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Dielectric Relaxation Processes of Some Nearly Spherical Dipolar Organic Molecules in a Few Glassy Media

Entazul M. Huque*

Department of Chemistry, Lakehead University, Thunder Bay, Ontario P7B 5El, Canada

Summary. Dielectric absorption studies have been carried out on some dipolar, almost spherical organic molecules (camphane derivatives) in a polystyrene matrix in the frequency range 10–10^5 Hz between 80 and 300 K. Some molecules have also been studied in other glass forming media such as carbon tetrachloride, glassy-*o*-terphenyl and polyphenyl ether (Santovac). All of these molecules show dielectric relaxation due to molecular reorientation in each dispersion medium with characteristic activation parameters. Alcohol molecules do not show dispersion due to hydrogen-bonded species below five percent concentration, a range usually used in dielectric studies. Relaxation due to the hydrogen-bonded species is observed at higher concentrations. High activation parameters for molecular reorientation of camphane derivatives are accounted for by the strong intermolecular interactions at low temperatures.

Keywords. Dielectric relaxation; Camphane derivatives; Glassy media; Molecular reorientation; Activation parameters.

Dielektrische Relaxationsprozesse einiger nahezu sphärischer dipolarer organischer Moleküle in glasartigen Medien

Zusammenfassung. Es wurden die dielektrischen Absorptionen einiger dipolarer, nahezu sphärischer organischer Moleküle (Camphan-Derivate) in einer Polystyrolmatrix im Frequenzbereich 10–10^5 Hz zwischen 80 und 300 K untersucht. Für einige Moleküle wurden auch andere glasbildende Medien herangezogen, z.B. Tetrachlorkohlenstoff, glasiges *o*-Terphenyl und Polyphenylether (Santovac). Alle untersuchten Moleküle zeigten eine dielektrische Relaxation mit charakteristischen Aktivierungsparametern, die auf molekulare Reorientierung in den jeweiligen Dispersionsmedien zurückzuführen sind. Alkoholmoleküle zeigen wegen wasserstoffbrückengebundener Spezies bei einer Konzentration unter 5% (ein bei dielektrischen Untersuchungen üblicher Bereich) keine Dispersion. Bei höheren Konzentrationen wird wegen wasserstoffbrückengebundener Spezies Relaxation beobachtet. Die hohen Aktivierungsparameter für die molekulare Reorientierung von Camphan-Derivaten wird auf starke intermolekulare Wechselwirkungen bei tiefen Temperaturen zurückgeführt.

Introduction

The dielectric study of a variety of organic dipolar rigid molecules in various glass-forming solvents such as polystyrene (*PS*), glassy-*o*-terphenyl (*GOTP*), polyphenyl

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* Correspondence to: Department of Biological Sciences, University of Calgary, Calgary, Alberta T2N 1N4, Canada

ether, commonly known as Santovac (*SV*), and *cis*-decalin at temperatures below T_g (glass transition temperature) have been reported [1–4]. Very broad loss curves were observed for numerous solutes, in which dipole reorientation necessarily involves rotation of the entire molecule. Davies et al. [5] studied camphor in a polystyrene matrix in the frequency range 5 to 10^9 Hz between 243–373 K and reported one dielectric dispersion. The Eyring plot $\log(T\tau)$ vs. $1/T$ for the dispersion was curved having two slopes above and below the temperature 293 K. The distribution parameter β was found to be decreased with decrease of temperature and became very pronounced at around 293 K. To explain this dispersion they suggested that the local molecular environment of camphor undergoes some changes at this particular temperature from a less rigid to a more rigid form. For generalization a more systematic study on large number of similar molecules seems to be desirable.

Clemett et al. [6] studied camphene, camphor and bornyl chloride in the pure solid state and also camphor in camphene solid solution. They obtained relatively low enthalpies of activation ($\Delta H_E = 8$ to $11\ \mathrm{kJ\ mol^{-1}}$) and entropies of activation ($\Delta H_E = 8$ to $11\ \mathrm{kJ\ mol^{-1}}$) for molecular reorientation. Increase of the former values with decrease of temperature was interpreted as being due to molecular interactions. Their Eyring plot $\log(\mathrm{T}\tau)$ vs. $1/T$ was bent, which is sometimes an indication of a cooperative process.

To obtain a clear picture, a systematic dielectric study on a series of camphane derivatives in a polystyrene matrix at low temperatures is reported here. This would enable the assessment that ΔH_E for molecular reorientation increases at low temperatures [5]. Molecular interactions may be assessed by varying dispersion medium to determine if the dielectric parameters change appreciably with the dispersion medium. A detail knowledge of molecular relaxation and the associated activation energy barriers is also essential for the assignment of a particular process in similar sized flexible and rigid molecules in different dispersion media.

The dielectric study of alcohols in the pure liquid state [7–11] and in liquid solutions [12–16] over a wide temperature and frequency range has shown three dielectric dispersions characterized by three relaxation times τ_1, τ_2 and τ_3. The τ_3 process, obtained at the highest frequency, has been assigned to $-\mathrm{OH}$ group rotation [9, 13] while the τ_2 process is attributed to contributions from $-\mathrm{O}R$ group rotation, molecular rotation and/or from small multimers [9, 10, 17]. The τ_1 process is the dominating process, appears at the lowest frequency, and has been accounted for in terms of several models [9–17]; however, it is not well understood. Recent dielectric studies by Huque and Walker [18] on long-chain aliphatic alcohols and thiols in a polystyrene matrix have shown two well resolved relaxations. The lower temperature process was assigned to the intramolecular motion, while the higher temperature process was shown to be related to molecular rotation which was influenced by the presence of some intermolecular hydrogen-bonding. A subsequent study on substituted alcohols showed additional absorption in the 200–270 K region [19]. The ΔH_E for this process was close to the energy required to break about three hydrogen bonds. This process, described as due to some associated species, was highly dependent on the dispersion medium as well as on the concentration of the solute. Alcohols obtained from camphane derivatives are sufficiently small to exclude contributions to the dielectric absorption from intramolecular process of the monomer. These molecules are potentially suitable to search for further evidence as to whether or not hydrogen-bonded equilibria in alcohols are medium and concentration dependent, as was observed recently in some simple alcohols [19]. The activation parameters of the corresponding rigid molecules help to distinguish molecular relaxation from the relaxation due to any associated species.

Experimental

The dielectric absorption measurements to obtain the loss factor (ε'') of a solute in a dispersion medium, were carried out in the frequency range 10–10^5 Hz with the use of a General Radio 1621 precision capacitance bridge. For polystyrene samples, a three terminal, circular, parallel plate capacitor, mounted in an air tight aluminum casing, was used. Liquid samples were placed in a three terminal, stainless steel, coaxial capacitor. The capacitors are mounted in temperature controlled chambers and are operational from 77–400 K.

The cell was cooled with liquid nitrogen. Both the cell and liquid nitrogen container were insulated with styrofoam. Temperatures were controlled to within 0.1 K and were recorded with a Newport 264-3 platinum resistance thermometer. The polystyrene matrices were prepared with atactic polystyrene according to the method of Davies et al. [20]. Preparation of the samples, the measurement technique and the apparatus have been described previously [1]. The compounds were purchased from the highest purity commercial sources and were appropriately purified, whenever necessary, before use. All compounds were rigorously dried.

Results

Typical plots of the loss factor against temperature at a fixed frequency are given in Figs. 1 and 2. Dielectric data ($\varepsilon'' = \varepsilon''_{matrix} - \varepsilon''_{solvent}$) as a function of frequency (e.g. Figs. 3 and 4) were analysed by computer for the best linear fit to the Fuoss-Kirkwood equation

$$\mathrm{Cosh}^{-1}(\varepsilon''_{max}/\varepsilon'') = \beta(\ln \nu_{max} - \ln \nu). \tag{1}$$

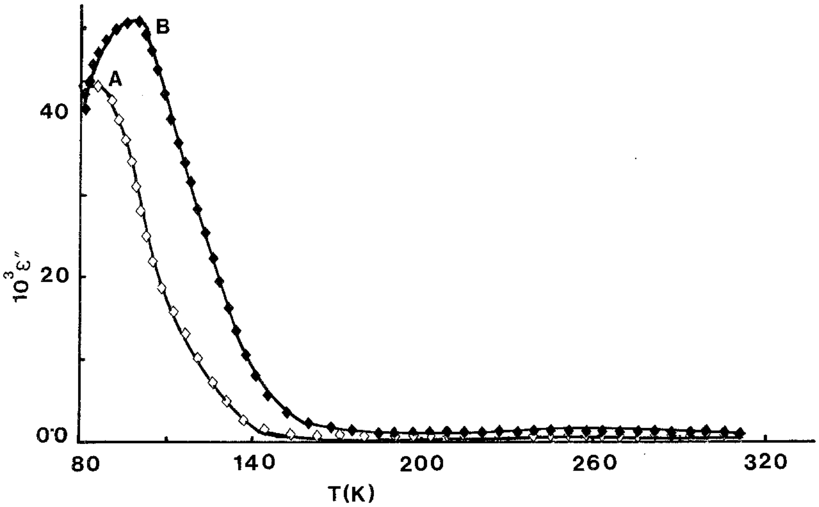


Fig. 1. Plots of dielectric loss factor ε'', against temperature, T(K) for norcamphor in a polystyrene matrix at $A = 50.2$ Hz and $B = 1.01$ kHz

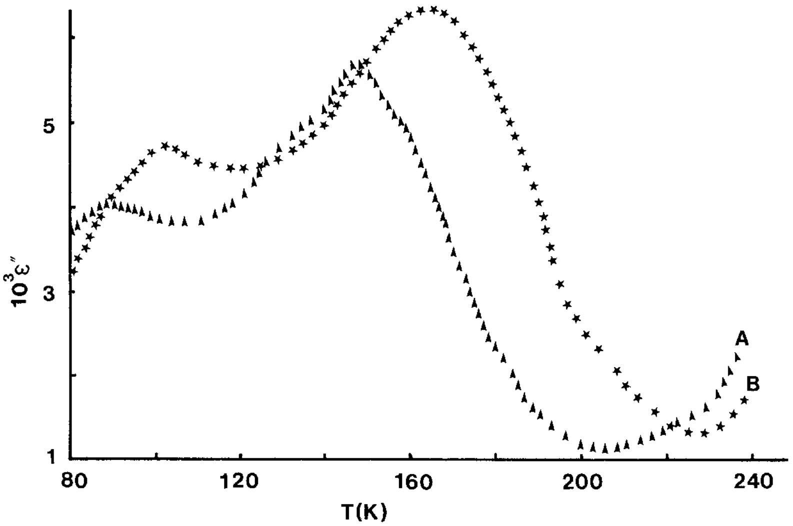


Fig. 2. Plots of dielectric loss factor, ε'', against temperature, T(K) for norborneol in glassy-*o*-terphenyl at $A = 50.2$ Hz and $B = 1.01$ kHz

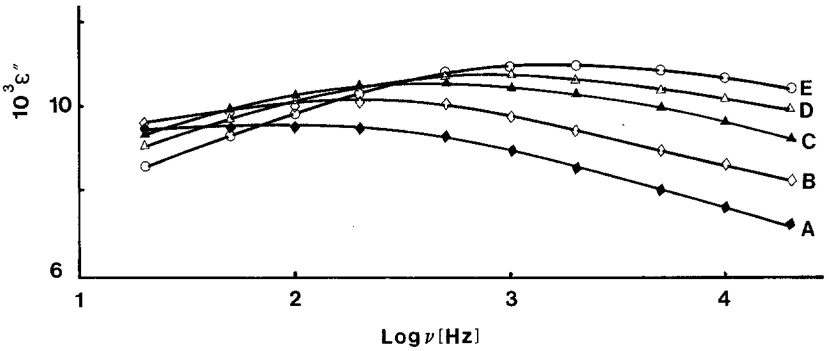


Fig. 3. Plots of dielectric loss factor, ε'', against log ν (Hz) for 1-fenchone in carbon tetrachloride at: $A = 109.5$K, $B = 114.7$K, $C = 120.1$K, $D = 123.7$K and $E = 127.4$K

The parameters generated as a result of the analysis are as follows: ε''_{max}, the maximum loss factor of the absorption at a fixed temperature, the mean relaxation time, $\tau = 1/2\pi\nu_{max}$, at the frequency ν_{max} of maximum loss, and β, the Fuoss-Kirkwood distribution parameter, which ranges between 0 and 1, with $\beta = 1$ corresponding to a single Debye-type relaxation and $\beta = 0.1$ an extremely broad distribution of relaxation times.

When log $T\tau$ is plotted against $1/T$, then the Eyring enthalpy of activation (ΔH_E) and entropy of activation (ΔS_E) for relaxation process can be determined from the slope and intercept of the line, respectively (Fig. 5). The Eyring parameters together with their 95 percent confidence limits for the molecules shown in the formula scheme are presented in Table 1.

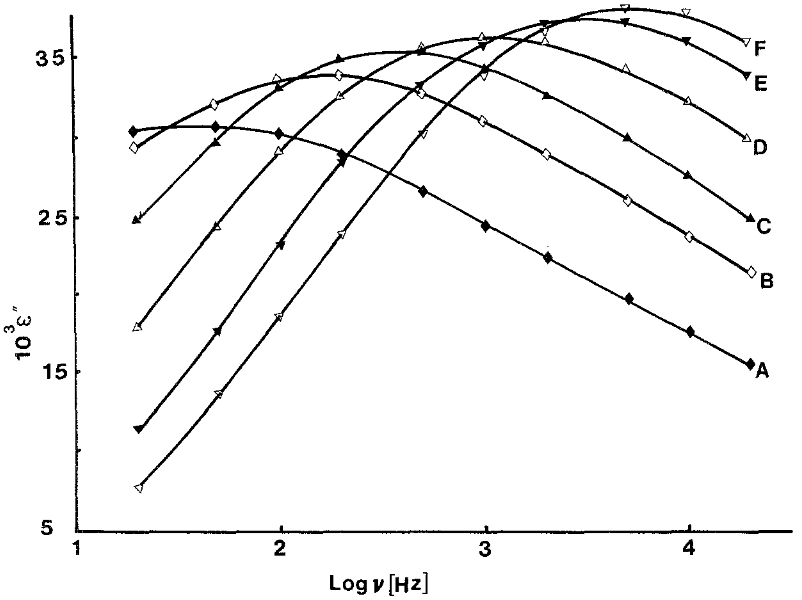


Fig. 4. Plots of dielectric loss factor, ε'', against log ν (Hz) for fenchyl alcohol in a polystyrene matrix at: $A = 126$ K, $B = 132$ K, $C = 134.5$ K, $D = 137.4$ K, $E = 140$ K and $F = 141.7$ K

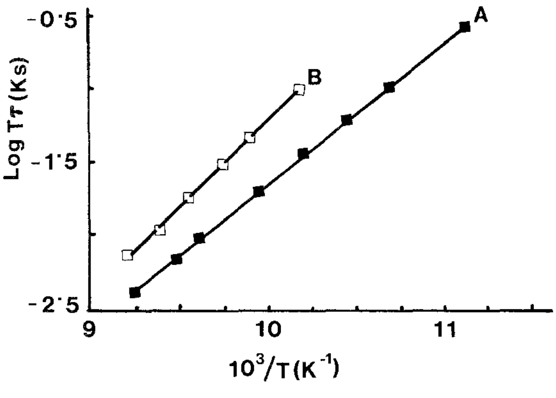
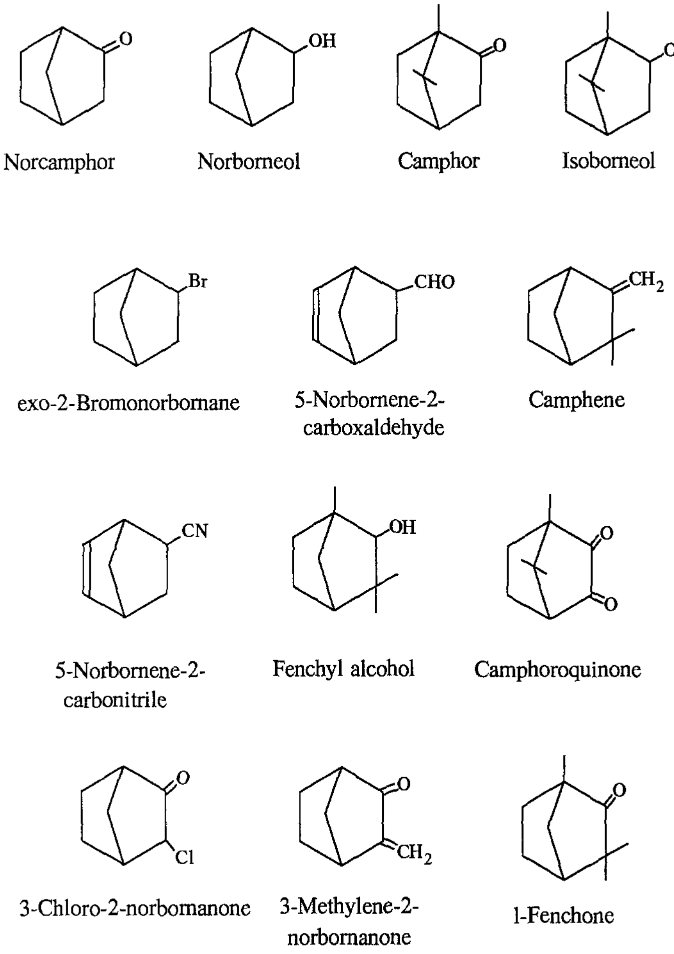


Fig. 5. Eyring plots of log $(T\tau)$ against $1/T$ for A = Camphor and B = Camphene in a polystyrene matrix

Discussion

Norcamphor has been studied in four different media viz., carbon tetrachloride, polystyrene (*PS*), glassy-*o*-terphenyl (*GOTP*) and santovac (*SV*). In each medium except CCl_4, norcamphor shows one dielectric dispersion. The β value ranges between 0.15–0.21, a typical value for molecular reorientation [1–4]. In CCl_4 the β value varies between 0.28–0.37 which seems rather high for molecular rotation. The relaxation parameters in the four media increases in the order $CCl_4 < PS < GOTP < SV$. Ahmed et al. [3] studied a number of rigid molecules in *PS*, *GOTP* and *SV* and reported that τ, ΔH_E and ΔG_E for molecular reorientation increases in the order $PS < GOTP < SV$. He explained the order for different viscosity of the dispersion media. Relaxation parameters obtained for norcamphor



Schema 1

follows the above order suggesting CCl_4 is least viscous among the four dispersion media, which is expected. Slightly high β and ΔS_E values in the latter may be accounted for by the size and shape of the dispersion medium. Both the solute and solvent being almost spherical and similar in size, at the time of rotation of norcamphor, a small range of environments is encountered at any one temperature and a little rotation would easily cause significant disorder in the system.

One dispersion region has been found for l-fenchone in the *PS* matrix and in *GOTP*. The β value ranges between 0.17–0.19. The activation parameters are comparable to those obtained for molecular reorientation of other similar sized rigid molecules (Table 1). The dielectric dispersion of the molecule in CCl_4 occurs in the temperature range 128–145 K. The β value for the dispersion ranges between 0.21–0.40, as compared to 0.10–0.28 for a normal molecular process.

The Cole-Cole plots are semicircular (not shown) and the process is insensitive to the variation of temperature. The activation parameters obtained for this process are fairly high for the molecular process. The relaxation of l-fenchone in CCl_4 seems to be reasonable to ascribe as a cooperative process. A cooperative process at such a low temperature may be reasonable owing to the similar shapes and sizes of both the solute and solvent molecules.

Seven other different rigid molecules (see formulae) have been studied in the *PS* matrix. Their β value varies between 0.13–0.22, the enthalpy of acitvation from

Table 1. Eyring analysis results for camphane derivatives in different dispersion media

Molecules	Medium	β-range	Temperature range (K)	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})	ΔG_E (kJ mol^{-1})			Relaxation time (s)		
						100 K	150 K	200 K	150 K	150 K	200 K
Norcamphor	*PS*	0.17–0.19	80–95	15 ± 1	12 ± 7	14	14	13	$1.3\cdot10^{-5}$	$1.8\cdot10^{-8}$	$6.2\cdot10^{-10}$
	GOTP	0.15–0.19	84–100	17 ± 1	16 ± 10	15	15	14	$5.4\cdot10^{-5}$	$4.0\cdot10^{-8}$	$9.8\cdot10^{-10}$
	SV	0.19–0.21	93–108	19 ± 8	25 ± 2	17	16	14	$7.7\cdot10^{-5}$	$8.0\cdot10^{-8}$	$1.3\cdot10^{-9}$
	CCl_4	0.28–0.37	82–94	13 ± 2	29 ± 20	13	12	11	$6.6\cdot10^{-6}$	$5.7\cdot10^{-9}$	$1.6\cdot10^{-10}$
Camphor	*PS*	0.19–0.22	89–108	18 ± 1	18 ± 11	17	16	15	$2.2\cdot10^{-4}$	$9.0\cdot10^{-8}$	$1.7\cdot10^{-9}$
Camphene	*PS*	0.18–0.22	95–109	21 ± 2	40 ± 20	17	15	13	$5.8\cdot10^{-4}$	$7.4\cdot10^{-8}$	$7.7\cdot10^{-10}$
5-Norbornene-2-carbonitrile	*PS*	0.13–0.18	113–138	24 ± 2	16 ± 14	22	21	21	$1.9\cdot10^{-1}$	$9.2\cdot10^{-6}$	$5.9\cdot10^{-8}$
3-Chloro-2-norbornanone	*PS*	0.16–0.18	104–122	21 ± 1	22 ± 13	19	18	17	$3.2\cdot10^{-3}$	$4.6\cdot10^{-7}$	$5.1\cdot10^{-9}$
Camphoroquinone	*PS*	0.18–0.20	103–121	20 ± 2	7 ± 15	19	19	19	$5.5\cdot10^{-3}$	$1.2\cdot10^{-6}$	$1.7\cdot10^{-8}$
exo-2-Bromo-norbornanone	*PS*	0.14–0.16	90–109	22 ± 3	47 ± 27	17	15	12	$4.0\cdot10^{-4}$	$4.4\cdot10^{-8}$	$4.2\cdot10^{-10}$
3-Methylene-2-nobornanone	*PS*	0.17–0.20	110–124	24 ± 1	36 ± 12	20	19	17	$2.0\cdot10^{-2}$	$9.3\cdot10^{-7}$	$5.8\cdot10^{-9}$
1-Fenchone	*PS*	0.17–0.19	110–126	23 ± 1	31 ± 11	20	19	17	$1.4\cdot10^{-2}$	$8.9\cdot10^{-7}$	$6.5\cdot10^{-9}$
	GOTP	0.17–0.19	117–135	20 ± 1	−7 ± 10	21	21	21	$3.3\cdot10^{-2}$	$7.0\cdot10^{-6}$	$9.4\cdot10^{-8}$
	CCl_4	0.21–0.40	128–145	54 ± 1	228 ± 20	31	20	8	$6.8\cdot10^{3}$	$2.2\cdot10^{-6}$	$3.5\cdot10^{-11}$
5-Norbornene-2-carboxaldehyde	*PS*	0.17–0.19	91–106	18 ± 1	20 ± 14	16	15	14	$1.5\cdot10^{-4}$	$6.7\cdot10^{-8}$	$1.3\cdot10^{-9}$
Norborneol	*PS*	0.16–0.18	80–98	15 ± 1	7 ± 13	15	14	14	$1.7\cdot10^{-5}$	$2.7\cdot10^{-8}$	$9.6\cdot10^{-10}$
	CCl_4	0.16–0.19	80–90	13 ± 2	36 ± 18	14	12	10	$6.8\cdot10^{-6}$	$4.5\cdot10^{-9}$	$1.0\cdot10^{-10}$
	GOTP	0.16–0.18	85–99	17 ± 1	22 ± 10	16	14	13	$7.3\cdot10^{-5}$	$2.3\cdot10^{-7}$	$1.2\cdot10^{-8}$
		0.12–0.23	144–166	30 ± 3	31 ± 17	27	26	26	$9.4\cdot10^{1}$	$3.2\cdot10^{-4}$	$5.3\cdot10^{-7}$
Isoborneol	*PS*	0.17–0.19	87–109	18 ± 1	10 ± 12	17	16	16	$2.2\cdot10^{-4}$	$1.3\cdot10^{-7}$	$2.9\cdot10^{-9}$
Fenchylalcohol	*PS*	0.14–0.15	114–127	29 ± 35	29 ± 35	21	20	18	$4.6\cdot10^{-2}$	$2.1\cdot10^{-6}$	$1.3\cdot10^{-8}$

18–24 kJ mol^{-1} and the activation free energy at 100 K between 14–22 kJ mol^{-1}. The low values of the distribution parameter of these rigid dipole molecular motions in the *PS* matrices agree well with the observations made by other workers for a series of rigid molecules in *PS*, *GOTP* and *SV* [1–5]. A slight variation in the activation parameters for molecular rotation can be accounted for by the fact that the volume swept out during relaxation by different camphane derivatives is slightly different due to different dipolar unit and their inclination to the principal axis.

5-Norbornene-2-carboxaldehyde with a flexible aldehyde group (−CHO) exhibits only one relaxation process in a polystyrene matrix. The β value for this dispersion ranges between 0.17–0.19 and the activation parameters are very close to those observed for the molecular rotation of camphor, an almost similar sized rigid molecule. The relaxation process for this flexible molecule seems to be reasonable to ascribe as due to the whole molecule rotation. The intramolecular dispersion due to the −CHO group rotation most probably lies below the liquid nitrogen temperature at the frequency range of this study. Low β value for this dispersion supports the molecular nature of the relaxation process.

Only one relaxation region was observed for each of the three alcohols norborneol, isoborneol and fenchyl alcohol in a *PS* matrix and also norborneol in CCl_4 in the usual concentration range less than five percent. The Fuoss-Kirkwood distribution parameter β for these dispersions ranges between 0.14–0.19. Such a low value of β indicates a wide distribution of relaxation times and is typical for molecular rotation of rigid molecules in various glass-forming media [1–4]. The relaxation parameters for these molecules are very close to those obtained for molecular rotation of the corresponding rigid molecules norcamphor, comphor and 1-fenchone (Table 1). Thus the dispersion of these three alcohols in *PS* and CCl_4 can be assigned as due to the molecular motion of the alcohol. No indication of intermolecular hydrogen bondig was observed in these systems in the concentration range below five percent. This result is consistent with the one obtained for long-chain aliphatic alcohols and thiols in a polystyrene matrix [18].

Two separate dispersion regions were exhibited by a higher concentration (8 percent by weight) norborneol in *GOTP* (Fig. 2). The β value for the low temperature dispersion ranges between 0.16–0.18. Within experimental error, the relaxation parameters for the process are very close to those obtained for molecular reorientation of the similar sized rigid molecule norcamphor in *GOTP* (Table 1). Relatively high enthalpy of activation (17 kJ mol^{-1}) cannot be accounted for by −OH group rotation. Reported enthalpy of activation for −OH group rotation in a 2,4,6-tri-*t*-butyl phenol in the pure solid state, where there is a significant contribution of conjugation and steric effects is 9.2 kJ mol^{-1} [21]. These results appear to suggest that the low temperature process obtained for norborneol in *GOTP* is due to the molecular rotation of the free monomeric unit. The low β value favors the molecular nature of the dielectric dispersion.

The high temperature relaxation of norborneol in *GOTP* yields the following activation parameters: $\Delta H_E = 30\,\mathrm{kJ\,mol^{-1}}$, $\Delta S_E = 31\,\mathrm{JK^{-1}mol^{-1}}$, $\Delta G_E = 27\,\mathrm{kJ\,mol^{-1}}$ and $\tau = 9.4 \cdot 10^1$ s at 100 K. The observed activation parameters for this molecule do not appear to correspond to its size, as might be expected for simple molecular rotation. The enthalpies of activation for molecular rotation of two similar sized molecules, 2-naphthol and 2-chloronaphthalene in a *PS* matrix are 52 and 32 kJ mol^{-1} [22]. The higher ΔH_E value for 2-naphthol in comparison to the latter is explained as being due to intermolecular hydrogen-bonding in the former. Clemett and Davies [6] interpreted higher ΔH_E value ($23\,\mathrm{kJ\,mol^{-1}}$) for molecular rotation of isoborneol, as compared to the similar sized rigid molecule bornyl chloride ($10.5\,\mathrm{kJ\,mol^{-1}}$) in the pure solid state as being due to intermolecular hydrogen-bonding. An approximate intermolecular hydrogen-bond strength in alcohols is reported to be $13\,\mathrm{kJ\,mol^{-1}}$ [18, 19]. If this is taken into account then $30\,\mathrm{kJ\,mol^{-1}}$ energy barrier for molecular rotation of norborneol is understandable as $13\,\mathrm{kJ\,mol^{-1}}$ energy is spent for breaking one hydrogen-bond and the remaining $17\,\mathrm{kJ\,mol^{-1}}$ for molecular rotation of the monomer, a value obtained for molecular rotation of the similar sized rigid molecule norcamphor in *GOTP*.

Conclusion

The nine spherical rigid, one flexible aldehyde and the three alcohol molecules of camphane derivatives do not have appreciable differences in their size and shape. The only variation is in the nature of the polar group. This is evident from the slight variations in their relaxation parameters (Table 1). In systems of similar character, there has frequently been a correlation between the activation enthalpies and entropies as has been found by many workers [2–5, 23]. This correlation does not hold here. The linear $\Delta H_E - \Delta S_E$ relationship is reasonable for any series of molecules when the shape as well as the inclination of the dipole to the principal axis is quite similar [4].

The results obtained for the camphane derivatives are in reasonable agreement with the previous report that the activation enthalpy increases with decrease of temperature [5, 6]. The observed activation enthalpies are appreciably higher than those reported by Davies et al. [5]. This discrepancy may be accounted for by the fact that this work was performed at much lower temperatures (liquid nitrogen) where the matrix has contracted and the molecular interactions between the solute and the dispersion medium becomes significant. Similar relaxation parameters in different dispersion media supports the view of increasing degree of molecular interactions with decreasing temperature.

One of the three alcohols in *GOTP* at high concentration has shown a dispersion due to the presence of intermolecularly hydrogen-bonded species. Similarities between the relaxation parameters at low concentration for these alcohols and the corresponding rigid molecules suggest that the relaxation process at low (less than 5 percent) concentrations is simply due to molecular rotation. In general, for a given alcohol, the H-bonded equilibria are concentration and medium dependent, as indicated previously [19, 24, 25] and this influences the rate process(es) detected by dielectric absorption studies. This study of small spherical alcohols confirms the view that the formation of hydrogen-bonded species and their relaxation are concentration as well as medium dependent. This was also observed earlier in some studies on simple alcohols in glassy media [19].

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