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The origin of β relaxation in organic glasses

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Using dielectric spectroscopy, some organic liquids consisting of mainly alkylhalides and acetic acid esters, have been studied over a wide frequency (10^6 to 10^{-3} Hz) and temperatures (down to 77 K). Measurements have also been made in the true liquid state at four microwave frequencies of 33, 22.4, 10, and 5.4 GHz in the temperature range 303–363 K. The high-temperature data reveals a significant contribution from the intramolecular (end- or side-group) rotation. The data corresponding to the supercooled state reveals a secondary (β) process in addition to the primary (α) process. The magnitude of the β process is found to be relatively large in systems which have greater contribution from the intramolecular process to the overall polarization at room temperature. The activation energies together with the side/end-group dependence of the magnitude of the β process suggest that the intramolecular process, though very much hindered during the process of supercooling, may survive to some extent in the glassy state to be realized as the β process. Our study suggests that the origin of the β process in these glasses may not be intermolecular in nature.

INTRODUCTION

Glass obtained by supercooling a liquid is often regarded as the low-temperature extension of the liquid, where the corresponding enthalpy relaxation time becomes comparable to that of the experimental time scale.¹ If the liquid under test consists of permanent dipoles, the approach to the glassy state can be seen in a dielectric relaxation experiment and the corresponding relaxation process is termed as the primary or α process, which gets arrested at the glass (transition) temperature T_g . In addition to the above process, supercooled liquids reveal yet another process of much smaller magnitude termed as a secondary or β process, which continues to the sub- T_g region.² The question of the origin of the β process is controversial. Some researchers^{3,4} believe it to be intramolecular in nature, whereas others^{2,5-7} believe it to be intermolecular. This matter is further complicated by the introduction of mode coupling theory⁸ which predicts a universal β process which is intermolecular in nature. We addressed this controversy in our previous publication,⁹ where we concluded that the origin of the sub- T_g processes probably lies in a side group and or segmental-rotation which still survive in the glassy state. However, a systematic study on liquids which have a significant contribution from the intramolecular process to dielectric polarization, is required to clarify this point further.

Therefore, in the present communication, we report our findings on a number of organic liquids, with the dipole located either at the end of the molecular chain or in the side group. Also of interest is the temperature variation of

the shape of the α process as the glass transition temperature is approached.

EXPERIMENT

The samples investigated are given in Table I, where samples 4 and 10 are obtained from M/s. Aldrich Chemicals; sample 3 from M/s.S.D. Fine Chemical, India, and the rest of the sample are obtained from Merck, India. All the samples are of purity >98% and are used as received.

Prior to the dielectric measurements all the samples are tested for their glass-forming ability using a DuPont TA2000 thermal analyzer. The samples are cooled to 95 K; equilibrated for 10 min, before heating it at a rate of $10^\circ/\text{min}$, for the glass transition temperature (T_g) measurement. The dielectric measurements are performed in three steps. In the microwave frequency range, measurements are performed at four spot frequencies: 5.6, 10, 22.4, and 33 GHz using microwave bridges. The temperature covered is 303–353 K. However, due to experimental difficulties the microwave data is not taken at all frequencies in some of the liquids. The accuracy of our microwave data is about 2% for ϵ' and 5% for ϵ'' values. In a temperature range below room temperature down to 77 K; we have used an HP4284 A precision LCR meter to cover the frequency range 10^6 –20 Hz and a dc step response technique is used for the range $10^{-0.5}$ – 10^{-3} Hz, which was described in Ref. 10. For all the low-frequency measurement, a two terminal dielectric cell is used and glass is formed by quenching the samples in the dielectric cell to the liquid nitrogen temperature. The cooling rate can be varied from 3–20°/min. For further experimental details, the reader may consult Refs. 10 and 11.

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TABLE I. DSC results of the glass formation in some flexible molecular systems.

Substance	T_g^a (K)	Comment on glass formation
1. 1-Bromopropane	107.0 ^b	bad
2. 1-Bromobutane	103.3	good
3. 1-Iodobutane	108.3	good
4. Vinylacetate	124.7	good
5. Ethylacetate	116.0 ^b	bad
6. <i>n</i> -Butylacetate	125.7	good
7. Benzylacetate	165.1	good
8. Di- <i>n</i> -butylether	114.3 ^b	bad
9. Aniline	146.5 ^b	bad
10. <i>n</i> -Propylbenzene	126.2	good

^a T_g : for heating rate of 10 K/min.

^bVery high cooling rates are required for glass formation.

RESULTS

We have chosen about ten samples for the study, all of which show a significant contribution to dielectric polarization ranging from 10% to 80%, from the intramolecular relaxation in their true liquid state. We have specifically chosen these samples in view of a large amount of information available about the nature of the dielectric relaxation in these systems.¹²⁻²⁵ We have tested these samples for glass formation using differential scanning calorimetry (DSC) to verify the suitability of the samples for dielectric studies in the supercooled state. In only six samples, the glass formation is found to be easier, i.e., glass is formed even for a normal cooling rate of 10 K/min. However, in the other samples, the high cooling rate of the order of 800 K/min is required, even for partial glass formation. The details of glass formation in the samples are given in Table I. (For further details on this subject, the reader may consult Ref. 11.) In view of the experimental difficulty in obtaining very high cooling rates in our dielectric cell only six samples are studied further in the supercooled state.

For the analysis of the dielectric data, use has been made of the Cole-Cole (CC) representation.¹² For the microwave data coupled with the static dielectric constant (ϵ_0) and the high-frequency limiting dielectric constant (ϵ_∞) (which is taken as $1.05n_D^2$, where n_D is the refractive index); can either be represented by the Cole-Cole (CC) equation¹² or Cole-Davidson (CD) equation,¹² which are specific cases of the more general Hevriliak-Negami equation²⁶ which is given by

$$\frac{\epsilon^*(f) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \left[1 + \left(i \frac{f}{f_0} \right)^{1-\alpha_{HN}} \right]^{-\beta_{HN}},$$

$$0 < 1 - \alpha_{HN}, \quad \beta_{HN} < 1. \quad (1)$$

In the above equation α_{HN} and β_{HN} are the symmetric and asymmetric distribution parameters, respectively. From the above equation the peak loss frequency f_m is calculated using the equation $f_m = f_0 \tan[\pi/2(\beta + 1)]$. Note that by putting $\beta_{HN} = 1$ in Eq. (1) one gets the CC equation and by putting $\alpha_{HN} = 0$ in Eq. (1) one gets the CD equation. Fur-

TABLE II. Details of the high-temperature relaxation frequency f_m (unresolved).

Substance	$\log f_m$ (Hz)			E (kJ/mol)	$\log f_0$
	303 K	323 K	343 K		
1. 1-Bromobutane ^a	10.29	10.37	10.44	7.53	11.58
2. 1-Iodobutane	10.05	10.27	...	13.74	12.50
3. Benzylacetate	10.17	10.32	10.44	13.45	12.40
4. <i>n</i> -Butylacetate	10.38	10.55	10.63	11.45	12.38
5. Vinylacetate	10.78	10.88	...	9.20	12.30

^aData taken from Ref. 13.

ther, for the high-temperature liquid, the apparent activation energy E per mole is calculated using the Arrhenius relation

$$f_m = f_0 \exp(E/RT). \quad (2)$$

The values of f_m , E along with the preexponential factor (f_0) for the high-temperature liquid side are tabulated in Table II. As our microwave data have some scatter, we have not made any attempt to find the f_m values in *n*-propylbenzene whose dipole moment (μ) is too low.²⁷

In Figs. 1-3, we have given the relaxation data of the true liquid along with that of the supercooled liquid, in the form of a normalized CC diagram, to get some insight about the change in the shape of the relaxation as the liquid is supercooled. The variation of $\tan \delta$ at 1 kHz test frequency is shown for all the samples in Fig. 4, which clearly reveals the presence of a β process in most of the samples. The f_m values corresponding to the α and β processes are calculated using Eq. (1). The β process can well be represented by a symmetric CC equation ($\beta_{HN} = 1$) (Fig. 5) unlike the α process which is more asymmetric. The temperature variation of the f_m values corresponding to the α process (f_m) are well represented by the power-law (PL) equation²⁹

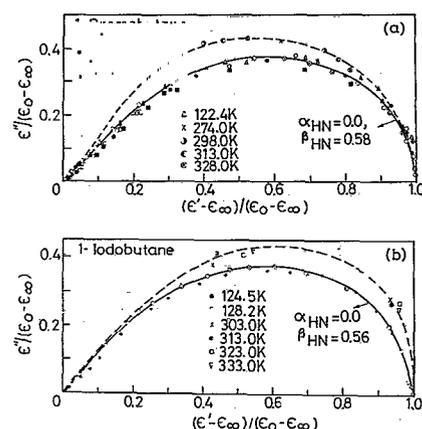


FIG. 1. Normalized Cole-Cole diagrams corresponding to the liquid relaxation above T_g in (a) 1-bromobutane and (b) 1-iodobutane. Also included in (a) is the high-temperature data of Symth *et al.* (Ref. 13) as given in Ref. 23.

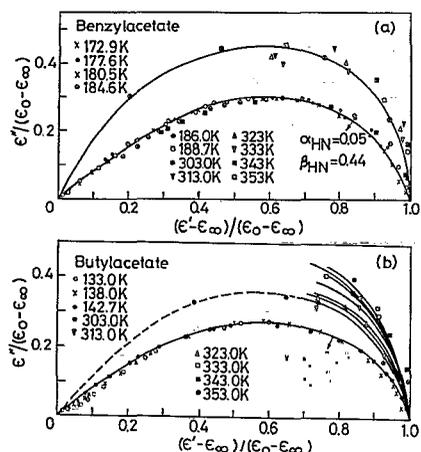


FIG. 2. Normalized Cole-Cole diagrams corresponding to the liquid relaxation above T_g in (a) benzylacetate and (b) *n*-butylacetate. Also included is the 37 GHz data at 303 K given in Ref. 28.

$$f_{m,\alpha} = f_{0,\alpha} \left[\frac{T - T'_g}{T'_g} \right]^r \quad (3)$$

as the PL equation is found to be a much better representation of the temperature dependence of the f_m as compared to the well-known Vogel-Fulcher-Tammann equation. In the above equation T'_g is the limiting glass transition, and r is the dynamic exponent. The f_m values corresponding to the β process ($f_{m,\beta}$) follow Eq. (2) and the corresponding parameters are given in Table III along with that of the parameters of Eq. (3) for the α process. In Table IV, we give the respective strengths of the α and β processes in the indicated temperature range.

DISCUSSION

For the sake of convenience, we split our discussion in three parts corresponding to the high-temperature (high- T) liquid regime, supercooled region, and the glassy state.

High- T liquid side

A quick look at the literature on dielectric relaxation in liquids as discussed, e.g., in Refs. 12, 24, and 25, reveals that the peak loss frequency (f_m) decreases with increase

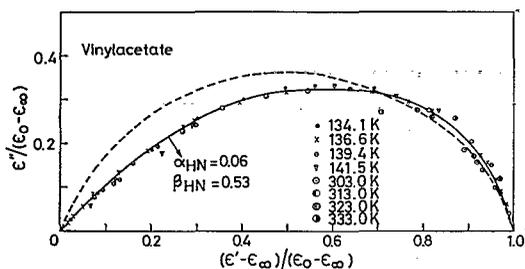


FIG. 3. Normalized Cole-Cole diagrams corresponding to the liquid relaxation above T_g in vinylacetate. The dashed line corresponds to the high-temperature liquid.

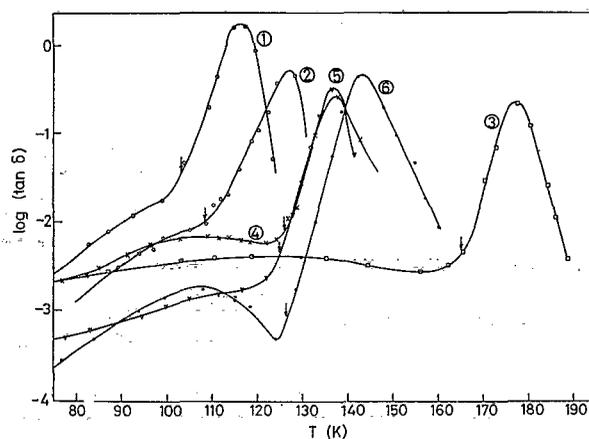


FIG. 4. Variation of the dissipation factor $\tan \delta$ at 1 kHz with temperature in (1) 1-bromobutane; (2) 1-iodobutane; (3) benzylacetate; (4) *n*-butylacetate; (5) vinylacetate; and (6) *n*-propylbenzene. The curve corresponding to (1) is shifted upwards by 0.5 units for the sake of clarity. The corresponding T_g 's are indicated by downward arrows.

in the size of the rotating unit and the apparent activation energy E increases. From this point of view, the initial temptation is to explain the decrease in f_m and increase in the E value as one moves from 1-bromo-butane (1BB) to 1-iodobutane (1IB) (see Table II) to an increase in the size of the molecule, and hence to attribute the relaxation process to the whole molecular rotation. But the previous work^{15-18,30} on 1BB has clearly established a significant contribution of end group $-\text{CH}_2\text{Br}$ to the total polarization. In view of this, if one looks critically at the actual f_m value of 1IB which is 11.2 GHz, one realizes that it is not of the right magnitude that is expected for the rotation of a molecule of the size of 1IB and hence there seems to be some contribution to the total polarization from the end group $-\text{CH}_2\text{I}$. Based on the previous work^{15-18,30} on alkyl bromides, the expected value for f_m for the whole molecular relaxation in 1IB is about 5.5 GHz (which is almost

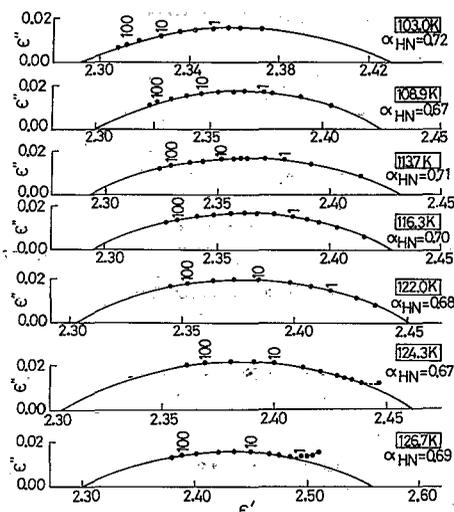


FIG. 5. Cole-Cole diagrams corresponding to β -process in *n*-butylacetate at various temperatures. Also shown is the value of α_{HN} ($\beta_{HN}=1$ for all the cases).

TABLE III. Details of Eqs. (2) and (3).

	α process				β process	
	T_g (K)	T'_g (K)	r	$\log f_0$	E (kJ/mol)	$\log f_0$
1-Bromobutane	103.3	94.0	15.47	12.51	18.5	12.8
1-Iodobutane	108.3	98.0	18.06	12.30	20.06	12.64
Benzylacetate	165.1	155.0	15.56	15.52	17,13 ^a	...
<i>n</i> -Butylacetate	125.7	116.5	15.38	13.96	21.45	13.49
Vinylacetate	124.7	110.0	21.17	15.51
<i>n</i> -Propylbenzene	126.0	114.0	15.27	11.87	15–19	...

^aCorresponds to the two weak β processes.

half of the experimentally observed value) and for $-\text{CH}_2\text{I}$ group relaxation is around 40 GHz. Depending on the contribution of the $-\text{CH}_2\text{I}$ group the resultant unresolved f_m value will be somewhere between 5.5–40 GHz, which is the case with 1IB. Since, one expects a greater hindrance to $-\text{CH}_2\text{I}$ group rotation as compared to the $-\text{CH}_2\text{Br}$ rotation its contribution to the overall polarization decreases, the corresponding f_m value (for the end-group relaxation) decreases. Also taking into view the size of 1IB, this should result in an overall decrease in the unresolved f_m value and an increase in the apparent E value; as compared to 1BB; which is the case (see Table II). Also one may notice from Fig. 1 that the CC diagram on the high- T side of 1BB is more symmetric than that of the corresponding CC diagram of 1IB, which is probably a reflection of the much greater contribution of the end-group rotation to the overall polarization in the former. [A symmetric CC diagram ($\beta_{\text{HN}}=1$) is generally taken as evidence of distribution of relaxation times whereas the asymmetric CD-type plot is generally taken as an indication of a cooperative process³¹ rather than a distribution of relaxation times.]

Replacing the Br atom in 1BB with a much bulkier acetate, the CH_3COO -group [which now becomes *n*-butyl acetate (NBA)]; one expects a large decrease in the f_m value corresponding to the whole molecular rotation as: (i) the overall size of the molecule increases and (ii) the acetate group offers more hindrance to the whole molecular rotation. Noting that the viscosities of 1BB and NBA at room temperature do not vary appreciably,³² the results

TABLE IV. Details of the magnitudes of α and β processes.

	α process		β process		$\frac{\Delta\epsilon_\alpha}{\Delta\epsilon_\beta}$
	Temp. range (K)	$\Delta\epsilon_\alpha$	Temp. range (K)	$\Delta\epsilon_\beta$	
1-Bromobutane	104–117.4	13.75–13.0	89–99	0.19–0.24	61.4
1-Iodobutane	120–128.0	13.20–12.9	89–108	0.10–0.17	94.0
Benzylacetate ^c	178–186.0	3.95–3.60	87.3	0.055	69.0
<i>n</i> -Butylacetate ^c	138–143.0	4.3–3.90	96–125	0.13–0.16	28.0
Vinylacetate ^c	...	0.334 ^a	...	0.0016 ^a	209 ^b
<i>n</i> -Propylbenzene	...	0.047 ^a	...	0.002 ^a	251 ^b

^aTan δ_{max} at 1 kHz from Fig. 1.

^bRatio of tan δ_{max} at 1 kHz for the α and β processes.

^cThe glasses formed are not fully amorphous.

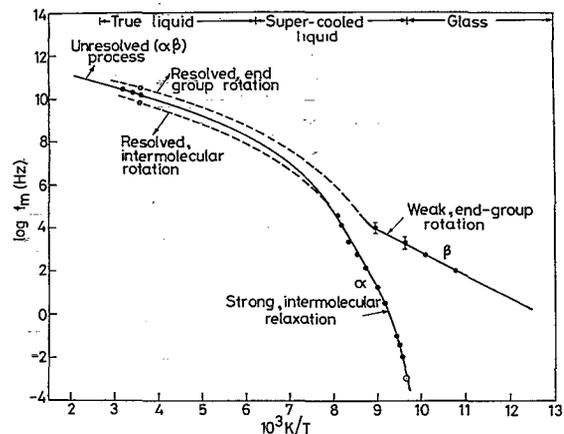


FIG. 6. Arrhenius plot of 1-bromobutane. Also shown is the high-temperature data of Smyth and co-workers (Refs. 13, 23, and 30) corresponding to the unresolved and resolved relaxation processes. The dashed line corresponds to the possible path of the resolved processes. Also shown in the figure is the DSC $T_g(\odot)$ which corresponds to an enthalpy relaxation frequency of 10^{-3} Hz.

given in Table II which show an increase in f_m value of NBA from that of 1BB clearly indicate a much greater contribution to overall polarization from the intramolecular rotation, probably coming from the acetate group. In this context it may be noted that the CC diagram at 303 K (Fig. 2) for NBA appears to be more like a symmetric ($\beta_{\text{HN}}=1$) CC diagram with an unrealistically large value of the distribution parameters α_{HN} .

Similarly, one can show a large intramolecular contribution to polarization in benzylacetate (BA) as the corresponding f_m value (=14.8 GHz) is much larger than that of a liquid of similar sized molecule and viscosity.^{12,24} (The viscosity of BA at room temperature is estimated to be of the order of around 7–10 cp.)

In the case of vinylacetate (VA), there is large uncertainty in the f_m values, as our experimental points in the microwave region are on the lower frequency side of the f_m and only constitute a small part of the CC arc (see Fig. 3). The f_m values measured with this uncertainty are slightly smaller than that of ethylacetate¹⁵ (which is of similar size). However, the f_m values are higher as compared to a molecule of similar size and shape. In addition, the CC diagram is also very symmetric with a large value for the distribution parameter α_{HN} (Fig. 3), indicating a significant intramolecular contribution to polarization.

Thus, our high- T data on these liquids indicate a significant contribution from the intramolecular process whose contribution to total polarization decreases in the order of NBA, BA, 1BB, and 1IB.

Supercooled regime

In the supercooled region, the f_m value corresponding to the α process strictly adhere to the power-law equation (3) and the DSC(T_g) corresponds to the freezing of the α process; where the corresponding f_m values are 10^{-3} Hz (Figs. 6 and 7). The α process is highly non-Debye in

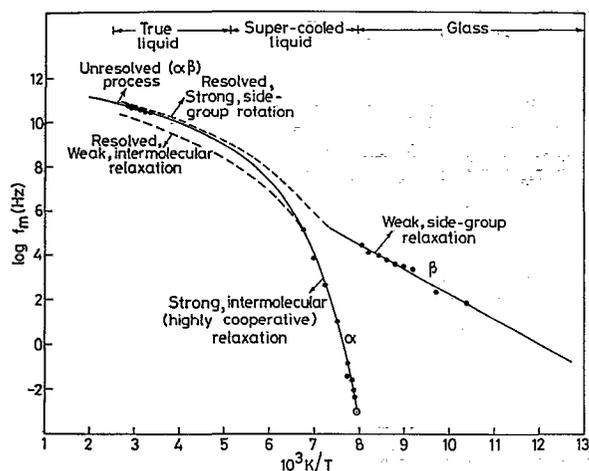


FIG. 7. Arrhenius plot of *n*-butylacetate. Also shown in the diagram are the possible paths of the resolved processes. Also shown in the figure is the DSC T_g (○) which corresponds to an enthalpy relaxation frequency of 10^{-3} Hz.

character and is of CD type³¹ ($\alpha_{HN}=0$) in the case of alkyl bromides (Fig. 1), where there is a small contribution from the presence of a second process on the high-frequency side. In the case of the NBA and BA, there is a deviation from CD type of behavior ($\alpha_{HN}=0$) where there is a significant contribution from the second process present on the high-frequency side. In fact, the deviation from CD type of behavior is very striking in NBA where there is a larger contribution to polarization from the second process as compared to the other samples. The case of *n*-propylbenzene (NPB) in the supercooled region has been studied in detail by earlier workers,^{22,32} whose data clearly show a CD-type behavior with no evidence of contribution from other processes.

It is interesting to note that only in the cases of NBA and BA, which have the largest contribution to polarization from intramolecular process, have a much larger change in the shape of the CC diagram as the liquid is supercooled as compared to the other cases (compare Fig. 2 with Figs. 1 and 3). Another significant observation is that the asymmetric parameter β_{HN} in alkylhalides (Fig. 1) is slightly larger than 0.5, a value which is of some significance in Glarum's defect diffusion model³³ of dielectric relaxation. Also, one may notice that the β_{HN} value determined for other alkylhalides by earlier workers^{9,34,35} is closer to the values found here. However, this value for NPB^{22,23} is about 0.65–0.71, much larger than that found in alkylhalides. (A value of 0.53 is also found for β_{HN} in tritolyphosphate as well.⁹) At present, we do not know the significance of the apparent universality in the value of β_{HN} in alkylhalides.

Thus our results in the supercooled region indicate that the α relaxation is cooperative and is due to reorientation of the molecule as a whole and the intramolecular process contributes less significantly to polarization as compared to the high-*T* liquid side. However, it may be noted that the contribution of the intramolecular process is still significant in NBA and BA.

Glassy state

The most curious of our observation is that the magnitude of the β process is larger in those systems where there is a larger intramolecular contribution to polarization on the high-*T* side of the liquids. From Fig. 4 and Table IV, one may notice that the magnitude of the β process relative to the corresponding α process decreases in the order NBA, IBB, BA, and 1IB, which is probably a reflection of the corresponding intramolecular contribution at room temperature.

1BB has an E_β value of 18.5 kJ/mol as compared to about 20 kJ/mol for 1IB. In addition, the magnitude of the β process is smaller in the latter. These observations indicate that it may be the end group, i.e., $-\text{CH}_2\text{Br}$ in the former and $-\text{CH}_2\text{I}$ in the latter which is responsible for the β process, because the latter will have more hindrance to rotation (and hence larger E_β) and lesser contribution to polarization. Our view is also supported by the experimental results of Ahmed and Walker,³⁶ on normal alkylhalides in various glassy matrices. The E value calculated from their low-temperature process which was attributed to $-\text{CH}_2\text{Br}$ rotation is approximately 18.5 kJ/mol which is what we have found in the case of 1BB.

In vinylacetate, since the main dipole (acetate group) is along the main molecular axis, it freezes along with the molecules at T_g and hence will not contribute to dielectric polarization below T_g . However, the vinyl group $-\text{CHCH}_2$ may survive to some extent below T_g but will not contribute to polarization significantly as the corresponding dipole moment is weaker. Note that the same acetate group which exists as the side group in NBA and BA gives rise to comparatively larger polarization below T_g . In NPB, since the main dipole is rigidly fixed to the phenyl ring it gets frozen at T_g along with the molecule and hence cannot be responsible for the β process below T_g . The E_β for NPB is about 15–17 kJ/mol, which we attribute to the "hindered rotation" of a small segment of the propyl radical, possibly a $-\text{CH}_3$ group, which by virtue of its much smaller dipole moment cannot contribute significantly to the polarization below T_g .

It is also of interest to note that the β process is highly symmetrical (Fig. 5), with a large value for the distribution parameter α_{HN} . A similar observation was made earlier^{9,10} in other liquids as well, the significance of which is not clear to us. Though one can explain it as due to a distribution of relaxation times, the actual explanation probably lies in the more constrained nature of the dipole, i.e., in the smallness of the local free volume around the dipole as the dipole is relaxing in a very rigid environment.

Based on the results discussed above, we can qualitatively visualize the origin of the β process in the glassy state, as given in Figs. 6 and 7. In 1BB and NBA, the high-*T* liquid relaxation as seen in a dielectric experiment is dominated by the $-\text{CH}_2\text{Br}$ group in the former and acetate group ($-\text{O}=\text{C}-\text{CH}_3$) in the latter which are capable of independent rotation about the C–C or O–C axis joining these groups to the main-butyl radical because the main dipole is in the $-\text{CH}_2\text{Br}$ or acetate group. There is

significant intramolecular contribution to the polarization on the high-temperature side. When the liquid is cooled, the viscosity increases drastically and the $-\text{CH}_2\text{Br}$ or acetate group finds it difficult to rotate freely and contribute fully to the polarization on its own, whereas the molecule can orient as a whole through a cooperative effort. Thus, one can expect a crossover from an intramolecular-dominated mechanism to an intermolecular-dominated mechanism during the process of supercooling. On further cooling, the intermolecular process, i.e., the α process freezes at T_g , whereas the highly hindered side group continues to the sub- T_g region and can be seen as the β process.

CONCLUSIONS

We have studied some glass-forming liquids over a wide temperature and frequency to find out the origin of the so-called β process. The liquids are chosen in such a way that the main dipole is at the end of the chain (1BB, 1IB), in the side chain (NBA, BA), and along the main molecular axis (VA and NPB). It is observed that the β process is very small in the last two samples and in the rest of the samples, the magnitude of the β process is found to be proportional to the magnitude of the intramolecular process on the high-temperature side. This, together with the activation energies corresponding to the β process, indicate that they are probably due to the intramolecular (side-group or end-group) rotation and not due to any intermolecular process as discussed in the mode coupling theory or due to any other kind of universal phenomena. It is also noticed that the β process may contribute significantly to polarization to invalidate the time (or frequency) temperature superposition principle for the α process.

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