



Solid binary mixtures of neopentanol with *tert*-Butyl chloride and carbon tetrachloride studied by thermal, X-ray and dielectric techniques



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ARTICLE INFO

Article history:

Received 5 August 2015

Received in revised form 12 February 2016

Accepted 6 March 2016

Available online 15 March 2016

Keywords:

Glass transition

Dielectric relaxation

Differential Scanning Calorimetry (DSC)

Neopentanol

tert-Butyl chloride

Carbon tetrachloride

ABSTRACT

The binary mixtures of Neopentanol (NPOH) with *tert*-Butyl chloride (TBC) and Carbon tetrachloride (CTC), have been studied using Differential Scanning Calorimetry, Dielectric spectroscopy and X-ray diffraction techniques. The results indicate the formation of the solid solutions. The crystalline solid thus formed is found to be orientationally disordered and supercools easily to form glassy crystal for mole fraction of NPOH in the range of 0.7–0.9. The T_g values are in the range of 140–147 K. In the dielectric study, a primary α -process and two sub- T_g processes are found for TBC-NPOH, whereas for CTC-NPOH only one sub- T_g process is found. The dielectric spectra of α -process follows the Havriliak–Negami equation. The sub- T_g processes follow the Cole–Cole equation, and are found to be of Johari–Goldstein type, indicating intermolecular nature.

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1. Introduction

Compounds of globular molecules are capable of forming plastic crystals [1,2]. In plastic crystals the enthalpy associated with the solid–solid transition is higher as compared to the solid–liquid transition [1–3] and this property can be utilized for thermal energy storage [4,5]. Since in plastic phase, the molecules are translationally ordered but orientationally disordered (OD), it is more advantageous to deal with these theoretically as compared to the structural glass formers and hence, are used as model systems [6] to understand the glass transition phenomenon. The molecular relaxation in the OD phase occurs in low-frequency region on supercooling [7–16]. On further cooling rotational degrees of freedom get kinetically frozen at glass transition temperature T_g and, this phase below T_g is referred to as the ‘orientational glass’ or ‘glassy crystal’ [7,17]. The relaxation in glassy crystals is similar to that observed in liquid glass formers [6]. Johari and Goldstein [18,19], based on their studies on many rigid-liquid glass formers, have observed that the glassy phase has one more relaxation, termed as the sub- T_g or β -process that is an intrinsic feature of the glass transition [20–23]. The β -relaxation involves

reorientational motion of the entire molecule in the cage formed by the surrounding molecules [11]. This β -process is often referred to as Johari–Goldstein (JG)-relaxation or β_{JG} -relaxation to honour their important discovery [24–26]. The identification of β_{JG} -relaxation is not always easy, and stringent criterion given by Ngai and co-workers [24,27–29] for identification needs to be looked into.

Most of the plastic crystals are less stable in their supercooled phase and collapse to the nonrotator phase. Due to this transformation, it is difficult to gain information regarding the various relaxations that occur in glassy crystalline phase. In case of neopentanol (NPOH), there is a lack of agreement about the T_g value, and it is not clear whether, β -process exists [11,30–37]. Johari [11] using the calorimetric technique determined T_g equal to 133 K, whereas Dworkin [30] reported it to be 143 K. Salud et al. [31] through X-ray diffraction technique found it to be 123 K. Recently, Singh et al. [36,37] using dielectric spectroscopy argued that the T_g is 144 K. Thus, there is lot of uncertainty in the reported behaviour of the plastic phase of NPOH in the supercooled state and, the lack of the details of the β -process such as activation energy, etc. make it difficult to find out its origin. Therefore, further investigations are required to clear the uncertainty and to understand the nature of sub- T_g process. Keeping this in mind we report the Differential Scanning Calorimetry (DSC), X-ray and dielectric measurements for

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two binary systems of NPOH that form solid solutions and extend the result to neat NPOH.

2. Experimental

The samples studied in this investigation are Neopentanol or NPOH [$C_5H_{11}OH$, molecular weight (MW) = 88.15 $g\ mol^{-1}$, 99% purity, obtained from Aldrich Co. USA]; *tert*-Butyl chloride or TBC [C_4H_9Cl , MW = 92.57 $g\ mol^{-1}$, 96% purity, obtained from Spectrochem Pvt. Ltd., INDIA] and Carbon tetrachloride or CTC [CCl_4 , MW = 153.82 $g\ mol^{-1}$, 99.5% purity, obtained from Thermo Fisher Scientific India Pvt. Ltd., INDIA]. They were used as received without any further purification. The sample Table is given in supplementary information S1.

The Differential Scanning Calorimetry (DSC) measurements were performed using PerkinElmer Sapphire DSC with quench cooling accessory. The DSC cell was calibrated using indium (melting transition = 429.75 K) and mercury (melting transition = 234.3 K) as standard materials. Power X-ray diffraction measurements were performed using PANalytical X'pert PRO diffractometer with PW 3011/20 Xe proportional detector. The X-ray tube was operated at 45 kV and 40 mA with diffraction angle ranging from 5° to 90° . Monochromatic Cu-K α_1 ($\lambda = 1.54056\ \text{\AA}$) radiation was used for this purpose. X-ray measurements at low temperature were performed using RICOR-Crydrive 3.0 (20–300 K) with argon gas. The X-ray results were analysed through Expo-2014 software using N-TREOR 09 [38] as the specific indexing program. The dielectric measurements were carried out with Agilent E4980A LCR meter with frequency range 20–2 MHz. The frequency range from $10^{-0.5}$ Hz to 10^{-3} Hz was covered by using d.c. step response technique in combination with a Keithley model number 617 programmable electrometer. For the further details of dielectric experimental setup, the reader may consult the previous publications from this laboratory [39–42].

3. Results

3.1. Neat NPOH

NPOH is found to exist in orientationally disordered (OD) phase at room temperature. This high-temperature phase (phase S_I) is fcc in structure [31,34,43] with unit cell parameter at room temperature as: $a = 8.83\ \text{\AA}$ [43] which is in agreement with our measurements reported below. On cooling, this OD phase transforms to an ordered phase S_{II} at 217 K that is triclinic in structure [31], which on subsequent heating transforms to plastic phase at 237.5 K. When phase S_I is cooled using fast quench cooling method and heated at a rate of 10 K/min, it transforms exothermally from S_{III} (which is a metastable phase and even may be a mixed phase of S_{III} , S_{II} and supercooled S_I) to phase S_{II} at (T_3) = 154.5 K. On further heating, the supercooled phase S_I transforms to phase S_{II} at (T_2) = 215.3 K. The enthalpy of transformation for $S_I - L$ and $S_{II} - S_I$ are 3.92 kJ/mol and 4.15 kJ/mol, respectively, which matches quite well with the previously reported values [3,31]. DSC curves for neat NPOH are shown in supplementary information SII and the details of transitions along with the reported value are given in supplementary information SIII.

3.2. Neat TBC

TBC, if cooled from its liquid state, freezes to an OD phase S_I below 244.4 K. This phase exhibits fcc structure [44–49] with unit cell parameter at 228 K, $a = 8.62\ \text{\AA}$ [46]. On further cooling, this OD phase transforms to phase S_{II} of unknown structure [47] below $T = 219.5\ K$, that is found to be stable only upto 2 K

temperature range. This phase (S_{II}) undergoes transformation to phase S_{III} at $T = 217.7\ K$ exhibiting tetragonal structure [48]. Finally, at a temperature $T = 184.8\ K$, phase S_{III} transforms to phase S_{IV} having monoclinic structure [48].

3.3. TBC-NPOH binary system

It is not easy to obtain the glassy crystalline state of NPOH. Extremely high cooling rate is required as the OD phase S_I quickly transforms to ordered phase [37]. This rapid transformation to ordered phase can be prevented by choosing a second compound that forms a solid solution with NPOH in the OD phase [31]. NPOH forms a solid solution with TBC (solid phase S_I) which is evident from DSC results. Fig. 1 shows the DSC curves for different concentrations of TBC-NPOH binary system. In this figure, x_m corresponds to the mole fraction of NPOH in the solution. These curves are recorded during heating at a rate of 10 K/min after the sample was cooled down to 100 K with a cooling rate nearly 10 K/min. The “melting” endotherms for these systems are not sharp, and they extend over 10–12 K temperature range, which is a characteristic feature of the formation of a solid solution. In this figure (Fig. 1), T_{Sol} and T_{Liq} are the solidus and liquidus temperature, respectively, and the region between T_{Sol} and T_{Liq} corresponds to the limiting temperature of the two-phase S_I + liquid equilibrium. T_1 and T_2 are the solid–solid transition temperatures. The transition at T_2 is observed at low concentrations ($x_m \leq 0.30$) only. At higher concentrations, the transition at T_1 is only observed if the sample is annealed at 193 K for a minimum of one hour. In the region $0.6 \leq x_m \leq 0.9$, the solid phase S_I supercools to form glassy crystal at T_g (Fig. 2 & Fig. 3). Fig. 2 depicts the DSC curve of TBC-NPOH binary system for $x_m = 0.71$ along with the curve for the annealed sample. In the same figure (Fig. 2), the inset shows the magnified portion of the curve near T_g region, showing a clear step-like change in baseline at T_g (145.4 K) for the unannealed sample. The specific heat changes taking place at glass transition temperatures is $\sim 0.23\ J/(g\ K)$ and the value of fragility index ‘m’ (discussed at the end of the section) is small; which indicates that the samples are ‘strong’ according to Angell’s classification of materials [50,51]. The solid–liquid sketch of the characteristic temperatures for TBC-NPOH binary system deduced from the DSC curves is shown in Fig. 3 (Table for the transition temperatures is given in supplementary information SIV). In the sketch of the characteristic temperatures three transitions at T_1 , T_2 and T_3 are shown. The transition at T_1 corresponds to a transition from the ordered phase S_{II} to plastic phase S_I , which is supported by dielectric measurement discussed in the later paragraphs, and is observed for entire concentration range. The transition at T_2 is observed for the low concentration range of $x_m \leq 0.30$ only and is similar to $S_{III} - S_{II}$ transition of pure TBC. Finally, the transition at T_3 is observed for $x_m \leq 0.95$ and coincides with $S_{III} - S_{II}$ transition of pure NPOH.

Due to a similarity in crystal structure and lattice parameters [31,43–46], TBC & NPOH form solid solutions in their S_I phase. X-ray diffraction measurements of solid phase S_I of TBC-NPOH binary system have been performed. The diffractogram exhibits few lines (Supplementary file SV) and indicate fcc structure as shown in Fig. 4. Variation of the lattice parameter of the fcc structure with composition is plotted in Fig. 4 for TBC-NPOH binary system along with that of pure NPOH (Table for the lattice parameters is given in supplementary information SVI). The variation of lattice parameter for TBC-NPOH is not continuous as a kink around $x_m \approx 0.75$ is observed. It is possibly due to the appearance of the demixing region [52,53] around this concentration between fcc of NPOH and tetragonal or even fcc phase of TBC.

For the concentration range from $x_m \approx 0.60$ to $x_m \approx 0.90$ the binary system behaves like a single component plastic crystal and gets supercooled on cooling from its plastic phase S_I at room

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