ODIC, glass of ODIC and glass of liquid will be discussed.

*Corresponding author. Tel.: +48 12 6628439; fax: +48 12 6628458.
E-mail address: Maria.Massalska-Arodz@ifj.edu.pl (M. Massalska-Arodź).

0921-4526/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2007.08.086

Table 1
Sequence of phase transitions for four dimethyl butanols

Substance	Cooling	Heating
2,2-DM 1-B	*Fast:* I→**C2**→**GC2**	**GC2** (∼150) **C2** (163) **C3** (∼200) **C2** (234) C1 (251) I
	sI (212) **C2**	**C2** (235) C1 (251) I
3,3-DM 1-B	*Fast:* sI (151) **LQG**	**LQG** (151) sI (196) **C1** (231) I
	Slow : sI **(** 195**) C1**	
3,3-DM 2-B	sI (268) **C4** (220) **GC4**	**GC4** (220) **C4** (249) C3 (272) C2 (274) C1 (275) I
2,3-DM 2-B	sI (234) **C2**	**C2** (249) C1 (261) I

Phase transitions temperatures are given in (K). Accuracy of estimation of the phase transition temperatures is equal to 0.5 K.

2. Experimental

Dimethyl butanols of 99% chemical purity have been purchased form the Aldrich Chemical Company and used in the measurements without further purification. IINS spectra and neutron powder diffraction (NPD) patterns have been registered at several chosen temperatures on fast (10 K/min) and on slow (1 K/min) cooling and heating of the sample within 20–300 K range. Samples have been placed in the cryostat in a flat hermetic aluminum vessel of a size of $16\times7\times0.1\,\mathrm{cm}^3$. The IINS spectra for dimethyl butanols have been measured in the energy range up to 250 meV. The inverted geometry time-of-flight spectrometer NERA installed at the high-flux pulsed reactor IBR-2 at the JINR, Dubna, Russia, was used [9,10]. The IINS spectra have been normalized to the monitor count and the background has been subtracted. Next, density of states $G(\omega)$ was calculated according to the following formula for double differential cross section $\mathrm{d}^2\sigma/\mathrm{d}\Omega\,\mathrm{d}\omega$ describing the scattering of neutrons on protons in the sample:

$$\frac{\mathrm{d}^2\sigma(\kappa,\omega)}{\mathrm{d}\Omega\,\mathrm{d}\omega}=\frac{k\hbar\kappa^2}{k_0 2M\omega}(b^{\mathrm{inc}})^2\frac{\exp(-2W)}{1-\exp(-\hbar\omega/k_{\mathrm{B}}T)}G(\omega), \qquad (1)$$

where k_0 and k are the wave vectors of incident and scattered neutrons, respectively, b^{inc} stands for the incoherent scattering length of hydrogen atom and κ is the momentum transfer of the neutron. M stands for molecular mass, $\exp(-2W)$ is the temperature Debye–Waller factor. When the harmonic approximation and one-phonon scattering process are assumed [11] $G(\omega)$ is defined by

$$G(\omega)=\sum_n\sum_j\int \mathrm{d}^3q[A_j^n(q)]^2\delta[\omega-\omega_j(q)], \qquad (2)$$

where $A_j^n(q)$ is the amplitude of displacement of the nth atom in the unit cell during the vibrational mode $\omega_j(q)$, j counts the dispersion curves of internal normal modes, and q is a reciprocal lattice wave vector in the Brillouin zone. The $G(\omega)$ functions registered for various temperatures have been normalized to the same area in the range 0–20 meV. Simultaneously with IINS spectra, the NPD patterns were measured by eight detectors in two scattering angles sectors, i.e., 30–65° and 115–150°. They were normalized taking into account the wavelength distribution of incoming neutron flux $\Phi(\lambda)$.

3. Results and discussion

3.1. Solid-state polymorphism

Interplay of the molecular structure, dynamics and interactions between molecules result in specific solid-state polymorphism of a compound. Four investigated dimethyl butanol isomers have nearly globular molecules and hydrogen bonds between them [6] but they differ in the number of molecular conformations available [7]. Low-temperature IINS method gives clear evidence of polymorphism of four dimethyl butanols and allows for comparison of the results. Fig. 1 presents the scattering intensity $I(\lambda)$ vs. incoming neutron wavelength for three solid phases of 2,2-DM 1-B at several temperatures. They were obtained in various regimes of temperature changes applied to the sample. Glass of the ODIC C2 (GC2) with frozen-in orientational/conformational disorder of molecules located in the well-defined crystalline lattice has been obtained on fast cooling down to 20 K. The spectra of glass GC2 observed on heating are shown for 100 K. On further heating first activation of rotational/conformational motions occurs during the softening of GC2 to C2. Then, a spontaneous transformation to a new crystal C3 was found (see $I(\lambda)$ at 200 K) which on slow cooling to 20 K shows a spectra typical for a well-ordered crystalline phase. When the C3 phase was heated up to 214 K the ODIC phase C2 was observed again. Then even on slow cooling glass GC2 has been obtained as on the fast cooling of the sample from the room temperature. In spectra of C2 ODIC phase shown for 214 K one can see a small quasi-elastic broadening caused by scattering of neutrons on the hydrogen atoms performing reorientations.

The diffraction patterns for all $C_6H_{13}OH$ substances are "quite poor" because of incoherent scattering on large number of hydrogen atoms in their molecules. At suitable angles of detection one can observe small, not very distinct peaks corresponding to a long-range structural order of molecules in crystalline phase as presented in Fig. 2 for 2, 2-DM 1-B (C3). For the crystal C2 and glass GC2 some regularity in a spatial distribution of H atoms can be traced only in measurements performed at several specially chosen angles of diffraction. The quality of NPD patterns obtained in solid phases of dimethyl butanols is not good enough for structural analysis. Anyway, diffractograms are useful for control of the phase changes on cooling and heating.

The densities of states $G(\omega)$ corresponding to $I(\lambda)$ measured for four dimethyl butanols at chosen temperatures are presented in Figs. 3–5. In Fig. 3, the $G(\omega)$ curves concern the same solid phases of 2,2-dimethyl 1-butanol as