

Effect of Dipole Position on Relaxation Parameters*

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Abstract. Dielectric absorption studies have been made on numerous monobromoalkanes and two α,ω -dibromoalkanes dispersed in polystyrene and polypropylene matrices in the frequency range 10–10⁵ Hz between 80–285 K. All compounds exhibited two clear cut dispersion regions in polystyrene except 3-bromopentane, 4-bromoheptane and 4-bromooctane. Nevertheless, when these three solute molecules are dispersed in polypropylene, they then show two dispersion regions. The low temperature process (LT) has been attributed to —CH₂Br group rotation about the C—C bonds and the high temperature (HT) process to molecular rotation. In the case of α,ω -dibromoalkanes, both —CH₂Br groups contribute to the low temperature absorption. For a bromoalkane of a given chain length the relaxation time alters with variation of the main dipole position from the terminal carbon atom to the middle of the chain for the low temperature absorption; this is related to the change in the size of the reorientating unit containing the —CH₂Br group. The effect of the same variation of the dipole position on the high temperature absorption is that the relaxation time decreases which is attributed to the decrease in volume swept out on molecular rotation. The ratio, $\varepsilon''_{(\max)LT}/\varepsilon''_{(\max)HT}$, increases with the variation of the dipole from the terminal to the middle of the chain.

Key words. Dielectric absorption, dispersion regions, dipole, bromoalkane.

1. Introduction

Anderson and Smyth [1] have studied the dielectric absorption of three isomeric dibromobutanes and α,ω -dibromopentanes as pure liquids. They found that the Cole–Cole distribution parameter, α , was almost zero and the mean relaxation time, τ_0 , for the three isomeric dibromobutanes was identical. However, since the mean relaxation time of 1,4-dibromopentane is somewhat longer than that of 1,4-dibromobutane, they suggested that the dielectric absorptions in these molecules could be attributed to the rotation of the whole molecule. There was also no indication of a second process.

Chandra and Prakash [2] carried out dielectric measurements on a number of α,ω -dibromoalkanes as pure liquids. Their data could be adequately represented by Cole–Davidson skewed arc plots. In addition, they were able to analyze their data

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in terms of a superposition of two noninteracting Debye type relaxations. The longer relaxation time, τ_1 , increases with chain length, which suggests that this corresponds to end-over-end rotation of the molecule as a whole. The shorter relaxation time, τ_2 , was independent of the chain length and was ascribed to terminal $-\text{CH}_2\text{Br}$ rotation about the C—C bond.

Tay and Crossley [3] dielectrically examined 1-, 2- and 4-bromo-octanes and 1,10-dibromodecane in dilute cyclohexane solution. Their results could be described adequately by a Cole—Cole symmetrical distribution function, but they were unable to obtain any sensible analyses of the data in terms of two discrete relaxation times. The location of the dipole did not influence these results for the bromooctanes while the relaxation times for 1,10-dibromodecane and 1-bromodecane were almost identical. The absorption in these molecules was interpreted in terms of a relaxation process which involves a variety of segmental motions including relaxation of the $-\text{CH}_2\text{Br}$ group.

Although the long chain polar compound having the dipole at the end of the hydrocarbon chain has been extensively studied, there have been relatively few studies on the variation of the dipole position along the hydrocarbon chain. It therefore, seemed worthwhile to carry out a systematic dielectric study of the variation of the dipole position along the hydrocarbon chain, in a matrix with a view to separating the intramolecular process from the molecular one. It was also considered that the variation of the dipole along the hydrocarbon chain and the introduction of a second dipole at the end of the chain might produce some alteration in the dielectric behaviour which could facilitate understanding of the relaxation mechanisms in long chain bromides.

2. Experimental

1-, 2-, 3- and 4-bromo-octanes, 1- and 3-bromopentanes, 1- and 4-bromoheptanes, 1,6-dibromohexane and 1,10-dibromodecane were examined in a polystyrene matrix and 4-bromo-octane and 4-bromoheptane in a polypropylene one. The apparatus and the experimental techniques employed in the preparation and measurements of polystyrene and polypropylene disks containing solute (at concentration of less than 8% by weight) in the $10-10^5$ Hz region were the same as described previously [4-11].

3. Results

The maximum value of the loss factor, ϵ''_{\max} , the relaxation time characterizing the dipole reorientation, $\tau = 1/2\pi \times v_{\max}$ (where v_{\max} is the frequency of maximum absorption) and the distribution parameter, β , were obtained by means of a computer program (written in APL) from a linear fit to the Fuoss—Kirkwood equation [12]:

$$\cosh^{-1}(\epsilon''_{\max}/\epsilon'') = \beta(\ln v_{\max} - \ln v).$$

The energy barriers opposing the dipole reorientation were evaluated by using the Eyring rate equation [13]:

$$\ln(T\tau) = (\Delta H_E/RT) - \Delta S_E/R + \ln(h/k)$$

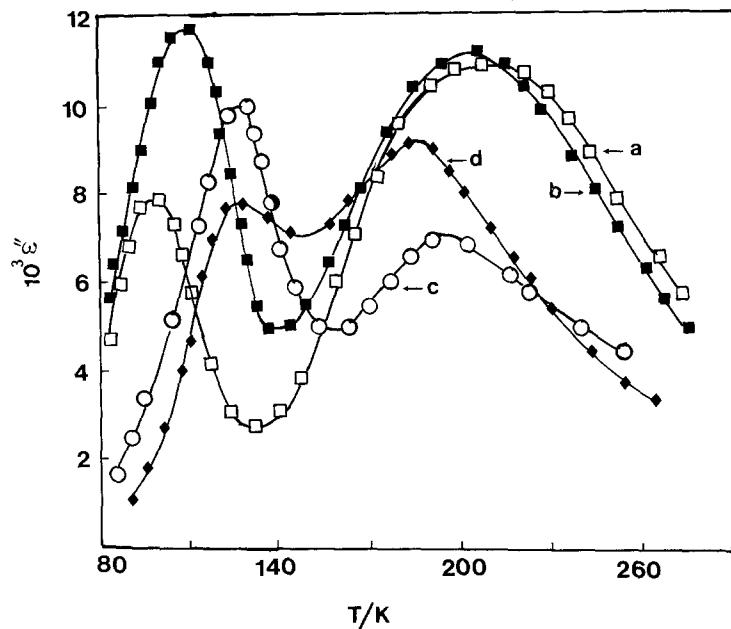
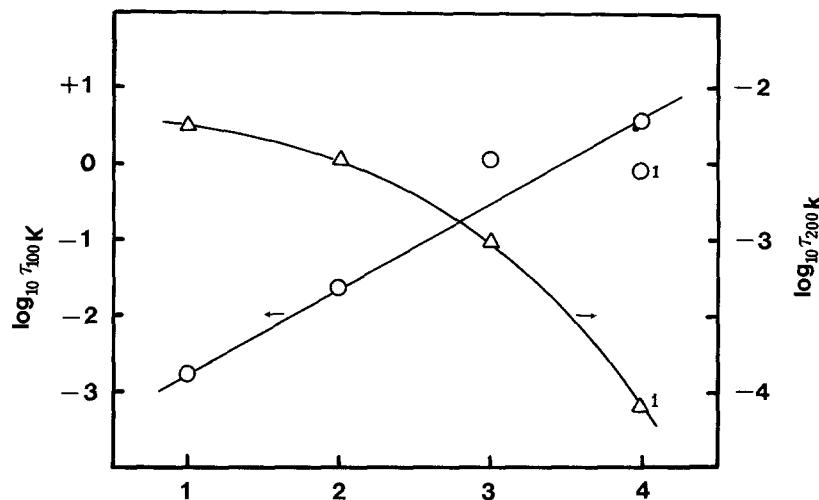


Fig. 1. Dielectric loss factor, ϵ''_{\max} versus temperature (K) at 50.2 Hz in a polystyrene matrix: (a) 1-bromoocetane (b) 2-bromoocetane (c) 3-bromoocetane and (d) 4-bromoocetane.

where the terms have their usual meaning. The enthalpies of activation, ΔH_E , and the entropies of activation, ΔS_E , were obtained from the slope and intercept, respectively, of the plot $\ln(T\tau)$ against $1/T$ by means of a computer program. The program also calculated the relaxation time, T , and the free energy of activation, ΔG_E , at different temperatures. Statistical analyses for the error estimation have been discussed in the previous publications [4-11]. Representative plots of the dielectric loss factor against temperature are given in Figures 1, 3-7, ϵ'' vs. \log (frequency) in Figure 8 and Eyring plots in Figure 9. The Eyring activation parameters are given in Tables I-IV and the loss factor maximum values in Table V.

4. Discussion

Before we discuss the present results, we shall review a few of the very basic points relating to the dielectric absorption of polar solutes dispersed in a polystyrene matrix where, at low concentrations, the solute molecule is monomolecularly dispersed amongst the polystyrene units (see later). The space in which the solute molecule resides is sometimes loosely termed a 'cavity'. However, the size of the 'cavity' is determined by both the local conformations of the polystyrene molecule(s) and the size and shape of the solute molecule itself. As Ahmed *et al.* [14] have pointed out (a) the molecular process of the trapped solute molecule may be considered to be relaxation between equilibrium positions of the dipole and (b)



Location of bromine atom along chain

Fig. 2. Log τ at (a) 200 K (high temperature absorption) and (b) 100 K (low temperature absorption) versus location of the bromine atom along the *n*-octane chain in a polystyrene matrix. Point 1 in the diagram is for the high temperature absorption of 4-bromo-octane in polypropylene.

on the time scale of the relaxation process the solvent 'cavity' does not need to alter appreciably to permit the solute molecule to relax.

Davies and Swain [15] showed that when solutes of low concentration (~5 to 10% by weight) are dissolved in a polystyrene matrix, they are in the form of a monomolecular dispersion. Later Borisova and Chirkov [16] demonstrated that the

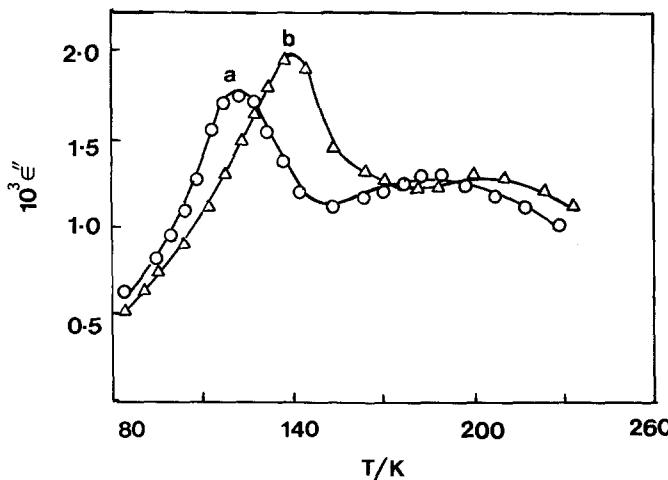


Fig. 3. Dielectric loss factor, ϵ''_{\max} versus temperature (K) for 4-bromo-octane in polypropylene: (a) 0.0502 kHz and (b) 1.01 kHz.

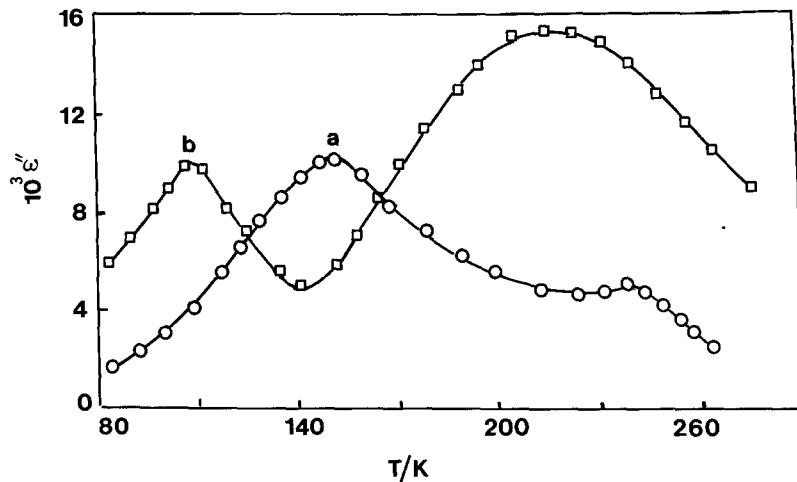


Fig. 4. Dielectric loss factor, ε''_{\max} versus temperature (K) at 1.01 kHz in a polystyrene matrix: (a) 4-bromohexane and (b) 1-bromohexane.

energy barriers for relaxation of small molecules in polystyrene matrices are independent of concentration in the range of 5–7 mol%.

Davies and Swain [15] also showed that for a rigid polar molecule at temperatures significantly less than room temperature the polystyrene matrix does not permit a complete relaxation of the dipole of the whole molecule. This is to be contrasted with the end-over-end rotation studied in the dielectric absorption of

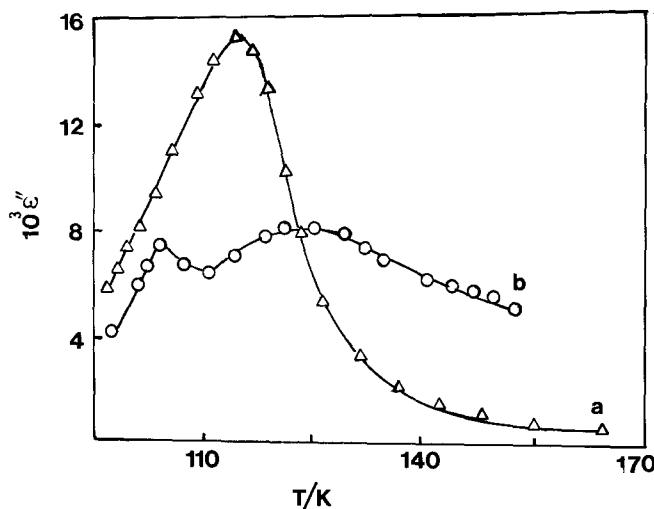


Fig. 5. Dielectric loss factor, ε''_{\max} versus temperature (K) at 50.1 Hz in a polystyrene matrix: (a) 3-bromopentane and (b) 1-bromopentane.

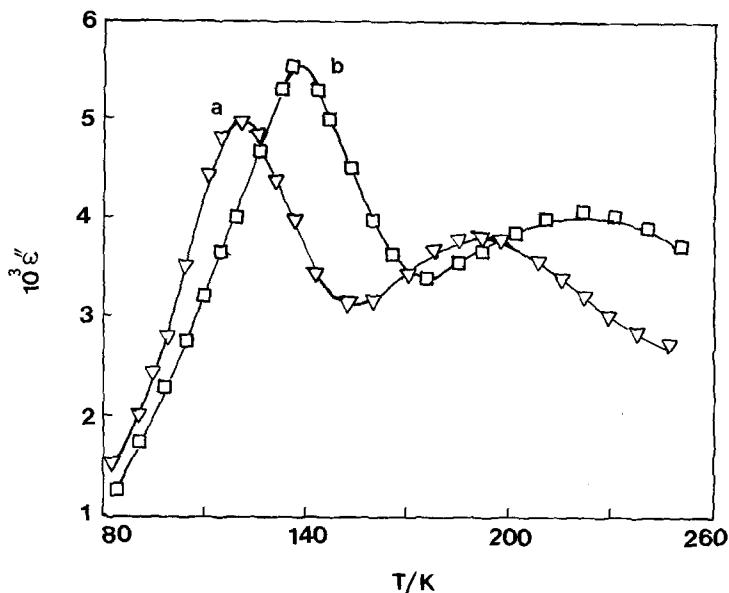


Fig. 6. Dielectric loss factor, ϵ''_{\max} versus temperature (K) for 4-bromoheptane in a polypropylene matrix: (a) 50.2 Hz and (b) 1.01 kHz.

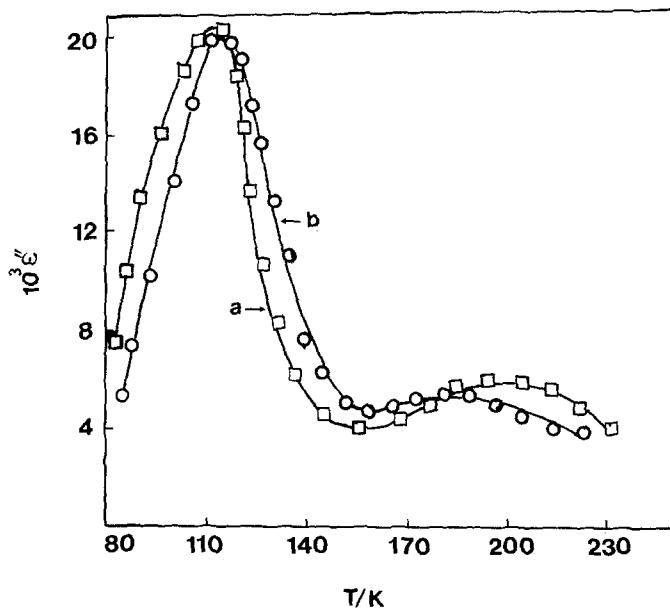


Fig. 7. Dielectric loss factor, ϵ''_{\max} versus temperature (K) at 50.2 Hz for (a) 1,10-dibromodecane and (b) 1,6-dibromohexane in polystyrene.

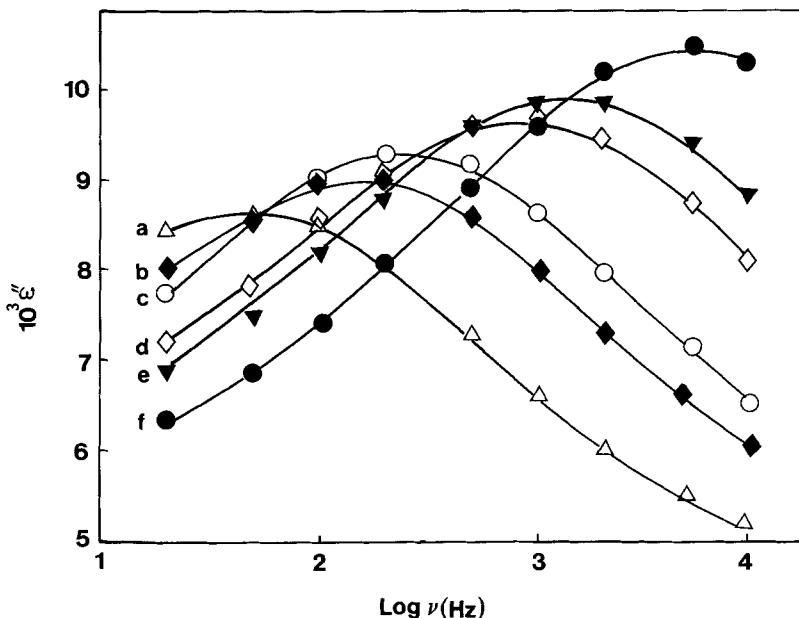


Fig. 8. Dielectric loss factor, ϵ''_{\max} versus $\log \nu$ (Hz) for the low temperature absorption of 4-bromoheptane in a polystyrene matrix: (a) 125.7 K (b) 131.6 K (c) 134.5 K (d) 141.6 K (e) 144.5 K and (f) 152.2 K.

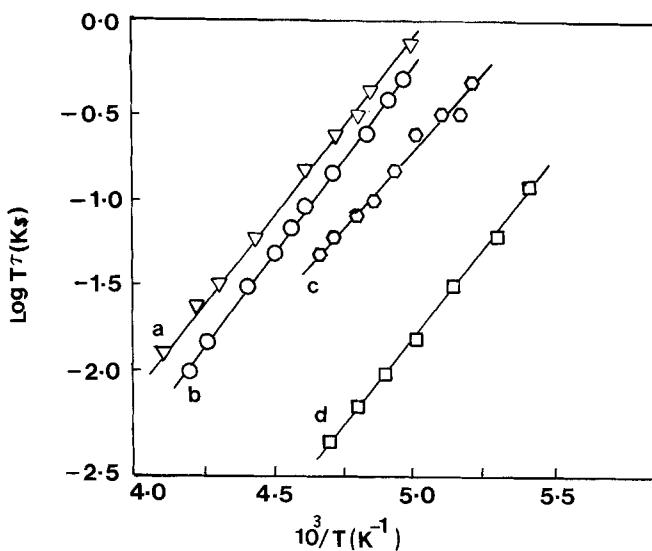


Fig. 9. Eyring rate plots of $\log T_r$ (Ks) versus $10^3/T$ (K^{-1}) for the high temperature absorption: (a) 1-bromoheptane (polystyrene) (b) 2-bromoheptane (polystyrene) (c) 3-bromoheptane (polystyrene) and (d) 4-bromoheptane (polypropylene).

Table I. Eyring parameters for the low temperature absorption of bromooctanes in a polystyrene (P.S.) or a polypropylene (P.P.) matrix

Molecule	$\Delta T/K$	Medium	β range	τ/s	ΔH_E		ΔS_E
					100 K	150 K	
1-bromooctane	98-124	P.S.	0.25-0.31	1.68×10^{-3}	6.23×10^{-7}	18.7 ± 1.3	4 ± 12
2-bromooctane	108-130	P.S.	0.17-0.21	2.48×10^{-2}	1.99×10^{-6}	22.5 ± 2.5	20 ± 22
3-bromooctane	122-152	P.S.	0.18-0.30	1.25×10^0	3.76×10^{-5}	25.0 ± 3.0	12 ± 9
4-bromooctane	127-161	P.S.	0.20-0.27	3.68×10^0	7.04×10^{-5}	26.1 ± 1.1	14 ± 8
4-bromooctane	122-142	P.P.	0.23-0.30	8.22×10^{-1}	2.52×10^{-5}	24.9 ± 1.5	15 ± 11

Table II. Eyring parameters for the high temperature absorption of bromooctanes in a polystyrene (P.S.) or a polypropylene (P.P.) matrix

Molecule	$\Delta T/K$	Medium	β range	τ/s	ΔH_E		ΔS_E
					200 K	kJ mol^{-1}	
1-bromooctane	205-249	P.S.	0.18-0.16	5.02×10^{-3}	39.3 ± 3.3	-2 ± 14	
2-bromooctane	199-238	P.S.	0.14-0.16	3.56×10^{-3}	41.5 ± 2.3	13 ± 11	
3-bromooctane	192-216	P.S.	0.12-0.16	1.01×10^{-3}	33.5 ± 3.4	-17 ± 17	
4-bromooctane	185-213	P.P.	0.18-0.27	7.89×10^{-5}	42.2 ± 3.6	48 ± 18	

Table III. Eyring activation parameters for some bromoheptanes and bromoheptanes in a polystyrene (P.S.) or a polypropylene (P.P.) matrix

Molecule	$\Delta T/K$	Medium	β range	τ/s			ΔH_E		ΔS_E	
				100 K	150 K	200 K	kJ mol ⁻¹	kJ mol ⁻¹	J K ⁻¹ mol ⁻¹	
1-bromoheptane	96-116	P.S.	0.22-0.27	1.10 \times 10 ⁻³	2.83 \times 10 ⁻⁷		19.6 \pm 1.4		17 \pm 13	
1-bromoheptane	189-213	P.S.	0.15-0.20		6.05 \times 10 ⁻⁴		35.4 \pm 2.8		-3 \pm 7	
4-bromoheptane	125-153	P.S.	0.22-0.25	2.42 \times 10 ⁰	5.38 \times 10 ⁻⁵		25.7 \pm 0.9		14 \pm 7	
4-bromoheptane	119-138	P.P.	0.25-0.29	1.15 \times 10 ⁻¹	2.45 \times 10 ⁻⁵		20.1 \pm 0.7		-17 \pm 5	
4-bromoheptane	217-238	P.P.	0.15-0.22		1.41 \times 10 ⁻²		33.5 \pm 3.8		-39 \pm 17	
1-bromopentane	95-106	P.S.	0.18-0.26	7.17 \times 10 ⁻⁴	7.28 \times 10 ⁻⁷		16.2 \pm 1.6		-14 \pm 16	
3-bromopentane	122-139	P.S.	0.27-0.32	4.25 \times 10 ⁻¹	1.14 \times 10 ⁻⁵		25.3 \pm 1.7		24 \pm 13	
1-bromopentane	142-162	P.S.	0.11-0.15	8.50 \times 10 ⁰	4.38 \times 10 ⁻⁴		23.6 \pm 1.8		-18 \pm 12	

Table IV. Comparison of Eyring activation parameters for 1-bromoalkanes and α,ω -dibromoalkanes in a polystyrene matrix

Molecule	$\Delta T/K$	β range	τ/s	ΔH_E			ΔS_E	
				100 K	150 K	200 K	kJ mol ⁻¹	kJ mol ⁻¹
1,6-dibromohexane	104-107	0.25-0.32	9.69 \times 10 ⁻³	1.23 \times 10 ⁻⁶		1.53 \times 10 ⁻²	21.4 \pm 0.6	16 \pm 5
1,6-dibromohexane	223-244	0.10-0.16					32.1 \pm 4.6	-46 \pm 20
1-bromohexane	95-117	0.18-0.23	3.66 \times 10 ⁻⁴	1.00 \times 10 ⁻⁷		6.60 \times 10 ⁻⁵	19.5 \pm 1.0	24 \pm 10
1-bromohexane	168-204	0.16-0.17					31.5 \pm 2.0	-4 \pm 11
1,10-dibromodecane	113-138	0.24-0.32	1.18 \times 10 ⁻¹	4.33 \times 10 ⁻⁶			24.5 \pm 0.4	27 \pm 3
1,10-dibromodecane								
decane	244-268	0.20-0.24			3.16 \times 10 ⁻¹		46.4 \pm 3.8	0 \pm 15
1-bromodecane	106-130	0.26-0.32	1.15 \times 10 ⁻²	1.13 \times 10 ⁻⁶			22.0 \pm 0.6	21 \pm 5
1-bromodecane	220-260	0.16-0.19			4.14 \times 10 ⁻²		46.9 \pm 4.5	19 \pm 19

Table V. Maximum loss factors for some molecules in a polystyrene or a polypropylene matrix at 50.2 Hz

Molecule	$\varepsilon''_{\max(\text{LT})}$	$\varepsilon''_{\max(\text{HT})}$	$\varepsilon''_{\max(\text{LT})}/\varepsilon''_{\max(\text{HT})}$
1-bromooctane	7.9×10^{-3}	11.0×10^{-3}	0.72
2-bromooctane	12.0×10^{-3}	11.0×10^{-3}	1.09
3-bromooctane	10.0×10^{-3}	7.0×10^{-3}	1.43
4-bromooctane	8.0×10^{-3}	9.2×10^{-3}	0.87
4-bromooctane (P.P.)	1.8×10^{-3}	1.3×10^{-3}	1.38
1-bromoheptane	10.0×10^{-3}	15.2×10^{-3}	0.66
4-bromoheptane	10.0×10^{-3}	5.1×10^{-3}	1.96
3-bromopentane (P.P.)	5.1×10^{-3}	3.8×10^{-3}	1.34
1-bromohexane	6.3×10^{-3}	8.9×10^{-3}	0.71
1,6-dibromohexane	21.0×10^{-3}	7.0×10^{-3}	3.00
1-bromodecane	12.9×10^{-3}	10.5×10^{-3}	1.23
1,10-dibromodecane	20.0×10^{-3}	5.0×10^{-3}	4.00

pure liquids and solutions. However, when the dipole moment values for these low concentrations of solute molecules in polystyrene obtained at lower temperatures are extrapolated to 330 K, then the dipole moment obtained corresponds with that obtained by the traditional Halverstadt-Kumler technique for the same solute in an inert solvent. The concentrations employed in the Halverstadt-Kumler approach are weight fractions of solute in the 0.001 to 0.01 range where the molecules are normally in a monomolecular dispersion. Davies and Swain [15] also demonstrated that for a flexible molecule exhibiting both an intramolecular and a molecular relaxation process extrapolation of the dipole moment for the intramolecular process (μ_s) and for the molecular process (μ_m) to 330 K followed by vectorial combination through the equation:

$$\mu = (\mu_m^2 + \mu_s^2)^{1/2} \quad (1)$$

led to the same dipole moment as that found by the Halverstadt-Kumler technique. The approach employing Equation (1) was recently applied by Ahmed and Walker [9] to the long chain 1-bromoalkanes:



where $n = 4, 5, 6, 8, 10, 12, 14, 16, 18$ and 20 and yielded dipole moments within $0.1(5)\text{D}$ of the dipole moment of a typical 1-alkylbromide in an inert solvent as determined by the Halverstadt-Kumler method. Thus, it follows for these alkylbromides that the molecules are monomolecularly dispersed in the polystyrene matrix and that the full components of the dipole moments, μ_m and μ_s , are exerted at 330 K. Hence, for example, the molecular process is not just limited to molecular reorientation about the long axis.

On consideration of our results given in Figure 3, it is apparent that for the isomeric octane bromides two absorption peaks appear when the dielectric loss factor ε'' is plotted against temperature at a fixed frequency. It is interesting to note that the low temperature absorption peaks, $\varepsilon''_{\max(\text{LT})}$ shift to the higher temperature

region whereas the higher temperature absorption peaks, $\varepsilon''_{(\max)HT}$, shift towards the low temperature region as the bromine atom is moved to a higher carbon number along the *n*-octane chain. Figure 2 shows that the relaxation time, $\tau_{100\text{ K}}$, for the low temperature absorption lengthens as the bromine atom is moved from the terminal carbon atom along the *n*-octane chain. However, the situation is quite different for the higher temperature absorption where the relaxation time, $\tau_{200\text{ K}}$, decreases as the bromine atom is moved along the chain.

The Fuoss-Kirkwood distribution parameters, β , for the low temperature absorption lie in the range 0.17–0.31 (see Table I) at 98–161 K. The half-width $\Delta T_{1/2}$, for the low temperature absorption is very similar for all and in the range 40–50 K. Such relatively high β values at these very low temperatures and small half-width values suggest that the low temperature absorption is an intramolecular process. This is in line with our previous investigations [9, 10] on flexible long chain polar molecules. In fact, it has been established for the 1-bromoalkanes [9], 1-aminoalkanes and 2-alkanones [10] that the low temperature absorption may be attributed to the segmental rotation involving movement by the polar end group. The enthalpy of activation, ΔH_E , for the intramolecular process in the bromooctanes increases in the order 18.7, 22.5, 25.0 and 26.1 kJ mol⁻¹ when the bromine atom is moved from C-1 to C-2 to C-3 to C-4 respectively. The increase of relaxation time, $\tau_{100\text{ K}}$ (see Figure 2) and enthalpy of activation, ΔH_E , for the intramolecular process could be accounted for by (a) the size of the smallest reorientating unit responsible for the low temperature absorption increases as the bromine atom is moved along the *n*-octane chain and (b) the steric effects increase when the bromine atom is moved from the 1-position along the chain.

In the bromoalkanes [9], 1-aminoalkanes and 2-alkanones [10] the higher temperature absorption has been shown consistently to correspond with molecular rotation. The relaxation time, $\tau_{200\text{ K}}$, for the higher temperature process decreases as the bromine atom is moved along the *n*-octane chain. It has been established already that the τ values increase with the increase in chain length of the 1-bromoalkanes [9], 1-aminoalkanes and 2-alkanones [10] for the molecular rotation. It was shown by Khwaja and Walker [17], for the relaxation of rigid molecules in a polystyrene matrix, that the relaxation time increases linearly with the increase of volume swept out on molecular relaxation. As the bromine atom is moved from C-1 to C-2 to C-3 to C-4, it is likely that the rotational volume swept out decreases since the centre of gravity lies near the heavier atom. This would account for the decrease of relaxation time, $\tau_{200\text{ K}}$, for the molecular process as the bromine atom is moved along the *n*-octane chain.

To study further the overlap of the two processes, 4-bromooctane has also been examined in a polypropylene matrix. The absorption curves are shown in Figure 3. In this case the intramolecular process has been separated more completely from the molecular one. The enthalpy of activation for the low temperature absorption of 4-bromooctane in a polystyrene matrix is 26.1 kJ mol⁻¹ which is in good agreement with 24.9 kJ mol⁻¹ in a polypropylene matrix.

Two completely symmetrically substituted compounds, 4-bromoheptane and 3-bromopentane, have been studied in a polystyrene matrix in order to examine the influence of the central dipole on the relaxation parameters (Figures 4, 5). These findings show that for a particular chain length, when the bromine atom is located

at the terminal carbon atom, the intramolecular process is adequately separated from the molecular one. However, when the dipole is located at the centre of the chain, appreciable overlap of the peaks occurs. Nevertheless, when the 4-bromoheptane is examined in polypropylene, better resolution is obtained (compare Figures 4 and 6). The difference in behaviour of the 4-bromoheptane in polystyrene and polypropylene could be accounted for by the latter having a greater microscopic viscosity effect on the molecular process.

Examination of the loss factors presented in Table V reveals:

- The variation of the bromo dipole from the end towards the middle of the chain tends to increase the $\epsilon''_{(\max)LT}/\epsilon''_{(\max)HT}$ ratio when polystyrene is the dispersion medium. 4-bromo-octane in polystyrene is an exception, and this may be accounted for by the appreciable overlap in the case of molecular and intramolecular processes. However, when 4-bromo-octane is examined in polypropylene, a better separation of the two processes is achieved, and then the ratio is of the same order as that for 3-bromo-octane in polystyrene.
- It is striking that the $\epsilon''_{(\max)LT}/\epsilon''_{(\max)HT}$ value of 1-bromohexane is only 0.71 whereas for 1,6-dibromohexane the value is 3.00; similarly for 1-bromodecane and 1,10-dibromodecane the values are 1.23 and 4.00 respectively. It would seem that two $-\text{CH}_2\text{Br}$ groups in the molecule as opposed to one substantially increase the contribution from the intramolecular process.

The absorption curves for 1,6-dibromohexane and 1,10-dibromodecane are given in Figure 7. The Cole-Cole plots for the low and high temperature absorption of 1,6-dibromohexane are adequately represented by a depressed centre, semicircular arc. From previous investigations [9, 10] it is known that the enthalpy of activation for the long chain polar hydrocarbons of the type: $\text{CH}_3(\text{CH}_2)_n\text{X}$ ($\text{X} = -\text{NH}_2$, $-\text{COCH}_3$ and $-\text{CH}_2\text{Br}$) increases linearly with each $-\text{CH}_2$ unit introduced. This suggests that in these molecules the chains tend to be extended rather than curled up. In fact, however, no precise evidence is available on the conformation of chains in a matrix. The large dielectric absorption for these α,ω -dibromoalkanes in the polystyrene matrix must be attributed to the rotation of both the $-\text{CH}_2\text{Br}$ dipoles, since the ratio of the $\epsilon''_{(\max)}$ for the low temperature and high temperature processes are appreciably greater for the α,ω -dibromoalkanes than for the corresponding 1-bromoalkanes; this reflects the more appreciable contribution of the intramolecular process in the former. Moreover, the ΔH_E value and the relaxation time for the low temperature absorption of α,ω -dibromoalkanes are greater than those of the corresponding monobromoalkanes (see Table III). For example, the ΔH_E value and the relaxation time for the low temperature absorption of 1,6-dibromohexane are 21.4 kJ mol^{-1} and $97 \times 10^{-4} \text{ s}$ at 100 K respectively whereas the corresponding values for 1-bromohexane are 19.5 kJ mol^{-1} and $3.7 \times 10^{-4} \text{ s}$, respectively.

Thus, it is reasonable to attribute the low temperature absorption of α,ω -dibromoalkanes to segmental motions of the chain involving the $-\text{CH}_2\text{Br}$ groups at each end of the chain. The ΔH_E value for the high temperature absorption of 1,6-dibromohexane is 32.5 kJ mol^{-1} which is in excellent agreement with that of the 1-bromohexane. In the case of 1-bromohexane, the high temperature absorption has been ascribed to molecular rotation. Thus, the high temperature absorption of 1,6-dibromodecane behaves in a similar way to 1-bromodecane and supports this interpretation.

Altogether, the present results for α, ω -dibromoalkanes in a viscous medium bear out what was previously inferred by Garg *et al.* [18] and Chandra *et al.* [2] for the dielectric absorption in α, ω -dibromoalkanes as pure liquids. The conclusions differ, however, in that the low temperature absorption is a segmental reorientation involving rotation about the C—C bonds in the chain and consequent rotation of the $-\text{CH}_2\text{Br}$ group. Thus, the relaxation is not limited to the sole rotation of the polar end groups. In fact, the relaxation time increases significantly with the increase of chain length while the plot of dielectric loss against dielectric permittivity (Cole—Cole plot) does not show any asymmetry in either process.

The conclusions from our results are (a) in partial agreement (see Figure 7) with Tay and Crossley [3] who concluded that the dielectric relaxation in 1,10-dibromodecane is dominated by $-\text{CH}_2\text{Br}$ group rotation, (b) in substantial disagreement (see Figure 7) with Anderson *et al.* [1] who considered that the dipole reorientation in α, ω -dibromoalkanes is dominated by whole molecule rotation, and there was no indication of a second relaxation process.

In the glassy media, on the other hand, the intramolecular process has been separated completely from the molecular one and characterized by means of its Eyring parameters whereas the work in the microwave region yields a mean relaxation time resulting from the overlap of the molecular and intramolecular processes. For the 1,6-dibromohexane and 1,10-dibromodecane, it is apparent from Figure 7 that the contribution from the intramolecular process is appreciably greater than that of the molecular one. It seems likely that in liquid solutions, where the two processes overlap, the relaxation time and weight factor for the molecular process would be subject to appreciable error if a Budó analysis were carried out.

5. Conclusions

The dielectric behaviour can be summarized as follows:

- (1) The increase of relaxation time for the low temperature absorption, when the bromine atom is moved along the *n*-octane chain, could be attributed to (a) the increase in the size of the smallest reorientating unit and (b) the steric effects.
- (2) The decrease in volume swept out on molecular rotation accounts for the decrease of relaxation time at 200 K for the high temperature absorption when the bromine atom is moved along the *n*-octane chain.
- (3) The results of α, ω -dibromoalkanes bear out that (a) we are dealing with a molecular and an intramolecular process, (b) the ends of the chains rotate involving both the $-\text{CH}_2\text{Br}$ groups, and the motion also involves rotation about the C—C bonds along the chain, (c) the α, ω -dibromoalkanes and 1-bromoalkanes for a given total number of carbon atoms have virtually identical ΔH_E values for the molecular relaxation process and presumably sweep out similar volumes.

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References

1. J. E. Anderson and C. P. Smyth: *J. Phys. Chem.* **77**, 230 (1973).
2. S. Chandra and J. Prakash: *J. Chem. Phys.* **54**, 5366 (1971).
3. S. P. Tay and J. Crossley: *Can. J. Chem.* **50**, 2549 (1972).
4. C. K. McLellan and S. Walker: *Can. J. Chem.* **55**, 583 (1977).
5. A. Lakshmi, S. Walker, N. A. Weir, and J. H. Calderwood: *Adv. Mol. Interaction and Relaxation Processes* **13**, 287 (1978).
6. S. P. Tay, J. Kraft, and S. Walker: *J. Phys. Chem.* **80**, 303 (1976).
7. M. A. Mazid, J. P. Shukla, and S. Walker: *Can. J. Chem.* **56**, 1800 (1978).
8. J. Crossley, M. A. Mazid, C. K. McLellan, P. F. Mountain, and S. Walker: *Can. J. Chem.* **56**, 567 (1978).
9. M. S. Ahmed and S. Walker: *J. Chem. Soc. Faraday Trans. 2* **81**, 479 (1985).
10. M. S. Ahmed and S. Walker: *Chem. Phys.* **113**, 453 (1987).
11. M. S. Ahmed and S. Walker: *J. Chem. Soc. Faraday Trans. 2* **83**, 2183 (1988).
12. R. M. Fuoss and J. G. Kirkwood: *J. Am. Chem. Soc.* **63**, 385 (1941).
13. S. Glasstone, K. J. Laidler, and H. Eyring: *The Theory of Rate Processes*, McGraw-Hill, New York, 1941.
14. M. S. Ahmed, J. Crossley, M. S. Hossain, M. A. Kashem, M. A. Saleh, and S. Walker: *J. Chem. Phys.* **81**, 448 (1984).
15. M. Davies and J. Swain: *Trans. Faraday Soc.* **67**, 1637 (1971).
16. T. I. Borisova and V. N. Chirkov: *Russ. J. Phys. Chem.* **47**, 949 (1973).
17. H. A. Khwaja and S. Walker: *Adv. Mol. Interaction and Relaxation Processes* **19**, 1 (1981).
18. S. K. Garg, W. S. Lovell, C. J. Clemett, and C. P. Smyth: *J. Phys. Chem.* **77**, 232 (1973).