CHAPTER III

GLASS FORMATION AND RELAXATION PROCESSES IN SUPERCOOLED ORGANIC LIQUIDS

1. INTRODUCTION

The approach to the glassy state, as has been discussed in chapter I, is relaxational in nature and can be detected by dielectric relaxation measurements [1,2]. The relaxation process is known as the primary relaxation or $\alpha$-process. In addition to this, almost all the supercooled liquids exhibit another process of much smaller magnitude which continues to the sub-$T_g$ region and is known as the $\beta$-process [3-6]. The origin of the $\beta$-process is not very clear. Some researchers [7,8] believe that it is due to some internal degrees of motion of the molecule which still survive in the glassy state. Examples of benzylchloride and polyvinylacetate, etc. are often cited for this purpose. However, others attribute it to some universal feature of amorphous packing rather than to some internal degrees of freedom [9-11]. Examples of halogen derivatives of benzene in nonpolar cisdecalin matrix are often cited in this context because the dipolar probe molecule, i.e., the halobenzene has no internal degrees of freedom. However, extension of the universality concept to liquids such as isopropylbenzene, o-terphenyl and alkyl halides, etc. is not very convincing since relaxation measurements [2,12-17] on these liquids have clearly revealed at least one additional process in the true liquid state which could be attributed to some intramolecular process (side group or segmental motion) surviving in the glassy state. Noting that the glasses studied so far are made from liquids whose molecules cannot strictly be considered as rigid, a critical examination of the sub-$T_g$ process is required before attributing to the $\beta$ process some kind of universality. Similarly, care must be exercised in the interpretation of the sub-$T_g$ processes in hydrogen (H-) bonded liquids as they are found to possess another glass transition process of much lower intensity below the main $T_g$ [18-20] and the corresponding $\alpha$-process can easily be mistaken for a $\beta$-process.
The study of the $\beta$-process has become more significant with the development of mode-coupling theories (MCT) [21] which, formulated for structureless particles, predict a universal $\beta$-relaxation process of intermolecular origin. This process was assumed to be the same as that giving rise to a secondary peak in the dielectric loss [3,4] and hence was called by the same name $\beta$-relaxation. Light scattering [22] and neutron scattering [23] experiments have shown substantial agreement with the theory in the high frequency region well above $T_g$. Their studies suggest a very fast $\beta$ process ($f_\beta > 10^{11}$ Hz) as compared to the slow $\beta$ process ($f_\beta < 10^6$ Hz) in the dielectric/nuclear magnetic resonance (NMR) experiments. There is no conclusive evidence to show that these two are one and the same [24]. Wu and Nagel [24] have argued that the $\beta$ process in dielectric measurements is of a different origin from what has also been called $\beta$ relaxation in MCT and light scattering experiments.

The main aims of this work are to see; (a) whether there is any sub-$T_g$ process which cannot be ascribed to internal degrees of freedom, and hence can be identified with the universal feature of amorphous packing; and (b) to see whether a different pattern exists in the relaxational behavior of supercooled plastic crystals (SCPC) as compared to the supercooled liquids (SCL).

This chapter is divided into parts A and B. Part A deals with the study of glass-forming ability in a wide variety of liquids and plastic crystals. Part B deals with the study of the relaxation processes in some of the liquids studied in part A.

2. PART A : THE ROLE OF MOLECULAR SHAPE IN GLASS FORMATION

2.1 EXPERIMENTAL DETAILS

The samples used in the study are all available commercially and were distilled prior to their use. All the solid samples were desiccated for a few days prior to use. Measurements in this part were made on a DSC instrument using quench cooling accessory and the fast quenching method described in chapter II. The latter method was used in the cases numbered 1-3, 11-15, 18, 19, and 21-24 mentioned in Table III.1.
**TABLE III.1: Details of glass formation in some organic liquids.**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Substance</th>
<th>$T_m$/K</th>
<th>$T_g$/K</th>
<th>$T_m/T_g$</th>
<th>comment on glass formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>1-Bromopropane</td>
<td>60.3</td>
<td>107.0</td>
<td>1.50</td>
<td>partial, 2%</td>
</tr>
<tr>
<td>(2)</td>
<td>2-Bromopropane</td>
<td>180.6</td>
<td>-</td>
<td>-</td>
<td>0%</td>
</tr>
<tr>
<td>(3)</td>
<td>Epoxypropane</td>
<td>160.2</td>
<td>114.7</td>
<td>1.40</td>
<td>partial</td>
</tr>
<tr>
<td>(4)</td>
<td>1-Bromobutane</td>
<td>159.2</td>
<td>103.3</td>
<td>1.54</td>
<td>full, 100%</td>
</tr>
<tr>
<td>(5)</td>
<td>1-Iodobutane</td>
<td>164.6</td>
<td>108.4</td>
<td>1.52</td>
<td>full, 100%</td>
</tr>
<tr>
<td>(6)</td>
<td>1-Chloro-2-methylpropane</td>
<td>142.7</td>
<td>89.4</td>
<td>1.60</td>
<td>full, 100%</td>
</tr>
<tr>
<td>(7)</td>
<td>1-Bromo-2-methylpropane</td>
<td>155.6</td>
<td>97.0</td>
<td>1.60</td>
<td>full, 100%</td>
</tr>
<tr>
<td>(8)</td>
<td>2-Chloro-2-methylpropane</td>
<td>247.5</td>
<td>137.5</td>
<td>1.80</td>
<td>partial, 2%</td>
</tr>
<tr>
<td>(9)</td>
<td>2-Methylpropan-2-ol</td>
<td>303.0</td>
<td>158.0</td>
<td>1.92</td>
<td>partial, 2%</td>
</tr>
<tr>
<td>(10)</td>
<td>Butan-1-ol</td>
<td>183.5</td>
<td>113.6</td>
<td>1.62</td>
<td>full, 100%</td>
</tr>
<tr>
<td>(11)</td>
<td>n-Butyl acetate</td>
<td>194.3</td>
<td>125.7</td>
<td>1.55</td>
<td>nearly full</td>
</tr>
<tr>
<td>(12)</td>
<td>Ethyl acetate</td>
<td>189.4</td>
<td>116.0</td>
<td>1.63</td>
<td>partial, 2%</td>
</tr>
<tr>
<td>(13)</td>
<td>Benzene</td>
<td>278.6</td>
<td>-</td>
<td>-</td>
<td>0%</td>
</tr>
<tr>
<td>(14)</td>
<td>Chlorobenzene</td>
<td>226.6</td>
<td>126.3</td>
<td>1.79</td>
<td>partial, 2%</td>
</tr>
<tr>
<td>(15)</td>
<td>Iodobenzene</td>
<td>241.6</td>
<td>149.7</td>
<td>1.61</td>
<td>partial, 20%</td>
</tr>
</tbody>
</table>

Continued
<table>
<thead>
<tr>
<th></th>
<th>Chemical Name</th>
<th>177.6</th>
<th>119.4</th>
<th>1.487</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>Methylbenzene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>n-Propylbenzene</td>
<td>173.6</td>
<td>126.2</td>
<td>1.38</td>
<td>full, 100%</td>
</tr>
<tr>
<td>18</td>
<td>Liquid crystal 1 (n=5, m=16)</td>
<td>329.4</td>
<td>212.0</td>
<td>1.55</td>
<td>partial, 22%</td>
</tr>
<tr>
<td>19</td>
<td>Liquid crystal 2 (n=4, m=14)</td>
<td>336.5</td>
<td>200.3</td>
<td>1.68</td>
<td>partial, 22%</td>
</tr>
<tr>
<td>20</td>
<td>OHMBBA</td>
<td>314.0</td>
<td>204.0</td>
<td>1.54</td>
<td>full, 100%</td>
</tr>
</tbody>
</table>

Liquid crystals

<table>
<thead>
<tr>
<th></th>
<th>Chemical Name</th>
<th>227.8</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>Tetrachloromethane</td>
<td></td>
<td></td>
<td>0%</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>2-Chloro-2-methylpropane</td>
<td>219.5</td>
<td></td>
<td>0%</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>Camphor</td>
<td>ca.213.0</td>
<td>156.7</td>
<td>1.36</td>
<td>partial</td>
</tr>
<tr>
<td>24</td>
<td>Cyclohexanol</td>
<td></td>
<td>151.0</td>
<td></td>
<td>partial</td>
</tr>
</tbody>
</table>

plastic crystals

---

*a* $C_nH_{2n+1}OC_6H_4·CH=N·C_6H_4C_mH_{2m+1}$

*b* Taken from ref.29.
2.2 DETAILS OF RESULTS

The DSC curve generally obtained after heating a glass at a certain rate is shown in Fig.III.1 for the case of 1-iodobutane. The glass first becomes liquid at $T_g$ (108.4 K), and then crystallizes at higher temperatures. On further heating, the crystal melts at the thermodynamic melting temperature, $T_m$ (164.6 K). The area under the exotherm gives the enthalpy of crystallization, and similarly the area under the endotherm gives the enthalpy of fusion [25]. For a 100% glass the above two quantities are equal. In a situation where the solid formed consists of a mixed phase of glass and crystal, the area of the melting endotherm has a value higher than that of the crystallization exotherm. Comparison of these quantities with the enthalpy of fusion of the 100% crystalline substance gives an indication of the amount of glass present in the solid formed by quenching the liquid. The data have been analysed using the Du Pont DSC standard data analysis program version 4.0. The areas under the DSC peaks are calculated using a sigmoidal baseline with two tangent lines fitted within selected limits on each side of the transition. Transition temperatures $T_g$ and $T_m$ are taken as the 'onset' temperatures. All the relevant quantities are given in Table III.1 along with the $T_g$ and $T_m$ values. This table is arranged so as to illustrate the effect of molecular structure on glass formation. Also given in Table III.1 are these values for some supercooled liquid crystals and plastic crystals. Results of the measurements of $T_g$ and $T_m$ values in a number of easily glass forming materials which require a cooling rate not more then $5-10^0$/min for complete elimination of crystallization are shown in Table III.2. As a representative of glass of liquids, the DSC curve of vinylacetate in the glass transition range is shown in Fig.III.2.

2.3 DISCUSSION

An interesting aspect of Table III.1 is that glasses have been formed even in liquids in which glass formation has hitherto been believed to be difficult. This is obviously because of the very high cooling rates employed in the experiments. Another feature of Table III.1 is that the tendency for glass formation increases with the molecular asymmetry of the liquid. For example, in the case of 2-bromopropane it is impossible to obtain even a minute fraction of glass, but for 1-bromopropane there is some glass formation. Similarly, increase
Figure III.1: DSC curve of iodobenzene; heating rate $10^9$/min.
Table III.2: Details of $T_m$ and $T_g$ in some glass-forming liquids$^a$

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Substance</th>
<th>$T_g$</th>
<th>$T_g$</th>
<th>$T_m/T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>3-Bromopentane</td>
<td>146.8</td>
<td>110.0</td>
<td>1.34</td>
</tr>
<tr>
<td>(2)</td>
<td>Isopropylbenzene</td>
<td>177.0</td>
<td>129.5</td>
<td>1.37</td>
</tr>
<tr>
<td>(3)</td>
<td>Dibutylphthalate</td>
<td>-</td>
<td>178.7</td>
<td>-</td>
</tr>
<tr>
<td>(4)</td>
<td>Diethylphthalate</td>
<td>273.0</td>
<td>182.5</td>
<td>1.49</td>
</tr>
<tr>
<td>(5)</td>
<td>Dioctylphthalate</td>
<td>-</td>
<td>184.4</td>
<td>-</td>
</tr>
<tr>
<td>(6)</td>
<td>Dimethylphthalate</td>
<td>274.4</td>
<td>194.9</td>
<td>1.41</td>
</tr>
<tr>
<td>(7)</td>
<td>Tricresylphosphate</td>
<td>-</td>
<td>214.4</td>
<td>-</td>
</tr>
<tr>
<td>(8)</td>
<td>Liquid crystal 2</td>
<td>336.5</td>
<td>200.3</td>
<td>1.68</td>
</tr>
<tr>
<td>(9)</td>
<td>α-Pheyl-o-cresol</td>
<td>325.6</td>
<td>220.1</td>
<td>1.48</td>
</tr>
<tr>
<td>(10)</td>
<td>Phenylsalicylate</td>
<td>316.2</td>
<td>221.6</td>
<td>1.43</td>
</tr>
<tr>
<td>(11)</td>
<td>O-terphenyl</td>
<td>331.5</td>
<td>247.7</td>
<td>1.34</td>
</tr>
<tr>
<td>(12)</td>
<td>Glucose</td>
<td>432.9</td>
<td>309.0</td>
<td>1.40</td>
</tr>
<tr>
<td>(13)</td>
<td>Sucrose</td>
<td>465.7</td>
<td>334.0</td>
<td>1.39</td>
</tr>
</tbody>
</table>

$^a$ All temperatures are in Kelvin for a heating rate of $10^0/min.$

$^b$ Below the lowest temperatures of our measurements.
Figure III.2: DSC curve of Vinylacetate in the range of glass transition.
in the carbon chain length, i.e. from 1-bromopropane to 1-bromobutane increases the glass-forming tendency (in this case to 100%) and glass formation is found to be possible for 1-bromobutane even at cooling rates of 10-20°/min. This is found to be true when other halogens are substituted for bromine on the above chain. Even after branching of this chain, as in 1-bromo-2-methylpropane, glass-forming tendency remains almost the same. For 2-chloro-2-methyl-propane, a nearly spherical molecule, glass-forming tendency is nearly zero. Indeed, glass-forming tendency remains almost zero even if one replaces the chlorine/bromine atoms in 2-chloro-2-methylpropane with an -OH group. This is an interesting result in the sense that the role played by hydrogen bonding in glass formation is not significant -- it is the change of molecular symmetry due to the introduction of the -OH group which is important. The effect of molecular shape on glass formation can also be seen in 1-butylacetate where the introduction of a bulkier acetate group in place of bromine in 1-bromobutane results in a decrease in the glass-forming tendency. For ethylacetate there is negligible glass formation, obviously because the molecular symmetry is higher.

Measurements on benzene and its derivatives show that the glass-forming tendency may be increased by replacing a hydrogen atom on one of the carbons by a much bulkier group. A glance at Tables III.1 and III.2 also reveals a tendency for a decrease in the \( T_m/T_g \) ratio with increasing non-sphericity or asymmetry [26] and an increase in the glass-forming tendency.

The liquid crystals studied are linear with varying lengths of the main chain. The trends are same in all these samples and hence only the results for two liquid crystals are shown in Table I:1.1. The development of mesophases on cooling the isotropic liquid is so fast that the glass obtained by quenching the sample is that of the anisotropic liquid. Here glass formation is partial. Note that liquid crystals with much lower molecular symmetry than those studied here, like PBBA [27], cholesteric hydrogen phthalate [28] etc. are good glass formers. The results on liquid crystals of linear molecules once again emphasize the role of molecular shape in glass formation. This can also be seen from the earlier results of Sori et.al. [29] on various isomers of OHMBBA.

On supercooling the plastic crystalline phases of tetrachloromethane, 2-chloro-2-methylpropane and 1,1,1-trifluoroethane no glassy crystal is formed.
An interesting point is that in the case of 2-chloro-2-methylpropane, it was not possible to form a glassy crystal but the isotropic liquid could be supercooled to form a positional glass (see Table III.1). However, a glassy crystal could be obtained in camphor and cyclohexanol. Note that the latter has already been studied by Suga and Seki [30] and the value of $T_g$ obtained above is close to their value.

Two points are very clear from these studies: (a) Considerable molecular asymmetry is required for facile glass formation; (b) It is easier to form a 'positional glass' of a spherical molecular liquid than to obtain an 'orientational glass' or glassy crystal of the same substance. These observations emphasize that glass formation in supercooled liquids may not be a simple kinetic event but is related to the specific structure of the liquid state. All the glass forming liquids have this specific structure as an additional property, and this must be the result of molecular asymmetry. Perhaps, it is this structure which is the cause of the large departure of the relaxation process from Debye behavior, and it may also lead to deviations of the liquid viscosity from Arrhenius behavior [28]. In this connection, it is worthwhile to consider the possible existence of anti-crystalline clusters in the true liquid state, as suggested by Ubbelhode [31].

3. PART B : DIELECTRIC MEASUREMENTS ON SUPERCOOLED LIQUIDS AND SUPERCOOLED PLASTIC CRYSTALS

3.1 EXPERIMENTAL DETAILS

The samples used in this study are (1) tritolylphosphate (TTP), (2) 3-bromopentane (3BP), (3) isopropylbenzene (IPB) (4) 1-bromobutane (1BB), (5) vinylacetate (VAc), (6) cyclohexanol (CHOL) and (7) camphor. Samples (2), (3) and (5) were obtained from Aldrich Chemicals; sample (1) from S.D.Fine Chemicals; sample (4) from Merck India; sample (6) from Qualingens, and sample (7) from G.S.C. India. All the samples were used as received except isopropylbenzene and cyclohexanol, which were distilled twice and then desiccated for a few days prior to use.
3.2 RESULTS

3.2.1 Details of the data analysis

The $\alpha$ - process is analyzed using Havriliak-Negami (H-N) [32] equation given by

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{[1 + (i\omega\tau_{HN})^{1-\alpha_{HN}}]^{\beta_{HN}}} \quad (\text{III.3.1})$$

where $\varepsilon_0$ is the static dielectric constant, $\varepsilon_\infty$ is the high frequency limit of the dielectric constant for the process under consideration and $\alpha_{HN}$ and $\beta_{HN}$ are the symmetric and asymmetric distribution parameters respectively. In the absence of any other process on the high frequency side $\varepsilon_\infty$ is approximately equal to $1.05n_D^2$, where $n_D$ is the refractive index of the material. The peak loss frequency $f_m$ is calculated from the relaxation time ($\tau_{HN}$) in Eq. (III.3.1) using the relation

$$f_m = (2\pi\tau_{HN})^{-1}\tan(\pi/2(1+\beta)) \quad (\text{III.3.2})$$

The sub-$T_g$ processes are analyzed assuming a depressed Cole - Cole arc behavior [33] as the peaks are not well-resolved and the equation used for this purpose, obtained by putting $\beta_{HN} = 1$ in Eq.(III.3.1), is

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{[1 + (i\omega\tau_{CC})^{1-\alpha_{CC}}]} \quad (\text{III.3.3})$$

The $f_m$ values corresponding to the $\alpha$ - process are fitted to a power law equation [34]

$$f_{m,\alpha} = f_{0,\alpha} \left( \frac{T - T_g'}{T_g'} \right)^r \quad (\text{III.3.4})$$
The power law equation is found to be a much better representation for the temperature dependence of $f_m$ as compared to the well known Vogel-Fulcher-Tammann equation [5,34]. The peak frequency $f_m$ corresponding to the $\beta$-process is analyzed by the Arrhenius equation

$$f_m,\beta = f_{0,\beta} \exp(-E/RT) \quad (III.3.5)$$

where $E$ is the activation energy per mole. The results of the fits to Eqs. (III.3.4) and (III.3.5) are given in Tables III.3 and III.4 separately.

3.2.2 Details of the results

(a). Tritolylphosphate (TTP)

The glass transition temperature ($T_g$) for this sample is 214.4K [19]. This sample was studied above $T_g$ using dielectric [35] and NMR [36] techniques. The present studies do not reveal a well resolved $\beta$ peak (Fig.III.3). A small shoulder on the $\alpha$ relaxation peak is found in the temperature range where a $\beta$ peak is expected for 1 KHz frequency ($\sim 0.7T_g$). However, the loss tangent ($\tan\delta$) shows a clear peak much below the $\beta$ peak shoulder in the temperature range 110-140K (Fig.III.3) corresponding to another process. The temperature variation of the shape of the $\alpha$ process is shown in Fig.III.4a in the form of normalized Cole-Cole (C-C) diagram. The Arrhenius diagram for the material is shown in Fig.III.5a. The open circle (○) point in the Arrhenius diagram is DSC $T_g$, which corresponds to an enthalpy relaxation frequency of $\sim 10^{-3}$Hz [19].

(b). 3-Bromopentane (3BP)

This sample shows a glass transition at 110 K [19] and the system has not been studied in the region below $T_g$ [37] prior to this work. The loss tangent curve shows two sub-$T_g$ processes (Fig.III.3). The $\beta$-process is not well resolved in the $\tan\delta$-$T$ plot, and is seen as a broad shoulder on the $\alpha$ relaxation peak. The $\beta$ and $\gamma$ processes are resolved assuming Cole-Cole behavior (Eq.(III.3.3)) for the $\beta$-process and the $\alpha$ and $\beta$ processes are further analyzed using Eqs.(III.3.1), (III.3.4) and (III.3.5) and the corresponding parameters are tabulated in Tables III.3 and III.4 (also see Fig.III.4b). Resultant relaxation behavior is shown in Fig.III.5b.
TABLE III.3: Details of the $\alpha$ process in systems studied.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Substances</th>
<th>Process</th>
<th>$T_g$</th>
<th>$T_{g'}$</th>
<th>$r$</th>
<th>$\log f_{0,\alpha}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>Glasses</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1)</td>
<td>Tritolylphosphate</td>
<td>$\alpha$</td>
<td>214.4</td>
<td>203.0</td>
<td>10.9</td>
<td>17.79</td>
</tr>
<tr>
<td>(2)</td>
<td>Isopropylbenzene</td>
<td>$\alpha$</td>
<td>129.5</td>
<td>123.0</td>
<td>12.75</td>
<td>13.27</td>
</tr>
<tr>
<td>(3)</td>
<td>3-Bromopentane</td>
<td>$\alpha$</td>
<td>110.0</td>
<td>95.0</td>
<td>18.07</td>
<td>11.49</td>
</tr>
<tr>
<td>(4)</td>
<td>1-Bromobutane</td>
<td>$\alpha$</td>
<td>103.3</td>
<td>94.0</td>
<td>15.47</td>
<td>12.51</td>
</tr>
<tr>
<td>(5)</td>
<td>Vinylacetate</td>
<td>$\alpha$</td>
<td>124.7</td>
<td>110.0</td>
<td>21.17</td>
<td>15.51</td>
</tr>
<tr>
<td>(B)</td>
<td>Plastic crystals</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(6)</td>
<td>Camphor</td>
<td>$\alpha$</td>
<td>156.7</td>
<td>153.0</td>
<td>8.33</td>
<td>10.29</td>
</tr>
<tr>
<td>(7)</td>
<td>Cyclohexanol</td>
<td>$\alpha_1$</td>
<td>151.0</td>
<td>139.0</td>
<td>8.94</td>
<td>7.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha_2$</td>
<td>80.0</td>
<td>72.0</td>
<td>9.43</td>
<td>6.00</td>
</tr>
</tbody>
</table>

TABLE III.4: Details of sub-$T_g$ processes.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Substances</th>
<th>$\beta$-process</th>
<th>$\gamma$-process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$E$(kcal/mol)</td>
<td>$\log f_0$</td>
</tr>
<tr>
<td>(1)</td>
<td>Tritolylphosphate</td>
<td>13.61</td>
<td>17.79</td>
</tr>
<tr>
<td>(2)</td>
<td>Isopropylbenzene</td>
<td>6.17</td>
<td>14.18</td>
</tr>
<tr>
<td>(3)</td>
<td>3-Bromopentane</td>
<td>5.52</td>
<td>14.03</td>
</tr>
<tr>
<td>(4)</td>
<td>1-Bromobutane</td>
<td>4.42</td>
<td>12.8</td>
</tr>
<tr>
<td>(5)</td>
<td>Camphor</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(6)</td>
<td>Cyclohexanol</td>
<td>4.04</td>
<td>12.59</td>
</tr>
</tbody>
</table>

*Plastic crystals
Figure III.3: Variation of dissipation factor tanδ or dielectric loss ε'' with temperature at 1KHz test frequency in: (1) tritolylphosphate; (2) 3-bromopentane; (3) isopropylbenzene; (4) cyclohexanol; and (5) camphor. The corresponding Tg's are indicated by arrows.
Figure III.4: Normalized Cole-Cole diagram at temperatures above $T_g$ in: (a) tritolylphosphate and (b) 3-bromopentane ($\epsilon_\infty$ is taken as $1.05n_D^2$) (ref.2). Note that the high frequency $\beta$-process is very small in magnitude.
Figure III.5a: Arrhenius diagram of tritolylphosphate. Also indicated in figure apart from our data (●) are the NMR data (ref.36) (×) and the dielectric data (ref.35) (○).
Figure III.5b Arrhenius diagram of 3-bromopentane. Also included in the diagram apart from our data (•) are the data of Berberian and Cole (ref. 37) (o) and our DSC data (ref.19) (•).
(c). Isopropylbenzene (IPB)

The glass transition temperature for this system is 129.5K [19]. This system was studied previously in both liquid [12,13] and glassy states and only one sub-\(T_g\) process was reported. The present results for the \(\alpha\) process agree quite well with those of earlier workers [3], but the measurements in the sub-\(T_g\) region show, in addition to the \(\beta\) process, another process located very close to the \(\beta\) process (Figs.III.3 and III.6). At lower temperatures it was very difficult to resolve the \(\beta\) process in the Cole-Cole diagrams as the magnitudes of the processes involved are very small due to the low dipole moments involved (Fig.III.6) and also due to the noise problems at lower frequencies. The \(f_\infty\) values corresponding to the \(\beta\) process are easily obtained by using the \(\tan\delta\) vs \(T\) plot which reveal peaks at lower frequencies in agreement with isothermal values. The \(f_\infty\) values corresponding to the \(\beta\) and \(\gamma\) processes at high temperatures have been estimated with a large uncertainty as shown in Fig.III.7. The sub-\(T_g\) process designated as the \(\gamma\) process is not resolved in the \(\tan\delta\) versus \(T\) plot. The variation of shape of the \(\alpha\) process with temperature is shown in Fig.III.8a.

(d). 1-Bromobutane (1BB)

The glass transition temperature for this sample is 103.3K [19]. This sample was not studied previously in the supercooled liquid state. The \(\tan\delta\) variation with temperature at 1KHz test frequency clearly shows a \(\beta\)-process (Fig.III.9). The normalized Cole-Cole diagram for the \(\alpha\) process is shown in Fig.III.8b. The Arrhenius diagram for this sample is shown in Fig.III.10. The temperature variation of \(f_\infty\) values corresponding to the \(\alpha\) process is well represented by the power law equation.

(e). Vinylacetate (VAc)

This sample shows a glass transition at 124.7K [19]. The variation of \(\tan\delta\) at 1KHz is shown in Fig.III.9. It does not show any shoulder below the main peak - an indication of the absence of the \(\beta\)-process. The normalized Cole-Cole plot is shown in Fig.III.8c.

(f). Cyclohexanol (CHOL)

This sample is in the plastic crystalline state at room temperature. On supercooling, it shows a glass transition at 151K [19]. This system was very well studied earlier in the liquid [38], plastic crystal (PC) [39,40] and supercooled
Figure III.6: Cole-Cole diagram in the sub-$T_g$ region of isopropylbenzene (frequency is indicated in KHz). Note the presence of two sub-$T_g$ processes designated as $\gamma$ and $\beta$ processes. Also included are the corresponding $\alpha_{CC}$ values of Eq.(III.3.3).
Figure III.7: Arrhenius diagram of isopropylbenzene (our data are indicated by •). Also indicated in the diagram are the data of others (refs. 3, 12, and 13) given as open circle (o). Also given in the diagram is the data corresponding to freezing temperature in the $C_p$ data (ref. 19, 30) (○).
Figure III.8: Normalized Cole-Cole diagrams at temperatures above $T_g$ in (a) isopropylbenzene, (b) 1-bromobutane and (c) vinylacetate.
Figure III.9: Variation of tanδ or dielectric loss $\varepsilon''$ with temperature at 1KHz test frequency in: (1) bromobutane and (2) vinylacetate. The corresponding $T_g$'s are indicated by downward arrows.
Figure III.10: Arrhenius diagram of 1-bromobutane. Also included are the high temperature data from ref.61. The dashed lines correspond to the possible path of the resolved processes. The corresponding DSC $T_g$ (o) is also shown.
plastic crystal (SCPC) [41,42] states. In view of the earlier observations [18-
20] of the existence of two non-Arrhenius processes in H-bonded systems, the sub-
$T_g$ region was critically examined using the dielectric method. Measurements
clearly reveal a process which is identified with the $\beta$ process of Adachi et.al.
[41] as shown in the Arrhenius diagram (Fig.III.11). This process is found to be
non-Arrhenius and freezes at 80K as a small step like change in specific heat
variation with temperature, as seen in calorimetric measurements [43]. In
addition to the above process, one more sub-$T_g$ process of very low magnitude has
been found as shown by large error bars in Fig.III.11. The primary (\(\alpha\)) process is
found only in the ultralow frequency region just above $T_g$, since at higher
temperatures, the material rapidly goes to a rigid crystalline state.

(g). Camphor

This material was studied earlier in PC state [44-46] as well as in the
rigid crystalline state [47]; but not in the SCPC state. The glassy crystal
formation can easily be achieved even for slow cooling rates. The DSC curve
corresponding to the SCPC phase reveals a glass transition at 156.7K. The Cole-
Cole diagram corresponding to the $\alpha$ process is found to be very symmetric
(Fig.III.12), unlike the supercooled liquids which show the asymmetric C-C
diagram. The symmetric distribution parameter $\alpha_{cc}$ (Eq.III.3.3) shows a step-like
rise as the material is supercooled (Fig.III.13a). In addition to the $\alpha$ process,
there are many sub-$T_g$ processes which are not well resolved in the loss tangent
curve (Fig.III.3). The sub-$T_g$ processes are resolved by assuming symmetric Cole-
Cole behavior for these processes and the resultant peak loss frequencies are
shown in Fig.III.13b.

3.3 DISCUSSION

3.3.1 PRIMARY RELAXATION ($\alpha$-PROCESS)

There are a few interesting points worth pointing out as far as the $\alpha$
process is concerned. In the case of TTP, 3BP and 1BB, the shape of the $\alpha$ process
is more or less Cole-Davidson type and does not change appreciably over the
temperature range shown in Figs. III.4 and III.8b. The corresponding dielectric
relaxation time and viscosity however change by many decades. In IPB
(Fig.III.8a), the shape of the $\alpha$-process deviates much from the Cole-Davidson
Figure III.11 Arrhenius diagram of cyclohexanol. Also included in the diagram is the true liquid data (o) of Garg and Smyth (ref. 38) and low temperature data of Adachi et.al. (ref. 41). The points indicated by o correspond to the transformation temperature as seen in DSC (ref. 19) and adiabatic specific heat ($C_p$) data (ref. 43).
Figure III.12: Cole–Cole diagrams corresponding to the $\alpha$-process at various temperatures in camphor (the frequency indicated is in KHz). Also shown in the diagram is the corresponding distribution parameter $\alpha_{cc}$ of Eq.(III.3.3).
Figure III.13a: The variation of the distribution parameter $\alpha_{cc}$ with temperature in camphor ($\Delta$-ours). Also included are the data from ref. 44 given by ($x$, $o$).
Figure III.13b: Arrhenius diagram of camphor. Also included in the diagram is the data of Williams and Smyth (ref.44) (o).
type and the shape of the C-C diagram changes appreciably with temperature. In this context, it is very interesting to note that the magnitude of the \( \beta \) process is smaller in the former three cases and is appreciable in the case of IPB (see Fig.III.3). Thus, it appears that the \( \beta \) process by merging with the \( \alpha \) process distorts the apparent shape of the \( \alpha \) process and hence, is at least partially responsible for the violation of frequency-temperature-superposition principle in IPB.

The interesting point in camphor is that the shape of the \( \alpha \) process is very symmetric (Fig.III.12) in contrast to that of supercooled liquids (Figs. III.4 and III.8). This kind of behavior is not seen in other supercooled plastic crystals studied earlier viz. 1-cyanoadamantane [48] or cyclohexanol [41]. The \( \alpha \) process in camphor follows the Cole–Cole equation (Eq.III.3.3), and interestingly enough, even the plastic crystalline phase of this sample studied by Williams and Smyth [44] shows a similar kind of behavior. The value of \( \alpha_{cc} \) is very high and the DSC baseline shift at \( T_g \) of camphor is spread over a few degrees of temperature contrary to that of SCL, implying a much wider distribution of relaxation times in camphor. The distribution parameter \( \alpha_{cc} \) also changes appreciably with temperature in the supercooled state (Fig.III.13a). There are four sub-\( T_g \) processes in camphor which contribute significantly to the dielectric polarization (Fig.III.13b). Since these processes have different activation energies, they are expected to influence the magnitude as well as the temperature dependence of the parameter \( \alpha_{cc} \). Though it is very difficult to say to what extent these processes contribute to \( \alpha_{cc} \), it is worth pointing out in this context that the recent theoretical work of Bagchi [49] predicts a symmetric Cole–Cole arc with a very high value of \( \alpha_{cc}(0.65) \) in the absence of translational degrees of freedom. The value of \( \alpha_{cc} \) predicted by this theory is very close to that found here.

Another difference between SCL and SCPC of camphor is that in the former case the corresponding liquid relaxation curve in the Arrhenius diagram merges smoothly with the corresponding \( \alpha \)-process (see Figs. III.5, III.7 and III.10), whereas in camphor the relaxation curve corresponding to the \( \alpha \) process is found to be discontinuous on supercooling, and this kind of behavior is not found in other plastic crystals (see Fig.III.11 and Ref.48). At this temperature, the corresponding DSC curve does not reveal any change except for a small endotherm.
At present, the significance of this change or its connection to the abnormality on supercooling camphor is not known.

3.3.2 SECONDARY RELAXATION ($\beta$-process)

In the following, the origin of the sub-$T_g$ processes is examined in order to see whether there is any process which is intermolecular in nature and hence may be identified with the universal feature of amorphous packing.

(a). TTP

The lower sub-$T_g$ process designated as the $\gamma$ process in Fig.III.5a has an activation energy ($E$) of the order of 5.13 kcal/mole. It is too low for the orientation of the TTP molecule as a whole, and may be due to some internal degrees of freedom associated with some small side groups. From the NMR measurements of Rossler [36], the $E$ value for the molecular rotation of TTP in the liquid state was estimated to be about 8.36 kcal/mole. The previous studies [10,50,51] clearly show that the $\beta$ processes associated with the dipolar solutes in a polystyrene matrix have much higher $E$ values than the corresponding liquid state values, which depend very strongly on the shape and size of the molecule. It is therefore, not unreasonable to expect an $E$ value in the range of 24–50 kcal/mole for the intermolecular process in TTP. The $E$ value for the higher sub-$T_g$ process designated as the $\beta$ process is 13.61 kcal/mole and is comparable to the out-of-plane phenyl flipping as found in o-terphenyl, salol, and $\alpha$-phenyl-$o$-cresol [52]. Also, since this process is much weaker in dielectric measurements as compared to that in NMR measurements [36], this indicates that it is not associated with the rotation of the main dipole. Hence, it can possibly be attributed to the weakly polar tolyl groups.

(b). 3BP

Bromoalkanes are known to have contributions to dielectric polarization from segmental rotation in addition to end-over-end rotation of the molecule [15–17,53–56]. However, in 3BP the bromine atom is on the middle carbon atom and hence the contribution to the electric polarization from the alkyl segmental relaxation on its own cannot be significant. If one of the sub-$T_g$ process is due to the main dipole rotation partially active even below $T_g$ (due to either the existence of liquid-like islands in an otherwise rigid matrix [11] or the small
angle rotation of each molecule [4]), there should be a considerable amount of contribution to the polarization from this motion at least above $T_g$. From Fig.III.4b, we see that this is not the case as the dielectric polarization above $T_g$ from the $\beta$ and $\gamma$ processes is very small.

Ahmad and Walker [56] obtained the $E$ value for $-\text{CH}_2\text{Br}$ rotation to be about 4.5 kcal/mole in lower 1-bromoalkanes in the polystyrene matrix. The $\beta$ process in 4-chlorotoluene [10] is found to be due mainly to the side group $-\text{CH}_2\text{Cl}$, with an $E$ value of about 5.5 kcal/mole. It appears that the rotation of the $-\text{CH}_2\text{CH}_3$ group in a rigid matrix should have an $E$ value in the range of 4.5-5.5 kcal/mole as the $-\text{CH}_3$ group is comparable in size to the chlorine (or bromine) atom. The $\beta$ process in 3BP has this amount of activation energy ($E=5.5$ kcal/mole) (Table III.4). The $\beta$ process may therefore be due to the $-\text{CH}_2\text{CH}_3$ group rotation. On the other hand, one may associate the $\gamma$ process to a $-\text{CH}_3$ group rotation as the corresponding $E$ value is low (this amount of $E$ value is generally associated with a small group rotation in rigid media).

(c). IPB

Previous dielectric measurements [12,13] in the true liquid state of this system clearly revealed two processes - the dominant process is found to be due to the rotation of the whole molecule with an $E$ value of 2.63 kcal/mole. The origin of second process is not definitely identified but it is speculated to be due to intramolecular motion. In the glassy state, i.e., below $T_g$, two processes have been found - the high temperature sub-$T_g$ process (designated as the $\beta$ process in Fig.III.4c) has an activation energy of 6.2 kcal/mole comparable to the intermolecular rotation of iodobenzene ($E=5.7$ kcal/mole) in polystyrene matrix as found in the study of Khwaza and Walker [50]. However, as the isopropyl group offers a much larger steric hindrance than the iodine atom to the rotation of the whole molecule in the plane of the phenyl ring the $E$ value for the rotation of IPB in the plane of the phenyl ring should be much higher than that of iodobenzene, which is not the case here. In fact, the $E$ value found for the $\beta$ process in IPB is comparable to the rotation of the $\text{CH}_2\text{Cl}$ group in 4-chlorotoluene [10] or acetyl group relaxation in aromatic ketones [57]. It is too early to say with certainty about the origin of the $\beta$ process in IPB. However, one cannot completely rule out the possibility of the rotation of the isopropyl group about the C-C bond joining it to the phenyl ring as the origin of the $\beta$
process.

Regarding the \( \gamma \) process, a value of \( \approx 2.9 \) kcal/mole has been assigned for the activation energy of rotation. Such low \( E \) values are often associated with \(-\text{OH}\) group relaxation in alcohols [20] and \(-\text{CH}_3\) group rotation in other organic systems in their glassy state. Thus, it is tempting to assign this process to the rotation of the \(-\text{CH}_3\) groups. However, before coming to any final conclusion further investigation using other techniques is needed.

(d). 1BB

From Fig.III.10 one can see that the \( \beta \)-process appears to be the same segmental or \(-\text{CH}_2\text{Br}\) group rotation seen at microwave frequencies at room temperature [58]. On supercooling the liquid, the segmental rotation gets increasingly hindered. This in turn increases the activation energy of \(-\text{CH}_2\text{Br}\) rotation while the strength of the corresponding relaxation process decreases. However, near \( T_g \) the \( \alpha \)-process gets arrested, while the \( \beta \)-process continues to the sub-\( T_g \) region.

(e). VAc

In this material the dipole is mainly located at the centre of the molecule and the side groups or the other segments do not have considerable dipole moments. Probably this is the reason for the absence of \( \beta \)-process in this system.

(f). CHOL

The sub-\( T_g \) process designated as the \( \beta \) process by Adachi et al. [41] (given as open circles in Fig.III.11) appears to be another non-Arrhenius process designated as an \( \alpha_2 \) process in Fig.III.11. Actually, this material was very well studied by Garg and Smyth [38] in the true liquid state and they found three processes. The main process was attributed to \( \text{H-bonded clusters} \); the intermediate frequency process was identified with the 'free' molecules; and the highest frequency process was attributed to the \(-\text{OH}\) group rotation. Interestingly, the \( \alpha_1 \) process merges more or less smoothly with their main process, and the \( \alpha_2 \) process merges with their intermediate frequency process. Note that the \( \alpha_2 \) process on extrapolation (using Eq.III.3.4) freezes at \( \approx 80K \), where the corresponding specific heat data of Kishimoto et al. [43] shows a small step-like change. The other sub-\( T_g \) process designated as the \( \beta \) process has an activation
energy of 2.9-4.1 kcal/mole. It may perhaps be identified with the -OH group rotation since the same E value is obtained for -OH group rotation in many other H-bonded systems as well [20].

(g). Camphor

The sub-$T_g$ processes seen as $\beta_1$ and $\beta_2$ processes in Fig.III.13b apparently have very high activation energies and may be due to the other isomers of impurities present here (the sample is a mixture of D and L camphor and the composition of this sample is not known). The other processes designated as $\gamma_1$ and $\gamma_2$ have very low E values and may be due to some internal degrees of freedom of the molecule.

In essence, the studies of the sub-$T_g$ processes in all the above systems reveal that these processes may be due to the intramolecular degrees of freedom which survive in the glassy state. From this point of view, the monomeric glasses differ from the glasses of binary liquids, e.g., halobenzenes in cis-decalin. In the later cases the $\beta$ process can only be explained as being due to the rotation of the dipolar halobenzene as a whole since the halobenzenes do not have any intramolecular degrees of freedom.

4. CONCLUSIONS

A large number of liquids of different molecular shapes have been examined for glass formation and it is observed that the glass forming tendency increases with the asymmetry of the molecules of the liquid. A clear distinction is noticed between spherical and non-spherical molecular liquids as far as their glass-forming efficiency is concerned.

Dielectric spectroscopy and differential scanning calorimetry techniques have been used to investigate the origin of $\beta$-process in organic liquids. Though this study does not completely rule out the possibility of some kind of intermolecular process as the origin of the $\beta$ process, the evidence that is available does not favor the above possibility. The sub-$T_g$ processes appear to be mainly due to some side group or segmental motion. It is also found that the sub-$T_g$ process thought to be the $\beta$ process in cyclohexanol is actually another non-Arrhenius process corresponding to another glass-like transition below the main
In this aspect, both the glasses and glassy crystals appear to behave in the same fashion.

The study of the $\alpha$ process in these systems indicates that the violation of frequency temperature superposition principle in some of the systems is due to a contribution to the polarization from the $\beta$ process. The $\alpha$ process corresponding to the SCPC phase of camphor is found to be very symmetric in contrast to the supercooled liquids studied.
REFERENCES