



# General specific heat dependences on temperature in neohexanol and its isomers

M. Gałązka\*, E. Juszyńska, P.M. Zieliński

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

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## ABSTRACT

The Gibbs free energy, in the form resulting from Landau considerations of the first order phase transitions, is used to describe resulting temperature behaviour of the specific heat of neohexanol and its isomers given by the general formula  $C_6H_{13}OH$ . Analyses of the data give power dependences of the specific heat on temperature with exponent one half in the vicinity of the melting points and almost one and a half far below phase transformation temperatures.

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## 1. Introduction

Full theoretical description of temperature behaviour of the specific heat and the entropy, the order parameter in the phase transition analyses involves applying one of the equations of state resulting from a rich family of models and theories proposed by Landau, Heisenberg, Ising, Wilson, Khmel'nitsky, Domb or Potts (for example see Refs. [1–5] and references cited therein) in the vicinity of the transition point in the first or in the second order phase transitions. All of the mentioned models and theories predict that in the vicinity of the phase transition temperature the physical quantities, such as the order parameter (polarisation, magnetisation, density or viscosity), the specific heat, the entropy and the susceptibility, are governed by the power law dependences on the reduced temperature with different values of exponents. However, far below the transition points all of dependences resulting from previously mentioned theories contribute to growing divergences between theoretically predicted dependences and those obtained from experimental measurements. To describe, for example, the behaviour of the specific heat in the broad temperature region, this means in the vicinity of the transition point as well as far below this point, one applies two different models to these regions or, as would be shown for isomers of neohexanol  $C_6H_{13}OH$  [6–9], use an effective description allowing quantities, being believed to take the constant values, to become temperature dependent. As it would be presented

\* Corresponding author.

E-mail addresses: [Miroslaw.Galazka@ifj.edu.pl](mailto:Miroslaw.Galazka@ifj.edu.pl) (M. Gałązka), [Ewa.Juszyńska@ifj.edu.pl](mailto:Ewa.Juszyńska@ifj.edu.pl) (E. Juszyńska), [PM.Zielinski@ifj.edu.pl](mailto:PM.Zielinski@ifj.edu.pl) (P.M. Zieliński).

for isomers of neohexanol in the vicinity of the transition temperature from the crystalline phase to the isotropic phase, being considered as the first or weak first order phase transition, one deals with a power law dependence of the specific heat on the reduced temperature with exponents whose values depend on a kind of fit procedure. The exponents can take the value one half, as for discontinuous case, under the condition that one allows some constant coefficient to appear in the temperature dependence of the specific heat, not resulting strictly from the phenomenological Landau theory of phase transitions. On the other hand, the exponents determined from the experimental measurements of the specific heat take a bit larger values than one half without the mentioned constant coefficient. However, far below the transition temperature one gets good agreement between theoretical and experimental curves of the specific heat with exponents equal to almost one and a half for all of the isomers of neohexanol. Summing up, this means that isomers of neohexanol despite having different properties and polymorphisms (described further within this section) are described very well by the power law dependences on the reduced temperature with closely located values of the exponents. This is in accordance with theories brought at the beginning of this section that all substances belonging to the same classes of universality (or to the same family) have the same exponent.

The dimethylbutanol (DM-B) molecules, i.e. 2,2-dimethylbutan-1-ol (2,2-DM-1-B)— $CH_3CH_2C(CH_3)_2CH_2OH$  [7,10–16], 3,3-dimethylbutan-1-ol (3,3-DM-1-B)— $(CH_3)_3CCH_2CH_2OH$ , 3,3-dimethylbutan-2-ol (3,3-DM-2-B)— $(CH_3)_3CCH(OH)CH_3$  and 2,3-dimethylbutan-2-ol (2,3-DM-2-B)— $(CH_3)_2CHC(CH_3)_2OH$ , belong to the “C1” symmetry group and their axes, planes and centres of symmetry cannot be determined. There is only one element of symmetry E. The 1-butanol

molecules have methylene groups  $\text{CH}_2$ , in contrast to the 2-butanols having the CH groups. Due to the molecular structure, 2,2-DM-1-B and 3,3-DM-1-B are the primary alcohols, 3,3-DM-2-B—the secondary and 2,3-DM-2-B—the tertiary one. Thanks to branched structure of C–C bonds the molecules of DM-B are nearly of globular shapes. Different molecular structures of the isomers influence strongly on dynamics and the polymorphism of solid phases. The geometry of molecules determines the appearance of the plastic ODIC type phases (orientationally disordered plastic crystal) in these substances, in addition to the completely ordered crystalline phases [10]. The ODIC phases are characterised by long-range arrangement of gravity centres of molecules in the crystal lattice but due to free rotation of molecules they are also called as rotational phases [17]. Thus in melting of the ODIC phase, only translational degrees of freedom are activated and the temperature of melting is lower than for the ordered crystalline phase. For organic substances several intermediate phases with the different degrees of freedom may occur between the ordered crystal and the disordered liquid phase [18]. The study of polymorphism of four DM-B substances was carried out using mainly three methods, namely, DSC [7], DTA [11,12,14,15] (only for 2,2-DM-1-B) and adiabatic calorimetry [9,10]. The isotropic liquid phase and crystalline or ODIC phases for isomers of neohexanol were found using calorimetry methods and different methods as well. A glassy phase of liquid was found on cooling for 3,3-DM-1-B [6,9,10]. Additionally, the crystallisation of supercooled liquid phase was observed there on heating after softening of the glass of liquid phase [6,9,10]. For 2,3-DM-2-B only crystallisation of an ordered crystal has been observed on cooling [9]. One transition of about 10 K below the melting temperature (with very small entropy jump) on heating has been observed [6,7]. No glassy phase was found there. A crystallisation of an orientationally disordered crystal (ODIC phase) occurs for 3,3-DM-2-B and 2,2-DM-1-B on cooling [6–9]. The softening of the glass of ODIC phase were observed on heating for mentioned samples [6,7,9]. However, on heating four [6,7,9] and two [6,7,9] ODIC phases were observed for 3,3-DM-2-B and 2,2-DM-1-B, respectively. Moreover, independent of cooling rate only glass of C4 ODIC phase for 3,3-DM-2-B, below about 240 K, and ordered crystalline phase for 2,3-DM-2-B, below about 195 K, were observed [6–9]. The polymorphisms in the isomers of neohexanol are determined by: the shapes and the geometries of the molecules, an existence of the hydrogen bonds, a location of the OH group and possible conformations of the molecules. In Table 1 the values of the melting temperature and related changes of enthalpy and entropy are collected. Small values of the enthalpy and the entropy of melting (smaller than 21 kcal/mol given by Timmermans criterion [19]) of 2,2-DM-1-B and, 3,3-DM-2-B alcohols confirm that the transformations occur for the ODIC phases. However, the large values of entropy of melting observed for 2,3-DM-2-B and 3,3-DM-1-B correspond to the transformation of the highly ordered crystalline phases into the liquid phase. These findings were confirmed by dielectric spectroscopy studies [8,10–12,14–16], the DSC method [6,7] and the DTA method [11–16]. Vibrational dynamics of the DM-B molecules was identified using the so-called incoherent inelastic neutron scattering (IINS) and optical spectroscopy in the far and mid infrared frequency ranges [9,20].

**Table 1**

Values of melting temperatures and changes of enthalpy and entropy at the melting points for isomers of neohexanol.

Quantity	Unit	2,2-DM-1-B	2,3-DM-2-B	3,3-DM-1-B	3,3-DM-2-B
$T_m$	K	233.11	261.90	235.68	275.55
$\Delta H_{fus}$	$\text{kJ mol}^{-1}$	4.4	7.2	9.5	1.7
$\Delta S_{fus}$	$\text{J K}^{-1} \text{mol}^{-1}$	17.9	27.4	40.9	6.2

Here, we consider a free energy density function in the Landau theory as presented in Section 3. The dependence of the specific heat on temperature, shown in Section 3, is for the first order phase transition. To the theoretical analysis some temperature  $T_M$ , higher than the melting temperature  $T_m$ , has been used. As it would be shown in Sections 4 and 5, using this procedure makes the description of behaviour of the specific heat easier.

## 2. Experimental

Heat capacity measurements of three isomers of neohexanol have been performed by adiabatic calorimetry in the temperature range from 100 K to 300 K with several experimental runs. A laboratory made adiabatic calorimeter at the Institute of Nuclear Physics, Polish Academy of Sciences [6,8] with the dedicated software [21], used to control parameters of the experiment and to acquire the data, was employed. Heat capacity measurements have been performed in the wide temperature range from 13 K to 302 K [10,22,23] for 3,3-DM-1-B at the Osaka University, Japan.

The masses of samples used for the calorimetric measurements were 5.528 g, 6.601 g, 5.368 g and 6.135 g with errors 0.001 g for 2,2-D-1-B, 2,3-DM-2-B, 3,3-DM-1-B and 3,3-DM-2-B, respectively.

The purities of the investigated samples of 2,3-DM-2-B and 3,3-DM-2-B were 99+ % and 98%, respectively. The neohexanol isomers 2,3-DM-2-B, 3,3-DM-1-B and 3,3-DM-2-B were bought from Aldrich Chemical Company and the 2,2-D-1-B sample was synthesised in the Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Cracow.

## 3. Specific heat dependence on temperature in the first order phase transition

### 3.1. Specific heat—general information

The specific heat  $C_p$  is the heat capacity per mole determined by the following formula:

$$C_p = \frac{C_p(\text{obs}) - C_p(\text{empty})}{m} \quad (1)$$

where  $C_p(\text{obs})$  is the total observed heat capacity of the sample and the sample cell,  $C_p(\text{empty})$  is the heat capacity of the empty cell and  $m$  is the mass of the sample in mole. The excess specific heat data associated with the Cr–Is transition (crystal–isotropic transition), related to the melting of the crystalline phase, is determined by the following relation:

$$\Delta C_p = C_p - C_p^{(\text{bg})} \quad (2)$$

where the specific heat  $C_p$  is obtained from Eq. (1) and  $C_p^{(\text{bg})}$  represents the background heat—a contribution of the vibrational degrees of freedom. The background heat  $C_p^{(\text{bg})}$  is shown as solid lines in Fig. 1(a)–(d) for all of the isomers of neohexanol. The Cr–Is transitions are of the first order for all of the neohexanol isomers.

### 3.2. First order phase transition in the Landau expansion

In accordance with the Landau assumptions related to the phase transitions the free energy density function  $F$ , also called the Gibbs free energy, can be expanded into a power series of an order parameter  $\varphi$  [1–3,5]

$$F = f_0 + a\tau\varphi^2 + b\varphi^4 + c\varphi^6 \quad (3)$$

where  $\tau = T/T_0 - 1$  is the reduced temperature,  $T_0$  is the temperature at which the coefficient of  $\varphi^2$  changes a sign (it is the critical temperature in the second order phase transition),  $a$ ,  $b$  and  $c$  are the

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