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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 pentachloroaniline (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 β_{JG}- 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 β_{JG}- relaxations in these materials are believed to originate from a common mechanism. However, the origin of β_{JG}- 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 β_{JG}-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,

$$\tau_{JG}(T) = t_c^n [\tau_{m\alpha}(T)]^{1-n}, \tag{1}$$

or in terms of frequency as,

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$$\log f_{m,\beta\ JG} = (1-n)\log f_{m,\alpha} - n(\log t_c + 0.80), \quad (2)$$

here $f_{m,\beta\ JG}$ 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 the α-relaxation, and t_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 − βKWW, where β_{KWW} is KWW exponent for α- 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 BPMB 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 α- and β_{JG}-relaxation occurring very close to each other [24,25]. The relaxation spectra were analyzed as superposition of two processes with α- relaxation being closer to Debye behaviour. The present work provides insight to the origin of the β_{JG}- relaxation in the two binary systems of HSBs and on the nature of α-relaxation in these materials. The binary solid solutions are investigated here to study the evolution of β_{JG}-relaxation with respect to concentration which explores the nature of the relaxation with much more clarity. The measurements corresponding to solid solutions of a very small amount of polar HSBs in non-polar HSB matrix presented in Part I of this work are also included here. In dilute solid solutions, the dipoles are mostly isolated with each other surrounded by non-polar molecules in the crystalline lattice. It is interesting to study the nature of orientational relaxation of dipoles under such crystalline environment. Also, the relaxation of HSBs dissolved in very small amount in glassy OTP-matrix is studied to have the idea of activation barrier for JG-relaxation in liquid glassy matrix. It is to be noted that the results of HBSs in OTP-matrix are in line with the predictions made in our earlier work.

2. Experimental

The samples studied here are hexachlorobenzene (HCB) (99%), hexamethylbenzene (HMB) (99%), and o-terphenyl (OTP) (99%) purchased from Sigma-Aldrich Co. USA, and pentachloroaniline (PCA) (≫ > 97%), bromopentamethylbenzene (BPMB) (≫ > 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 BPMB-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],

$$\frac{\varepsilon^*(f) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \left(1 + i\left(\frac{f}{f_0}\right)^{1-\alpha_{HN}}\right)^{-\beta_{HN}}, \quad (3)$$

where f_0 is the characteristic relaxation frequency, α_{HN} and β_{HN} are the spectral shape parameters, and ε_0 and ε_∞ are the limiting dielectric constants for the process under consideration. When $\alpha_{HN} = 0$, the HN equation reduces to Cole-Davidson equation [27] (with β_{HN} designated as β_{CD}) and similarly to Cole–Cole equation [28] when $\beta_{HN} = 1$ (with α_{HN} represented as α_{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],

$$f_m = f_0 \exp(-E/RT), \quad (4)$$

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 BPMB − HMB in the entire concentration range.

3.1. PCA − HCB system

Pure PCA exist in orientationally disordered phase (S_I) at room temperature having monoclinic space group $P2_1/c$ with lattice parameters as $a = 8.45 \pm 0.04$ Å, $b = 3.81 \pm 0.02$ Å, $c = 16.86 \pm 0.05$ Å, $\beta = 123°50' \pm 20'$, $Z = 2$, [31] and transforms to liquid phase around 508.5 K (Table 1). The phase S_I in PCA is isomorphous with HCB (HCB has monoclinic structure with space group $P2_1/n$ and lattice parameters $a = 8.047(6)$ Å, $b = 3.836(3)$ Å, $c = 14.820(8)$ Å, $\beta = 92.13(14)°$, $Z = 2$) [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 S_I in pure PCA as well as in solid solutions is stable against crystallization to more ordered phase and forms orientational glass on cooling. The orientationlly disordered phase S_I 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 0.982, 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.

Sample	Nature of transition	Transition temperature (K)	Enthalpy (ΔH) (J/g)
PCA	S_I − L (T_m)	508.5 (508-9[a])	69.7(70.4[b])
PCA–HCB, x_m = 0.09	S_I − L (T_{liq})	508.7	71.0
PCA–HCB, x_m = 0.29	S_I − L (T_{liq})	506.2	75.4
PCA–HCB, x_m = 0.48	S_I − L (T_{liq})	506.1	78.6
PCA–HCB, x_m = 0.69	S_I − L (T_{liq})	504.2	82.0
PCA–HCB, x_m = 0.84	S_I − L (T_{liq})	504.8	83.0
HCB	S_I − L (T_m)	504.0(505.0[c])	84.0(83.75[c])

L: Liquid, S: Crystalline solid, [a]Ref. [32], [b]Ref. [33], [c]Ref. [34]. The standard uncertainties in T and ΔH are u(T) = 0.5 and u(ΔH) = 0.6 kJ/mol, respectively (The standard uncertainty u = s/√n, where 's' is standard deviation given as $s = \sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2/(n-1)}$, x_i is the result of the i^{th} measurement and $\bar{x}$ is the arithmetic mean of the 'n' results considered).