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Experimental study of the nature of the glass transition process in monohydroxy alcohols

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The nature of the glass transition process in six monohydroxy alcohols, viz., the isomers of butanol, 2-propanol, and 3-methyl-1-butanol had been studied in detail using dielectric spectroscopy (frequency range 10^{+6} – 10^{-3} Hz) and differential scanning calorimetry (DSC). Measurements were made down to a temperature of 77 K in dielectric experiments and a temperature of 95 K in DSC. These results together with the published microwave data on these liquids reveal the existence of two glass transition processes—one due to the hydrogen bonded network which is very dominant and the other one due to the nonhydrogen bonded molecules, which is much weaker. Associated with the latter process, there is a secondary (or β -) relaxation process whose activation energy varies from 4.8 to 6.7 kcal/mol which is dependent on the shape and size of the liquid molecules. In addition to the β process, all the alcohols revealed yet another sub- T_g (γ) process whose activation energy varies from 2.1 to 2.6 kcal/mol and is found to be little dependent on the molecular shape. These results perhaps indicate that the β process is somehow connected to the relaxation of the free monomeric molecule and the γ process to that of hydroxyl group rotation, respectively.

INTRODUCTION

When a simple (van der Waals) liquid is supercooled fast enough to avoid crystallization, its relaxation time as seen in a dielectric relaxation experiment keeps on increasing, but splits into the so-called primary (or α) and secondary (β) processes.¹⁻⁵ On further lowering the temperature, the α branch gets arrested when the associated relaxation time is of the order of 200 s or its relaxation frequency is of the order of 10^{-3} Hz, and this happens at a temperature designated as T_g (dielectric) [or $T_g(D)$]. This temperature is often found to agree well within the experimental uncertainty with the temperature designated as T_g (calorimetric) (or simply T_g), where the calorimetric experiments for a cooling rate of 10^0 /min reveal a major step-like change in the specific heat data.^{6,7}

However, the experiments of Johari and Goldstein⁸ clearly reveal that this is not the case with alcohols where $T_g(D)$ and T_g differ considerably from each other. If one assumes that the error involved in the estimation of $T_g(D)$ from an extrapolation of the α process to much lower frequencies is negligible, then two possible explanations can be offered for the above behavior. One is the decoupling of dielectric and calorimetric (enthalpy) modes and the second is the possible existence of yet another glass transition process that is difficult to be resolved.^{9,10} It is interesting in the present context to note that many alcohols are found to possess at least one more non-Arrhenius process in the audio- and radiofrequency ranges, the origin of which is not well understood.^{9,10} In order to resolve this issue, it is absolutely required to examine the T_g region critically using both calorimetry and low-frequency dielectric spectroscopy.

The alcohols generally exhibit three well-resolved relaxation processes at room temperature.^{11,12} Though a lot of work¹³⁻¹⁸ has been done on supercooled alcohols, it is

not clear to us as to how these three processes terminate as the liquid is supercooled to form a glass. There are many other problems as well. For example, the nature of the β process in these liquids is not very clear as there are conflicting views on this.^{12,19} Some researchers²⁰ choose to explain it as being due to –OH group rotation, whereas some workers⁸ choose to explain it as some intermolecular process which is a universal feature of the glass.

In order to resolve the above issues, we have undertaken a critical study of some of the alcohols which have been studied extensively in the past both in the liquid and supercooled states.

EXPERIMENT

The samples studied are 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-propanol, and 3-methyl-1-butanol (of which the first three are the isomers of butanol) and are obtained from Merck India. All the samples are distilled twice and desiccated for a few days prior to their use.

Two kinds of measurements have been made on the samples: (i) one is the differential scanning calorimetry (DSC) measurements using a DuPont 2000 Thermal Analyzer using a quench cooling accessory, the details of which are given in our earlier reference.¹⁰ First the samples are quench cooled to the starting temperature and equilibrated for 15 min. Then the data are taken on reheating the samples at a rate of 10^0 /min. The DSC cell is calibrated for temperature using *n*-pentane and indium as the standards and a two-point temperature calibration is used for this purpose.

The second kind of measurements performed on the samples are the dielectric relaxation measurements. For this purpose, the samples are cooled in a two terminal dielectric cell with a guarded electrode arrangement, which has an empty cell capacitance of 61.7 pF. The glass is

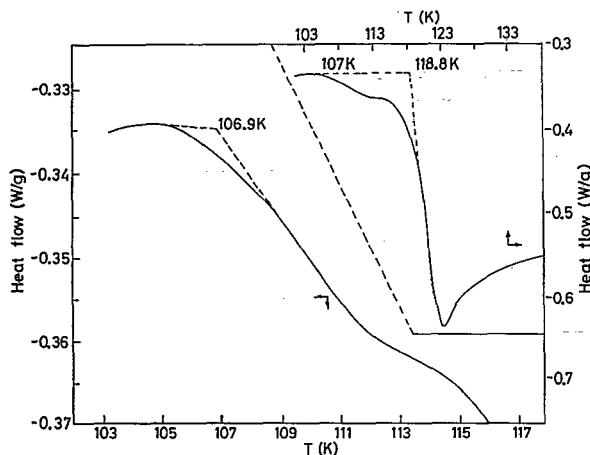


FIG. 1. (a) The DSC curve of 2-propanol in the region of the glass transition temperature. Note that the base line shift occurs in two steps—one ~ 107 and the other ~ 118.8 K (heating rate= $10^\circ/\text{min}$). (b) A magnified portion of the DSC curve in the region of the lower glass transition temperature.

formed by dipping the cryostat directly into liquid Nitrogen which gives an average cooling rate of $50^\circ/\text{min}$ and dry nitrogen gas is used for purging purposes. The samples are equilibrated at 77 K and are slowly heated to the measuring temperature. The samples are kept at the measuring temperature for about 20 min for equilibration before taking the measurements. A heating coil wound around the sample cell and a temperature controller are used for this purpose. All the samples are studied from 77 K up to a few degrees above the melting temperature of the samples. The dielectric measurements are taken in two steps. The frequency range from 20 to 10^6 Hz is covered by using a HP4284A Precision LCR meter and the frequency range from $10^{-0.5}$ to 10^{-3} Hz is covered by using a d.c. step response technique.²¹ In the latter technique, only the dielectric loss measurements are determined, and for this purpose, the Hamon's approximation^{21,22} is used for the estimation of the loss data from the absorption current. A programmable electrometer (Keithley Model No. 617) is used for this purpose. The sample is charged initially by applying a 100 V d.c. step from the d.c. source (part of the electrometer) and the sample is then discharged after charging it for a sufficient amount of time.²² The discharging current is digitized and is stored in the memory of the electrometer. The digitized data are then used for the estimation of the dielectric loss.

RESULTS

All the samples are studied critically using DSC for a possibility of two resolved glass transition temperatures.^{9,10} As an example, we show the DSC curve of 2-propanol in the T_g region (Fig. 1), which shows a major glass transition process at 118.8 K, but if the part of the curve just below this temperature is magnified, it clearly reveals another small step-like change characteristic of the glass transition. As another example, we show the DSC curve of 2-butanol (Fig. 2), where again one can see two T_g 's. We

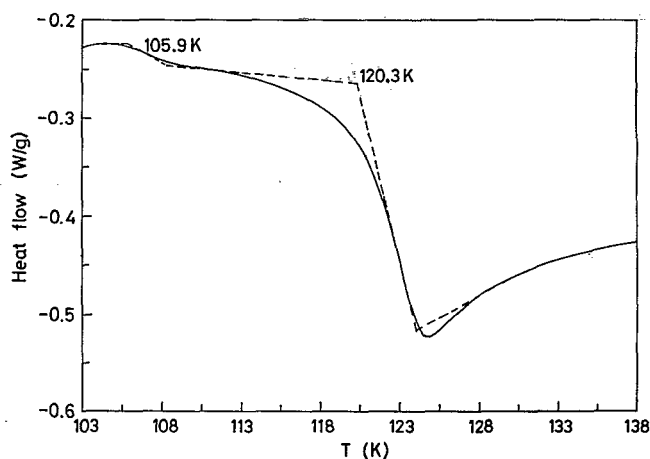


FIG. 2. The DSC curve of 2-butanol in the region of the glass transition temperature. Note that the base line shift occurs in two steps—one at 105.9 and the other at 120.3 K (heating rate= $10^\circ/\text{min}$).

designate these two calorimetric glass transition temperatures as T_{g1} and T_{g2} in the order of decreasing temperature.

The dielectric loss in the frequency range $10^{-0.5}$ – $10^{-3.0}$ is obtained from the Hamon's approximation^{21,22}

$$\epsilon''(f) = \frac{i(t) \cdot t}{0.63 \cdot C_0 \cdot V_0}, \quad ft = 0.1 \quad (1)$$

where $i(t)$ is the discharging current at a time t , C_0 is empty cell capacitance, and V_0 is the applied voltage. Equation (1) is strictly not valid for a material showing Debye behavior, but is still a good approximation for the loss above the loss peak frequency f_m . The error estimated²³ from Eq. (1) in the calculation of $\log f_m$ for a Debye process is ~ 0.20 . The values of ϵ'' thus obtained, along with that of the bridge values in the frequency region 20– 10^6 Hz are shown in Fig. 3, at temperatures above T_{g1} . The loss peaks are "Debye" in character, and even on lowering the temperature, the loss peaks do not appear to

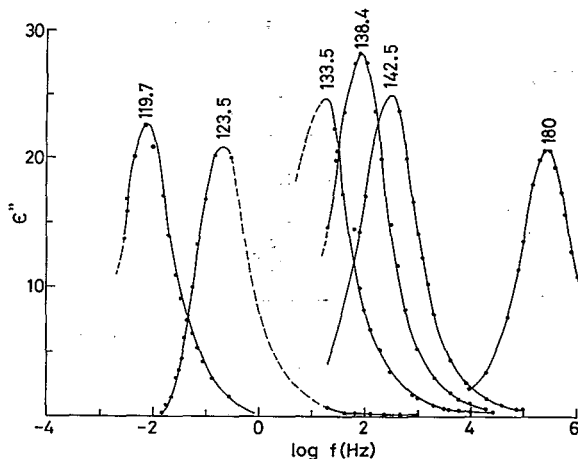


FIG. 3. A variation of dielectric loss with frequency in 2-propanol at different temperatures. The corresponding temperature is indicated at the top of each curve.

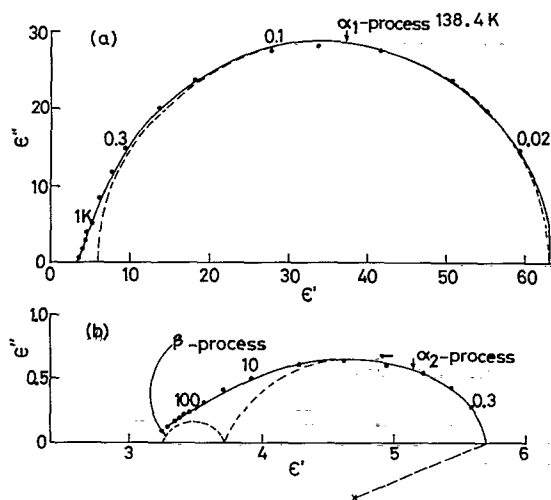


FIG. 4. (a) A complex plane diagram for 2-propanol at 138.4 K. The dotted semicircles indicate the best fit for the lower frequency points ($\alpha_{cc}=0$, $\epsilon_0=63.1$, $\epsilon_\infty=5.7$, and $f_m=82$ Hz) which corresponds to the α_1 process. The numbers beside the points indicate the corresponding frequency in kiloHertz. (b) The resultant complex plane diagram after subtracting the contribution of the α_1 process from the experimental data. Note that the resultant complex plane can be shown to be a superposition of two depressed Cole-Cole arcs—one with $\alpha_{cc}=0.26$, $\epsilon_0=5.7$, $\epsilon_\infty=3.73$, and $f_m=1.67$ kHz; and the second one with $\alpha_{cc}=0.22$, $\epsilon_0=3.73$, $\epsilon_\infty=3.25$, and $f_m=30$ kHz.

deviate from the Debye character as the half-width is found to be not detectably different from that of the Debye which is 1.14. However, it is not clear to us why the peak loss decreases on lowering the temperature in the region of T_{g1} . We could not measure the losses below T_{g1} in our ultralow frequency setup as the loss is found to be below the detection level of our measuring system.

The Cole-Cole diagrams²⁴ corresponding to the sample whose loss curves are shown in Fig. 3, are as shown in Fig. 4(a). The low frequency data could well be fitted to a Debye arc. The data thus calculated at all frequencies if subtracted from the experimental data yield a Cole-Cole diagram for the high frequency processes as shown in Fig. 4(b), which can again be resolved into two depressed Cole-Cole arcs, where the Cole-Cole arc is given by

$$\epsilon^*(\omega) - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{(1 + i\omega\tau)^{1-\alpha_{cc}}}, \quad (2)$$

where $\tau (= 1/2\pi f_m)$ is the mean relaxation time and α_{cc} is the symmetric distribution parameter. In other words, the relaxation data in our frequency window at temperatures a few degrees above T_{g1} can well be represented as a superposition of three processes—one Debye type and two depressed Cole-Cole arc type processes which are designated as α_1 , α_2 , and β processes, respectively, in Fig. 4. The low temperature data below T_{g2} corresponding to the glassy state of the same sample are shown in Fig. 5 again in the form of Cole-Cole diagrams which show a gradual appearance with increasing temperature of a process which can be identified as the β process in addition to existence of another process which is designated as a γ process.

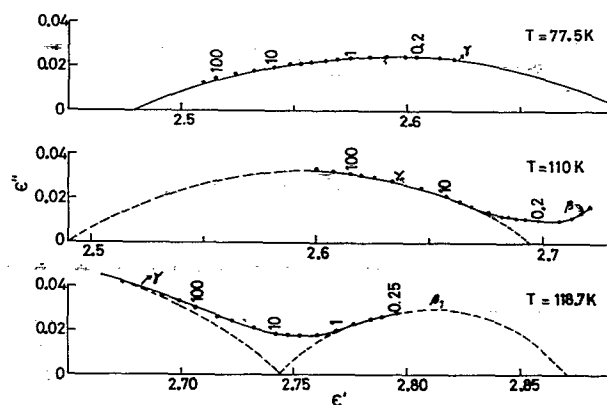


FIG. 5. The behavior of 2-propanol in the sub- T_g region, shown in the form of complex plane diagrams. The numbers by the side of the points indicate the corresponding frequency in kiloHertz. (a) A complex plane diagram at 77.5 K. The thick line is given by Eq. (2) with $\alpha_{cc}=0.72$, $f_m=450$ Hz, $\epsilon_0=2.694$, and $\epsilon_\infty=2.48$. (b) A complex plane diagram at 110 K. The dashed line corresponds to Eq. (2) with $\alpha_{cc}=0.61$, $f_m=2.5$ KHz, $\epsilon_0=2.695$, and $\epsilon_\infty=2.491$. Note that there is another process on the lower frequency side. (c) A complex plane diagram at 118.7 K. Note that there are two well-resolved processes—one on the higher frequency side and one on the lower frequency side.

The behavior is found to be similar in all the other samples as well and as another example; we show the case of 1-butanol in Fig. 6 where one can see three processes identified as α_1 , α_2 , and β processes. The low temperature data below T_{g2} of the same sample appears as a difficult to resolve combination of two processes, namely, β and γ processes (Fig. 7).

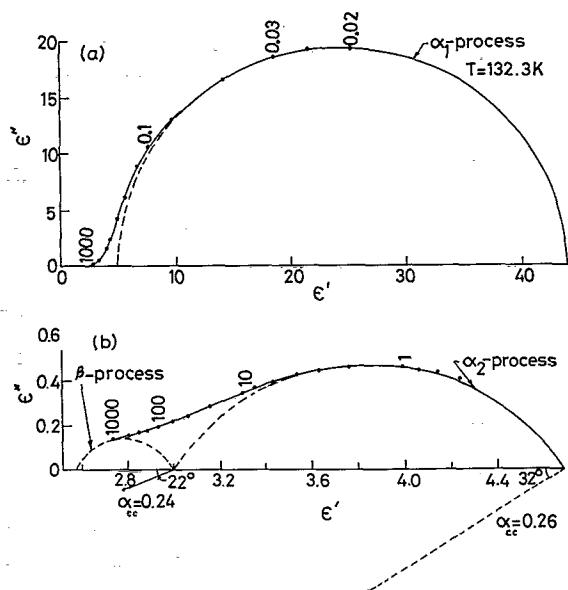


FIG. 6. (a) A complex plane diagram 1-butanol at a temperature of 132.3 K. The dotted semicircle is the best fit to the experimental data on the lower frequency side which corresponds to the α_1 process. (b) A resultant complex plane diagram after subtracting the contribution of α_1 process from the experimental data. Note that it is actually a superposition of two depressed Cole-Cole arcs given by Eq. (2), with $\alpha_{cc}=0.36$ and 0.24, respectively.

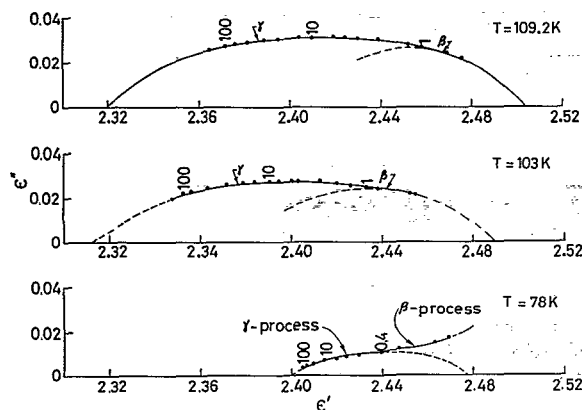


FIG. 7. A complex plane diagrams of *n*-butanol on the lower temperature side. Note that at $T=78$ K, the β process appears only as a spur on the lower frequency side and the γ process can be described by Eq. (2) quite well. At higher temperatures, the β process can be seen as a hump on the lower frequency side, but is difficult to be resolved. Also note that the magnitudes of the β and γ processes increase with temperature.

The existence of various relaxation processes can be seen if one plots $\tan \delta$, the dissipation factor against the temperature (Fig. 8). If one compares it to a similar plot for a van der Waals liquid as given in Ref. 25 with that of the alcohols shown in Fig. 8, one can see that the region below T_{g1} has a lot of shoulders or peaks which cannot be well resolved. The peak loss frequency (f_m) values obtained for various (resolved) relaxation processes are plotted in the form of Arrhenius diagrams for all the samples as shown in Figs. 9–13. Also shown in these diagrams are the data reported by earlier workers on these samples and the T_g 's obtained by the DSC method. The curves designated as α_1 and α_2 could be well fitted to a power law equation^{4,26}

$$f_m = f_0 \left(\frac{T - T'_g}{T'_g} \right)^{-r} \quad (3)$$

for all f_m below 10^6 Hz, as the power law equation is found to be more appropriate for the description of the temperature dependence of f_m than the well-known Vogel-Fulchers-Tammanns equation.⁴ In the above equation $T'_g < T_g$ is the limiting glass transition temperature, where f_m is expected to become zero. The corresponding parameters are given in Table I along with that of the DSC T_g 's.

The β and γ processes can be fitted to the Arrhenius equation

$$f_m = f_0 \exp \left(\frac{-E}{RT} \right), \quad (4)$$

where E is the activation energy per mole. The parameters corresponding to Eq. (4) are given in Table II.

DISCUSSION

For the convenience of discussion, we split our discussion into a number of points as given below.

(1) The glass transition process as seen in calorimetric measurements is a two-step transition⁹ (the two glass tran-

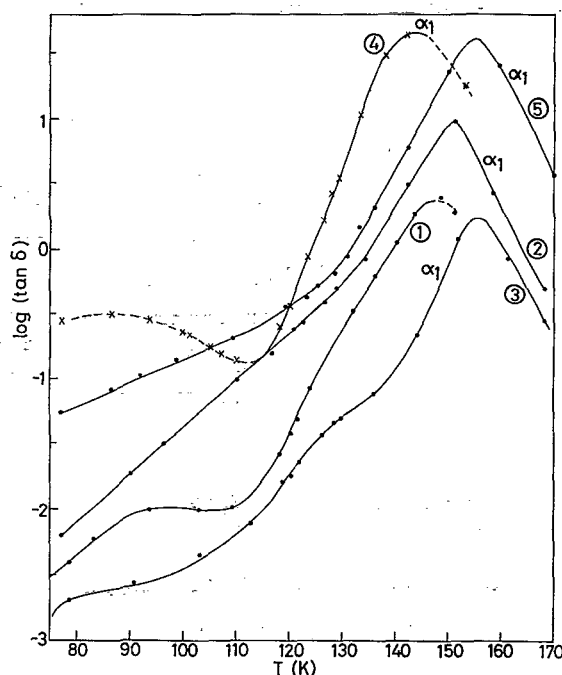


FIG. 8. A variation of dissipation factor with temperature at 1 KHz test frequency in (1), 1-butanol; (2) 2-methyl-1-propanol; (3) 2-butanol; (4) 2-propanol; and (5) 3-methyl-1-butanol. The curves labeled (2), (4), and (5) are shifted vertically by -0.8 , 1.5 , and 1.6 units, respectively. Note that in addition to the large α_1 peak, the sub- T_g region consists of many small humps or shoulders, indicating the presence of two or more hard to resolve processes.

sition temperature are designated as T_{g1} and T_{g2} in the order of decreasing temperature) (see Figs. 1 and 2). If one takes the specific heat change at T_g as the strength of the process, one can see that the strength of the lower glass transition is about 5%–10% of that of the first transition at T_{g1} .

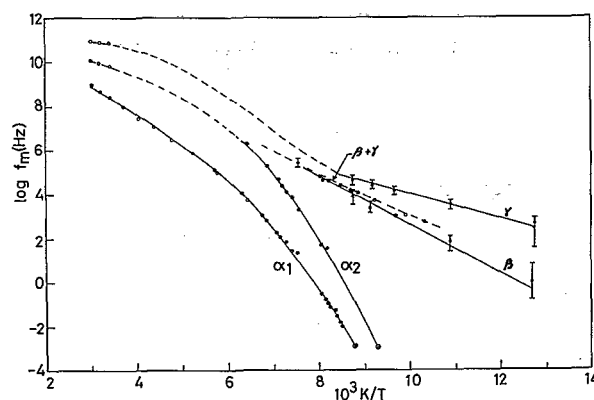


FIG. 9. A relaxation map of 1-butanol. Also included in the figures are the microwave data of Garg and Smyth (Ref. 11), the radiofrequency data of Dannhauser and Cole (Ref. 13) and that of Johari and Goldstein (Ref. 8) and our (Ref. 10) DSC T_g 's (which correspond to an enthalpy relaxation frequency of 10^{-3} Hz). Note that the sub- T_g process of Johari and Goldstein (Ref. 8) is actually a combination of two processes designated as β and γ , respectively. The points given by \bullet and \circ are ours.

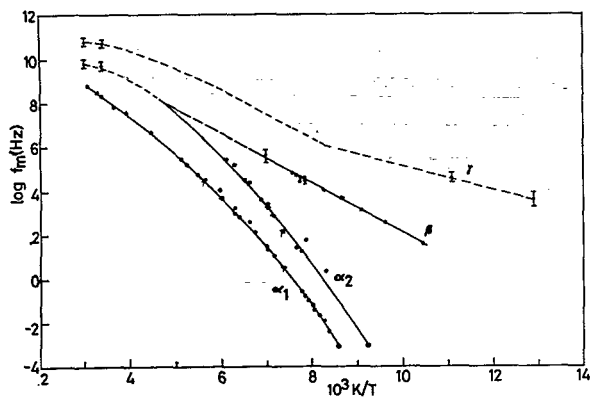


FIG. 10. A relaxation map of 2-methyl-1-propanol. Also included in the figure are the data given in Refs. 11, 13, and 24 and our DSC T_g 's ($f_m=10^{-3}$ Hz). The points given by \bullet and \odot are ours.

(2) All the alcohols studied here more or less reveal the presence of four relaxation processes in the temperature range above 77 K. However, the processes designated as α_2 , β , and γ processes could not be seen in the usual $\log \tan \delta$ vs temperature plots (Fig. 8) since these processes are located in a narrow range of temperature below T_{g1} and also since the low temperature processes are weaker as compared to the α_1 process (see Figs. 3–7 and 13). We are able to separate these processes by assuming a depressed Cole–Cole behavior [Eq. (2)] for the low temperature processes, which appears to be a good approximation as can be seen from the fits given in Figs. 3–7.

(3) The most dominant process designated as the α process, which is Debye in nature, freezes at the calorimetric glass transition T_{g1} (Figs. 9–13). This process was very well studied in the past at temperatures much above T_{g1} and was found to be Debye in nature, in agreement with the present work. Also, our measurements at temperatures much closer to T_{g1} reveal that this process still retains its Debye character (Fig. 3) (which seemed to be contradicting the results of Forsman *et al.*¹⁸). The agreement of our

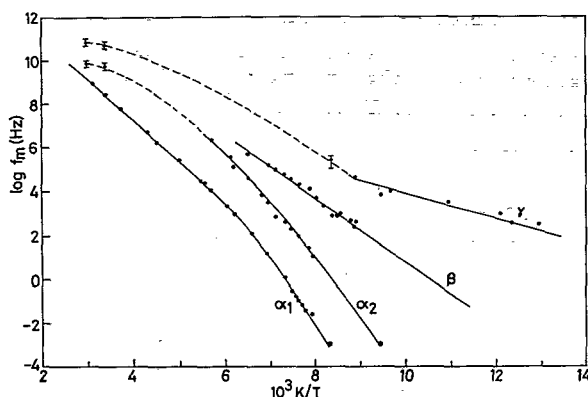


FIG. 11. A relaxation map of 2-butanol. Also included in the figure are the data given in Refs. 11, 13, and 24 and our (Ref. 10) DSC T_g 's ($f_m=10^{-3}$ Hz). The points given by \bullet and \odot are ours.

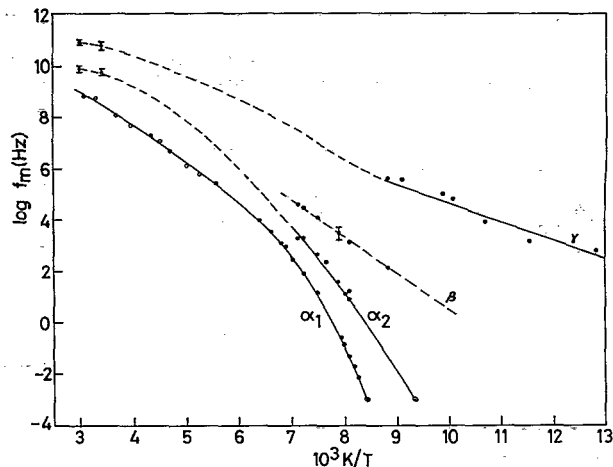


FIG. 12. A relaxation map of 2-propanol. Also included in the figure are the data given in Refs. 11 and 24 and our (Ref. 10) DSC T_g 's ($f_m=10^{-3}$ Hz). The points given by \bullet and \odot are ours.

results with that of earlier work,^{13–18,24} as shown in Figs. 9–13, leads us to attribute T_{g1} to the freezing of the H-bonded network.

(4) The process designated as the α_2 process on extrapolation to lower temperatures, freezes at a temperature which is exactly the lower glass transition temperature T_{g2} , determined calorimetrically (Figs. 9–13). (This process could not be studied by dielectric relaxation method, at temperatures closer to T_{g2} , since its magnitude is found to be about 2% to 5% of that of the α_1 process and the corresponding polarization currents are much below the detection level of our ultralow-frequency experimental setup.) This process is found to be non-Debye in nature (see Figs. 4 and 6) and our f_m values corresponding to this process agree quite well with that of the values reported by Hassion and Cole¹³ (HC) about four decades back (see Figs. 9 and 10). We are able to resolve the α_2 process in all the samples. Both α_1 and α_2 processes follow point (3) for f_m (for all f_m values below 10^6 Hz) and the corresponding parameters are given in Table I.

It is interesting to note in the present context that the earlier work^{11,12} on these alcohols more or less reveal three relaxation processes at room temperature in the microwave and very high-frequency (VHF) regions of which the two lower-frequency processes correspond to the α_1 and α_2 processes of our work, respectively (see Figs. 9–13). Symth and his co-workers^{11,12} interpret these processes to the H-bonded network and the reorientation of the free molecules, respectively. In this context, it is tempting to interpret the α_2 process as due to the free molecules since this process freezes at a temperature (T_{g2}), where the corresponding van der Waals liquid freezes.¹⁰ For example, T_{g2} for 1-butanol is 106.5 K, which is closer to the T_g ($=106.7$) of 1-butyliodide, whose molecules are of similar size and shape as that of 1-butanol. For more details on this subject, the reader may refer to Ref. 10.

(5) In addition to the α_1 and α_2 processes, all the alcohols studied here more or less reveal the presence of

TABLE I. Details of the α processes in the samples studied.

Sample	Details of the α_1 process				Details of the α_2 process			
	T_{g1} (K)	T'_{g1} (K)	r	$\log f_0$ (Hz)	T_{g2} (K)	T'_{g2} (K)	r	$\log f_0$ (Hz)
1-butanol	113.4	100	10.86	6.43	107.4	91	15.65	8.65
2-methyl-1-propanol	116.5	96	12.92	5.69	108.6	85	16.56	6.21
2-butanol	120.3	92	15.68	5.02	105.9	90	12.12	6.12
2-propanol	121.3	102	14.41	8.36	107.1	95	11.49	7.24
3-methyl-1-butanol	123.2	102	13.46	6.18	106.8	90	11.71	5.53

two other processes (designated as β and γ processes), but which are Arrhenius in nature. The relaxation process situated immediately below T_{g2} has an activation energy (E_β) between 4.5–7.0 kcal/mol (Table II). A closer examination of Table II reveals that the value of E_β is molecular shape dependent as can be seen in the case of the isomers of butanol, where the E_β value increases as one moves from more symmetric 1-butanol to the more asymmetric 2-butanol. This possibly indicates that the β process is due to the rotation of the molecule as a whole.²⁸ However, one cannot completely rule out the possibility of segmental rotations involving one or two carbon atoms in the backbone as responsible for the β process.

The other interesting aspect in the present context is that the β process on extrapolation to the high temperature side does not appear to meet the α_1 process at any temperature below the boiling temperature of the liquid (see Figs. 9–13), but appears to merge with the α_2 process, indicating that the β process found in these liquids belongs to the α_2 process. This possibility of merging/bifurcation²⁷ of α_2 and β processes leads us to conclude that the β process is perhaps connected to the “free” molecules.

(6) The relaxation process situated on the lowest side of the temperature designated as the γ process has an E value of 2–2.5 kcal/mol, which cannot definitely be associated with the rotation of the molecule as a whole,²⁸ as it is too low. In addition, this value does not vary much from liquid to liquid. Thus one can attribute this to the –OH group rotation. The value of E is of the same order as that found for the –OH group rotation in a number of H-bonded systems in the polystyrene matrix.^{29,31} It is also interesting to note that the γ process has a tendency to become non-Arrhenius above T_{g2} and meets the –OH group rotation that is found at room temperature in the

frequency range of a few tens of gigaHertz (see Fig. 9–13). The non-Arrhenius dependence is probably due to a change of the E value with viscosity or free volume around the –OH group, as the temperature is raised above T_{g2} as described in Ref. 32.

(7) The non-Debye parameter designated as α_{cc} is found to have a value of 0.30–0.45 for the α_2 process, 0.55–0.6 for the β process, and about 0.7 for the γ process. One may explain this as being due to an increase in distribution of relaxation times for which one cannot give any convincing physical meaning.²² However, we wish to explain this as being due to a increasing rigidity²² of the local environment around the rotating dipole. This is consistent with the observation that α_{cc} increases in the order of α_2 , β , and γ processes.

The magnitudes of the β and γ processes have a general tendency to increase with temperature, as against the inverse temperature dependence for the molecular relaxation process²⁸ seen in the liquid state. We have noticed this trend in van der Waals liquids as well.²⁵ However, as the accuracy in the absolute values of α_{cc} , ϵ_0 , and ϵ_∞ for these processes is not very good, we do not wish to discuss the temperature dependence of these parameters any more.

The highlight of this present study is the evidence of the existence of two glass transition processes in monomeric alcohols. The existence of two non-Arrhenius processes in the dielectric relaxation studies was detected by

TABLE II. Details of β and γ processes in the samples studied.

Sample	β process		γ process	
	E_β (kcal/mol)	$\log f_0$ (Hz)	E_γ (kcal/mol)	$\log f_0$ (Hz)
1-butanol	4.78	...	~2.4	~9.13
2-methyl-1-propanol	5.20	13.51	~2.4	...
2-butanol	6.62	15.25	2.63	9.65
2-propanol	6.74	15.28	3.31	11.92
3-methyl-1-butanol	2.08	8.33

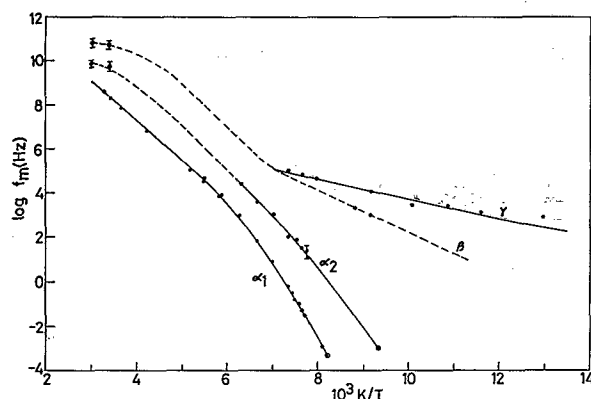


FIG. 13. A relaxation map of 3-methyl-1-butanol. Also included in the figure are the data given in Refs. 11, 14, and 24 and our (Ref. 10) DSC T_g 's ($f_m = 10^{-3}$ Hz). The points given by ● and ○ are ours.

Cole and his co-workers^{13,15} way back in 1950s and was also evidenced in the relaxation studies of other workers^{14,24} as the ϵ_∞ values corresponding to the α_1 process are significantly higher than n_D^2 values, where n_D is the refractive index of the liquid. However, Cole and his co-workers¹³ opined that both α_1 and α_2 processes were of the same origin as the limiting temperatures of these processes were found to be the same within their experimental accuracy, but unfortunately, it was not supported by any calorimetric data. In our case, the increased frequency window of the measurements, use of sensitive DSC measurements, and an increase in the accuracy of bridge measurements due to modern electronic circuitry have helped us in resolving the two glass transition processes. In fact, we had the advantage of the accessibility of the microwave data^{11,12} on these liquids which was published 10 to 12 years after the publication of the work by Cole and his co-workers.¹³

CONCLUSIONS

Our measurements on about five alcohols clearly reveal the existence of two closely located glass transition temperatures in calorimetric measurements and associated with this there are two non-Arrhenius processes in dielectric relaxation measurements. The temperature dependence and the origin of these two processes are found to be different. The two glass transition temperatures are attributed to the freezing of the H-bonded network and the free molecules, respectively. We have not noticed any decoupling²⁷ of dielectric and calorimetric modes.

All the liquids show two sub- T_g processes, one of which is possibly connected to the free molecules (either molecular or segmental rotation) and the other to the -OH group, respectively. The former has an activation energy of 4.5–7 kcal/mol, whereas the latter has an activation energy of 2.5 kcal/mol. Our measurements clearly indicate a more restricting environment for the latter process. Because of the difficulty in measuring the absolute magnitudes of the strength β process, we are not able to determine why this process is weaker in some alcohols.

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