Full Length Article

Experimental study of relaxation dynamics in solid solutions of benzene, hexa-substituted benzenes. II

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ABSTRACT

In continuation with Part I of current study, we present here the orientationally disordered materials penta-chloroaniline (PCA), bromopentamethylbenzene (BPMB), and their solid solutions with hexachlorobenzene (HCB) and hexamethylbenzene (HMB), respectively, encompassing the entire concentration range, studied employing dielectric spectroscopy, differential scanning calorimetry, and powder X-ray spectroscopy. The α-relaxation in these systems gets closer to Debye behaviour on non-polar rich side and is analyzed employing Havriliak-Negami equation, whereas the β-relaxation is found to be symmetric everywhere and follows Cole–Cole equation. In both the systems studied here, the temperature dependence of relaxation rates could be described by Arrhenius equation. The β-relaxation evidenced in these two binary systems appears to originate from the different microscopic mechanism that is discussed based on their spectral behaviour. Further, we probe the liquid glasses of very dilute concentrations of dipolar HSB solutes in OTP matrix, and compare it with the spectral features of the dilute dipolar solid solutions of HSBs.

1. Introduction

Secondary relaxations are reported in many orientationally disordered systems [1–15]. Very few of these secondary relaxations, only those arising from the dynamics of molecular unit as a whole, and not from the intramolecular degrees of freedom, are termed as Johari-Goldstein (JG) relaxation. In some orientationally disordered materials (e.g., ethanol, cyclo-hexanol, cyclo-octanol, 2-adamantanone, etc.) [1,4,9–11], the βJT relaxation appears on the high frequency side of the α-relaxation with much weaker dielectric strength as compared to the main or α-relaxation. The α- and βJT relaxations in these materials are believed to originate from a common mechanism. However, the origin of βJT relaxation in these materials is still controversially discussed. It is not clear whether all molecules contribute to JG-process or only those in the island of mobility do [16–18]. The other class is formed by materials where the βJT-relaxation are attributed to originate from different microscopic origin [7,8,12]. The two relaxation times observed in halogenomethanes [7,8] studied employing Nuclear Quadrupole Resonance (NQR) method along with dielectric spectroscopy are attributed to the molecules in the asymmetric unit that are non-equivalent with respect to their molecular environment. Similar results were obtained in pentachlorotoluene studied employing Deuterium NMR technique [19]. The Hadamard quadrupole exchange NMR technique was developed by Kubo et al. [19], to efficiently measure the close relaxation rates for reorientational jumps between non-equivalent sites in the crystalline pentachlorotoluene. It is clear from Part I of the present work that addition of even small amount of dipolar substituents in the non-polar crystalline matrix induces disorder that appears as an aggregate of two relaxation processes. In a relevant work by Johari, et al. [20], it was discussed that a mixed crystal may have a second type of disorder that is in coexistence with the orientational disorder, and was designated it as “substitutional disorder”. It was suggested that the lattice site may randomly be occupied by two type of molecules, the molecular motions in which freezes and unfreezes upon cooling and heating, respectively, identical to the metallic glasses. It is difficult to clarify by observing the step like change in DSC if the freezing is corresponding to a mixed crystal of atoms, an ordinary glass forming liquid, or a pure ODIC. Further, temperature dependent study of the nature of disorder in the system can be exploited further to have much deeper analysis [21]. Attempts were made previously to correlate such JG-type β-relaxation to the primary or α-relaxation. To identify the genuine β-relaxations, Ngai, et al. [22,23], proposed criteria in the framework of Coupling Model (CM) that relates the β-relaxation to the parameters of the α-relaxation as,

\[ \tau_{JG}(T) = \tau_{a}^n \tau_{a}(T)^{1-n}, \]  

or in terms of frequency as,
log \( f_{m,\beta} \) \( \propto \) \( (1 - n) \log f_{m,\alpha} - n(\log \tau_c + 0.80) \),

(2)

where \( f_{m,\beta} \) \( \propto \) is the primitive frequency of Coupling Model, \( n \) is coupling (or non-Debye) parameter, \( f_{m,\alpha} \) is the peak loss frequency \( f_m \) for \( \alpha \)-relaxation, and \( \tau_c \) is the time characterizing the crossover from independent to cooperative fluctuations found to be close to 2 ps for the molecular glass-formers. The coupling parameter \( n \) is defined as, \( n = 1 - \beta \text{KWW} \), where \( \beta \text{KWW} \) is KWW exponent for \( \alpha \)-relaxation.

The experimental results presented in this manuscript is in continuation with our investigation on molecular motions in orientationally disordered crystals of HSBs of apparently non-polar hexa-substituted benzenes with rigid dipolar molecules containing a benzene ring (Part I of this work). We report here the dielectric data on two hexa-substituted benzenes (HSBs), PCA and BMBM in their pure materials as well as their solid solutions with HCB and HMB, respectively, encompassing the entire concentration range. The dielectric relaxation of HSBs studied in our earlier work revealed the existence of \( \alpha \)- and \( \beta \text{KWW} \)-relaxation occurring very close to each other \([24,25]\). The relaxation spectra were analyzed as superposition of two processes with \( \alpha \)-relaxation being closer to Debye behaviour. The present work provides predictions made in our earlier work.

2. Experimental

The samples studied here are hexachlorobenzene (HCB) (99%), hexamethylybenzene (HMB) (99%), and \( \alpha \)-terphenyl (OTP) (99%) purchased from Sigma-Aldrich Co. USA, and pentachloroaniline (PCA) (\( \geq 97\% \)), bromopentamethylbenzene (BMBM) (\( \geq 97\% \)), purchased from Tokyo Chemical Industry Co. Ltd., Japan. They are all used as received without any further purification except OTP, which we have purified through recrystallization from its solution with benzene.

The Differential Scanning Calorimetry (DSC) measurements were performed using a PerkinElmer Sapphire DSC with a quench cooling accessory. The DSC cell was calibrated for temperatures using indium and tin as standards, and for enthalpy using indium as the standard material. The measurements were performed at a controlled heating rate of 10°/min. Dielectric measurements were carried out with HP4284 LCR meter with the frequency range of 20 Hz–1 MHz, for binary samples of PY, FB, CB, and BB with benzene, in a three terminal cylindrical dielectric cell, whereas the measurements on PCA-HCB and BMBM-HMB solid solutions were performed on Agilent-E4980A LCR meter in the frequency window of 20 Hz – 2 MHz, with the sample pressed in the form of pellets. The measurements on liquid samples of HSBs dissolved in OTP matrix were also performed using three terminal cylindrical cell.

The dielectric relaxation spectra was analyzed using Havriliak-Negami (HN) equation \([26]\),

\[
\varepsilon'(f) - \varepsilon_{\infty} \approx \left( 1 + \left( \frac{f}{f_0} \right)^{-\alpha_{\text{HN}}} \right)^{-\beta_{\text{HN}}},
\]

(3)

where \( f_0 \) is the characteristic relaxation frequency, \( \alpha_{\text{HN}} \) and \( \beta_{\text{HN}} \) are the spectral shape parameters, and \( \varepsilon_0 \) and \( \varepsilon_\infty \) are the limiting dielectric constants for the process under consideration. When \( \alpha_{\text{HN}} = 0 \), the HN equation reduces to Cole-Davidson equation \([27]\) (with \( \beta_{\text{HN}} \) designated as \( \beta_{\text{CD}} \)) and similarly to Cole–Cole equation \([28]\) when \( \beta_{\text{HN}} = 1 \) (with \( \alpha_{\text{HN}} \) represented as \( \alpha_{\text{CC}} \)). The peak loss frequencies \( f_m \) corresponding to the loss curves are calculated using the parameters of HN-equation \([29]\). The temperature variation of \( f_m \) is analyzed using Arrhenius equation \([30]\),

\[
f_m = f_0 \exp(-E/RT),
\]

(4)

where \( f_0 \) is ‘pre-exponential factor’ and \( E \) is the ‘activation barrier’ for the process under consideration.

3. Results

In this part, we present the study on orientationally disordered phase in pure samples as well as solid solutions of PCA – HCB and BMBM – HMB in the entire concentration range.

3.1. PCA – HCB system

Pure PCA exist in orientationally disordered phase (SI) at room temperature having monoclinic space group \( P2_1/c \) with lattice parameters as \( a = 8.45 \pm 0.04 \, \text{Å}, \ b = 3.81 \pm 0.02 \, \text{Å}, \ c = 16.86 \pm 0.05 \, \text{Å}, \ \beta = 123.50^\circ \pm 20^\circ, \ Z = 2, [31] \) and transforms to liquid phase around 508.5 K (Table 1). The phase SI in PCA is isomorphous with HCB (HCB has monoclinic structure with space group \( P2_1/c \) and lattice parameters \( a = 8.047(6) \, \text{Å}, \ b = 3.836(3) \, \text{Å}, \ c = 14.820(8) \, \text{Å}, \ \beta = 92.13(14)^\circ, \ Z = 2) [35]. Due to isomorphous structure and identical lattice parameters, PCA forms solid solution with HCB throughout the concentration range. The crystal structure of the solid solutions (diffractograms are provided in supplementary material SI) is found to be identical to that of the pure components. The phase SI in pure PCA as well as in solid solutions is stable against crystallization to more ordered phase and forms orientational glass on cooling. The orientationally disordered phase SI is studied in pure PCA as well as in solid solutions with HCB at six different concentrations \( (x_m = 0.09, 0.29, 0.48, 0.69, 0.84, \) and \( 0.92) \) here \( x_m \) corresponds to the mole fraction of the second component HCB in the mixture). The solid solutions on heating begin to liquefy that can be seen as melting endotherm in DSC measurements (Fig. 1(a)). The corresponding solid-liquid phase diagram of PCA – HCB systems is shown in Fig. 1(b). It is to be noted that the DSC measurements did not show any step like change that could be assigned as glass transition event throughout the concentration. The dielectric measurements corresponding to the

![Table 1: Details of phase transitions in PCA – HCB systems.](image)
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