



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



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ABSTRACT

The NMR study revealed that the 60° reorientational jumps in non-polar crystalline benzene do not give to a new configuration, and therefore benzene behaves as orientationally ordered system from thermodynamic perspective. All the non-polar symmetric crystalline hexa-substituted benzenes, such as hexachlorobenzene, hexamethylbenzene, etc., are supposed to be characteristically similar like benzene. We selectively probed solid solutions of these non-polar crystalline matrices with polar crystalline species employing dielectric spectroscopy, and differential scanning calorimetry. An additional process, close to Debye in nature, was observed in dielectric spectroscopy with higher activation energy, which was absent in NMR, and based on spectral behaviour we designate it as α -relaxation. Moreover, the single strong process that appears in NMR study of non-polar benzene, hexachlorobenzene, and hexamethylbenzene matrices is identical to a relatively weak process observed in dielectric spectroscopy, which we designate as secondary relaxation. In all the cases, the temperature dependence of the relaxation rates follow Arrhenius equation.

1. Introduction

The molecules like benzene C_6H_6 [1,2], hexafluorobenzene C_6F_6 [3], hexachlorobenzene C_6Cl_6 [4], and hexamethylbenzene $C_6(CH_3)_6$ [4,5] in the crystalline phase just below their melting temperature show reorientational motion in NMR relaxation which is attributed to 60° jump. These substances do not have an orientational disorder from thermodynamic perspective, as rotation of molecules by 60° do not give rise to a new configurational state [1,2]. These substances are non-polar, and therefore, cannot be studied by well established relaxation technique like dielectric spectroscopy. However, it would be interesting to study these non-polar crystals using some dipolar probe molecules which can occupy regular lattice site and form substitutional solid solution.

It is with this motive in mind, we probed benzene with the least possible structural change in the dipolar substituents (such as fluorobenzene (FB), chlorobenzene (CB), bromobenzene (BB), and pyridine (PY)) in the form of solid solution with crystalline benzene (B) with very dilute concentrations of the polar counterparts. All these polar hexa-substituted benzene (HSB) materials are rigid in their pure crystalline phase. Cioffi et al. [6], have shown that pyridine forms solid solution with benzene with limited solubility of pyridine in benzene. Therefore, we probed very low concentration pyridine in benzene in the form of solid solution, in order to study the relaxation dynamics of

pyridine in benzene. The results of B-PY system lead us to study the other species like FB, CB, and BB in benzene in the form of solid solutions. It is to be noted that the solubility of CB and BB are very low in benzene as compared to FB and PY, which may be attributed to structural dissimilarity with benzene. Similar results were obtained when polar HSBs such as pentachloroaniline (PCA) and bromopentamethylbenzene (BPMB) were studied in very dilute concentrations in hexachlorobenzene (HCB) and hexamethylbenzene (HMB), respectively, in the form of solid solutions. In all the cases, the entire dielectric relaxation spectra can be characterised as an aggregate of two processes designated as α - and β -relaxation. The β -relaxations in all these solid solutions are collinear with the T_1 -spin relaxation time of the reorientational motion of non-polar counterpart of the solid solutions. Thus, the NMR reorientational mode which is a major and only process in the non-polar HSBs, appears as a weak process in the dielectric spectra of the solid solutions, and the complete absence of α -relaxation in NMR spectra is notable.

The present contribution is divided in two parts: in the first paper (Part I), we present the experimental results of very dilute concentration of polar HSB solutes in non-polar HSB solvents in the form of solid solution. Out of the systems studied here, PY-B, FB-B, CB-B, and BB-B form solid solutions in the low concentrations of their polar solutes, and not in the entire concentration range. The PCA-HCB and BPMB-HMB systems form solid solution in the entire concentration range, however,

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Table 1
Details of solutes studied in crystalline benzene.

Solutes	Molecular weight (M)	Dipole moment (μ)	Crystal Structure
Benzene (B)	78.11	0 ^a	Orthorhombic (Pbca) ^c
Pyridine (PY)	79.10	2.26 ^b	Orthorhombic (Pna2 ₁) ^d
Fluorobenzene (FB)	96.10	1.58 ^e	Tetragonal (P4 ₃ 2 ₁ 2) ^e
Chlorobenzene (CB)	112.56	1.57 ^e	Orthorhombic (Pbcn) ^f
Bromobenzene (BB)	157.01	1.50 ^e	Orthorhombic (Pmnn) ^f

^a Ref. [15].

^b Ref. [16].

^c Ref. [17].

^d Ref. [18].

^e Ref. [19].

^f Ref. [20].

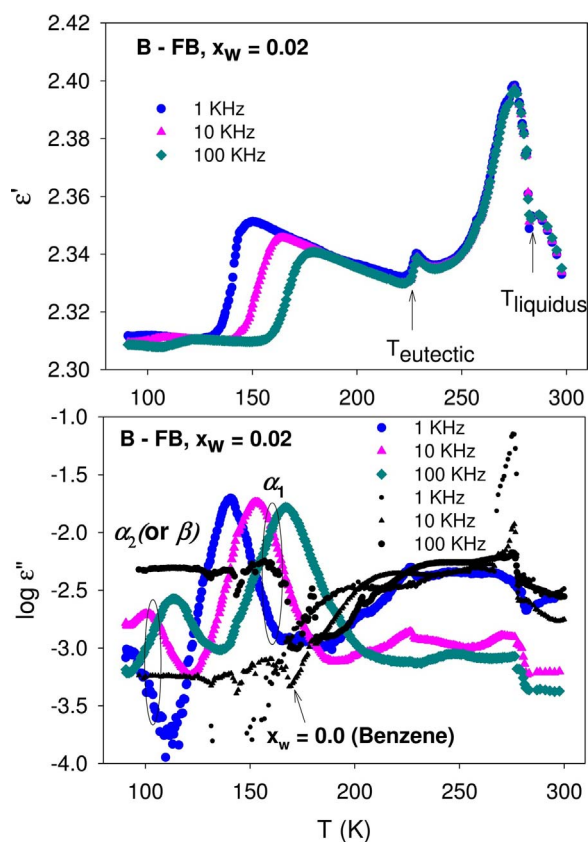


Fig. 1. Temperature variation of (a) ϵ' and (b) ϵ'' at different test frequencies in B-FB, $x_w = 0.02$. Also shown in the figure is temperature variation of $\log \epsilon''$ for crystalline benzene (black symbols) for comparison.

in this Part (I), the dielectric spectra of only the dilute concentrations of the polar solutes are presented for the sake of comparison with the other systems. In the present work, we studied the phase diagram of all the systems under consideration. The dielectric measurements were performed in all the systems with solid solutions of dilute concentration of PY, FB, CB, and BB in benzene, PCA in HCB, and BPMB in HMB. In the second Part (II), we present the experimental data on PCA-HCB and BPMB-HMB, which form the solid solution in the entire concentration range, demonstrating the existence of secondary relaxation in the orientationally disordered phase of these systems. The work is in continuation with our longstanding interest in the characteristics of relaxation spectra of orientationally disordered phase in hexa-substituted

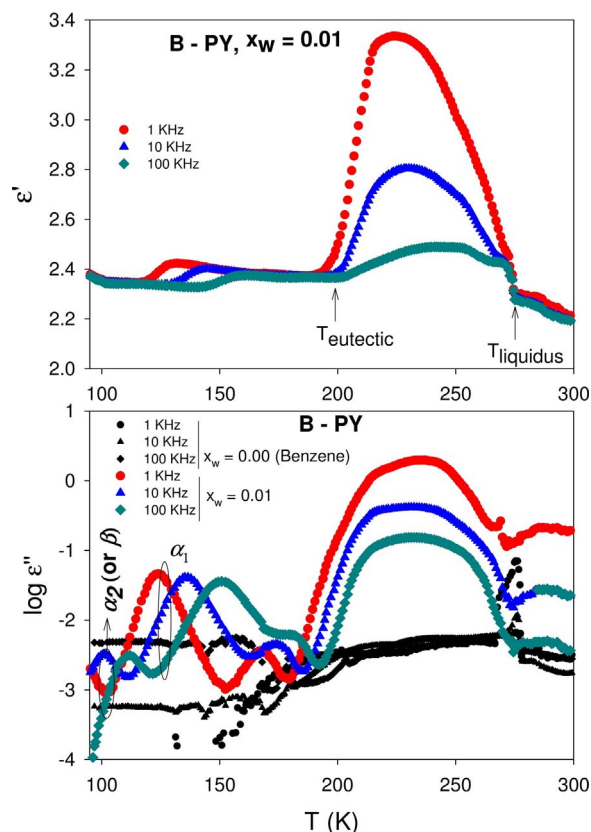


Fig. 2. Temperature variation of (a) ϵ' and (b) ϵ'' at different test frequencies in B-PY, $x_w = 0.01$. Also shown in the figure is temperature variation of $\log \epsilon''$ for crystalline benzene (black symbols) for comparison.

benzenes, and the results in the present work are compatible with the earlier research from this lab [7,8]. In the second paper, we also present the liquid glass forming systems of very dilute solution of polar HSBs dissolved in OTP order to access the potential barrier for the reorientation of HSBs in liquid glassy matrix. We further compare the microscopic environment of liquid glassy matrix studied in binary mixtures of HSBs in OTP with that of the orientational glasses of HSBs in non-polar crystalline matrix.

2. Experimental

The samples studied here are benzene (B) (99.9%) and fluorobenzene (FB) (99% purity), chlorobenzene (CB) (99%), bromobenzene (BB) (99%), pyridine (PY) (99%), hexachlorobenzene (HCB) (99%), and hexamethylbenzene (HMB) (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.

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. 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 details of the experimental setup can be seen in the earlier

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