



Relaxation in rotationally disordered phase of hexa-substituted benzenes



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ABSTRACT

We have studied pentafluoroaniline ($C_6F_5NH_2$), pentachlorophenol (C_6Cl_5OH) and one solid solution of pentachlorophenol-hexachlorobenzene (C_6Cl_6) using dielectric spectroscopy ($f < 2$ MHz) and differential scanning calorimetry. The dielectric spectra in the disordered phase I of the first two samples did not conform to the Havriliak–Negami shape function; however, another process of smaller magnitude was noticed on the higher frequency side. The resulting relaxation rate of the dominant process along with the literature data suggests that the primary relaxation process in the rotationally disordered phase of hexa-substituted benzenes (HSBs) conforms to Arrhenius equation with apparent activation energy (E) in the range of 30–80 kJ/mol, dependent on molecular weight/size. The JG-relaxation of a number of HSBs in glassy *o*-terphenyl matrix was also been studied which allowed us to propose that the observed primary or α -relaxation in the neat HSBs is due to the hexad-rotation. Deviation of dielectric spectra from Debye behaviour is discussed.

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1. Introduction

Reorientational motion of molecules occurs in some hexa-substituted benzenes (HSBs) in rotator phase below the melting temperature [1–9], though not all HSB samples exhibit this phenomenon. This rotator phase may fail to transform to a non-rotator phase on lowering the temperature because of kinetic reasons [10,11]. Unlike the cubic plastic crystals of simple molecules such as neopentanol, 2,3-dimethylbutane or cyclohexanol [3,12–15], the rotator phase of HSBs occurs in less symmetrical crystalline structures such as monoclinic, triclinic or rhombohedral structures [3,16–21]. Often discussed in this context is the Arrhenius equation [22,24]:

$$f_m = f_0 \exp\left(\frac{-E}{RT}\right) \quad (1)$$

where E is the activation energy and f_m is the maximum loss frequency corresponding to the relaxation process of orientational process and f_0 is the vibrational frequency of the molecules (which is of the order of 10^{12} – 10^{13} Hz). Deviation from Eq. (1) is much more pronounced in plastic cubic crystals [12,13] than in HSBs [6,7,9].

In the context of such a T -dependence on the relaxation of a dipole, discussed is the so-called Debye process [23,25] given by:

$$\frac{\varepsilon''(f) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \left[1 + i\left(\frac{f}{f_m}\right)\right]^{-1} \quad (2)$$

where ε_0 and ε_∞ are asymptotic limits of the real part of the dielectric constant and f_m is peak loss frequency where temperature (T)-dependence of f_m is governed by Eq. (1) [26–29].

The simplest molecular system of HSBs is the benzene itself where the nuclear magnetic resonance (NMR) spin-lattice relaxation of crystalline benzene [19,30,31] follows Eq. (1) with an E value of ~ 17 kJ/mol and is explained as due to the reorientation along the 6-fold axis normal to the plane of the ring [32]. The E value increases from ~ 22 kJ/mol in hexamethylbenzene (HMB) [21,33] to 29.4 kJ/mol in hexafluorobenzene (HFB) [34]. Unfortunately these three samples viz. benzene, HMB and HFB can not be studied in its crystalline state using dielectric spectroscopy owing to their non-polar nature, and also are thermodynamically not disordered [32]. For polar HSBs, the E value, estimated from dielectric measurements, shows an increase with molecular weight [35–37]. The corresponding spectra [6–9,36,37] show deviations from the Debye behaviour.

As shown by Johari and Goldstein [38,39], supercooled liquids and glasses do possess another relaxation of smaller magnitude below the glass transition temperature (T_g) of the binary solution due to the inter-molecular degrees of freedom and is often referred to as JG-relaxation or β_{JG} -process [40–43]. The origin of this

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process is greatly debated in literature. According to one particular model referred to as coupling model (CM) given by Ngai [29,44], the main (or α)-process, and β_{JG} -process are inter connected to each other via the non-Debye parameter n :

$$\log f_{m,\beta_{JG}} = (1 - n)\log f_{m,\alpha} - n(\log t_c + 0.80) \quad (3)$$

where $f_{m,\beta_{JG}}$ is the primitive frequency of CM, n is coupling (or non-Debye) parameter, $f_{m,\alpha}$ is the f_m of the α -process, 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.

According to the classification of supercooled disordered phases proposed by Angell, the HSBs may be classified as “strong” because of their apparent adherence to Eq. (1) [11,45,46]. For such a process the corresponding structural relaxation has to be Debye, i.e., $n=0$ in Eq. (3) which in turn leads to the identity that $f_{m,\beta_{JG}} = f_{m,\alpha}$. In this context, it is interesting to note that the molecules of rigid HSBs relax (only) by hexad-rotation [30–34], and the previous publications [6,7,9] from this laboratory do not indicate a well-defined secondary process in the sub- T_g region.

In view of the academic interest in the secondary relaxation process in the supercooled HSBs as described in the previous paragraphs, we have under taken the study of JG-relaxation of HSBs in glassy matrix of *o*-terphenyl, and compared the results with the relaxation of orientationally disordered phase of neat HSBs.

2. Experiment

The samples studied here are 2,3,4,5,6-pentachlorophenol or PCP (97% purity); 2,3,4,5,6-pentafluoroaniline or PFA (99% purity); 2,3,4,5,6-pentafluoronitrobenzene or PFNB (98% purity), 2,3,4,5,6-pentabromophenol or PBP (96% purity); 2,3,4,5,6-pentafluorophenol or PFP (99% purity); 2,3,4,5,6-pentafluorotoluene or PFT (99% purity); hexachlorobenzene or HCB (99% purity) and *o*-terphenyl or OTP (99% purity) which were obtained from Aldrich Co., USA. They are all used as received without any further purification except OTP which we have purified through recrystallization from its solution of benzene. The materials have been desiccated well prior to use and are heated to 383 K to remove low volatile impurities and water.

The differential scanning calorimetry (DSC) measurements are done by using a PerkinElmer Sapphire DSC with a quench cooling accessory. The DSC cell has been calibrated for temperatures using indium and mercury as standards, and for enthalpy using indium as the standard material. Dielectric measurements were carried out with HP 4284 A precision LCR meter with frequency range 20 Hz–1 MHz and Agilent E4980A LCR Meter with frequency range

20 Hz–2 MHz. A three terminal liquid dielectric cell is used for PFA. A different cell assembly has been used for PCP which is a crystalline solid at room temperature. A disk of 2.5 cm in diameter and about 0.82 mm of thickness is made out of the sample by pressing the sample in a pressure die at 10 kbar. Two electrodes are made from silver powder pressed at the same pressure. For further details of the measurement set-up and measurement accuracy the reader may refer to the previous articles [12,47] from this laboratory. Also in case of PCP–HCB system, dielectric measurements are performed on a disk (pellet) as in the case of PCP. The solid solution of PCP–HCB (weight fraction of HCB $x_w=0.10$) is obtained by slow evaporation of their benzene solution for seven days as described elsewhere [48].

3. Results

The two samples namely pentafluoroaniline ($C_6F_5NH_2$) or PFA and pentachlorophenol (C_6Cl_5OH) or PCP could be supercooled in plastic or rotator phase. The glass forming tendency of phase I of PCP can be increased by adding a small amount of hexachlorobenzene (C_6Cl_6) with which it forms a solid solution [48]. The details of the various first order transitions found in the DSC scans in the three samples studied here are shown in Table 1 along with the literature values. All the calorimetric measurements are performed at a heating rate of $10^\circ/\text{min}$.

3.1. 2,3,4,5,6-Pentafluoroaniline (PFA)

PFA exists in rotationally disordered phase at room temperature, the structure of which is not known to the best of our knowledge. On cooling below room temperature it crystallizes to S_{III} (Table 1). Dielectric measurements in PFA are made in plastic phase S_I formed by cooling the liquid in the dielectric cell. In Fig. 1, the dielectric measurements of slow cooled sample from phase I followed by subsequent heating are shown. The ϵ_0 values in liquid (L) as well as disordered phase S_I are also shown in the figure to give the reader an idea of the extent of supercooling of the disordered phase. The calorimetric measurement of slow cooled sample is included in the Fig. 1 as inset. As evident in the figure, the orientationally disordered phase S_I during cooling crystallizes to S_{III} around 272.8 K. During heating S_{III} transforms to S_{II} at temperature T_2 and to S_I at T_1 . The transformation from S_{III} to S_{II} takes a few days for completion. The absence of transition at T_2 in the DSC scans of the sample kept in the desiccator for a few weeks may be noted. The dielectric transition temperatures agree well with the DSC measurements. In DSC measurements no step like change of the base line characteristic of glass transition phenomenon is observed in low temperature regions of even quench cooled S_I indicating

Table 1
Details of 1st order phase transitions as measured in DSC experiments.

Sample	Nature of transition	Designation of transition temp.	Transition temp.* (K)	ΔH^* (kJ/mol) Enthalpy of transition
PFA	$S_I - L$	T_m	305.7 (306.8 ^a)	15.4 (14.28 ^a)
	$S_{II} - S_I$	T_1	288.6 (287.4 ^a)	4.3 (3.94 ^a)
	$S_{III} - S_{II}$	T_2	261.5	–
PCP	$S_I - L$	T_m	464.8 (464.0 ^b)	15.4 (15.17 ^b)
	unknown	T_{tr}	441.6 (435.0 ^c)	–
	$S_{II} - S_I$	T_1	340.2 (341.0 ^b)	9.0 (8.28 ^b)
	$S_{III} - S_{II}$	T_2	287.4	–
PCP–HCB ($x_w=0.10$)	$S_I - L$	T_1^d	466.7	60.2 (J/g) ^d

L: Liquid, S: Crystalline solid.

*Average of four runs.

^a Literature value from Ref. [20].

^b Literature value from Ref. [16].

^c Literature value from Ref. [52].

^d T_1 is the liquidus temperature and accordingly the enthalpy has been measured (in J/g) using the software with onset at 463.0 K.

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