

CHAPTER 4

DIELECTRIC STUDIES OF ORTHO- AND PARA-BROMOANISOLE AND β-BROMOPHENETOLE IN THE LIQUID STATE

4.1 Introduction

In the previous chapter the relaxation mechanisms in aromatic molecules with rotatable polar groups -SH and CH_2SH were discussed. In this chapter it is proposed to discuss the results of the OCH_3 and OC_2H_5 group rotation in haloanisoles and halophenetole respectively. Relaxation studies in anisole and dimethoxy benzene in pure liquid as well as in dilute solutions were reported by various workers¹⁻⁵.

Vaughan et al.¹ and Garg and Smyth² reported that the OCH_3 group relaxation time τ_2 and its weight factor C_2 in anisole in the liquid state are about 3 p.sec at 20°C and .2 respectively. But the values of τ_2 and C_2 in anisole as well as in p-dimethoxy benzene in dilute solution reported by different workers³⁻⁵ are about 7-9 p.sec at 20°C and .7 respectively.

So it appears that the methoxy group relaxation time and its contribution C_2 in anisole or dimethoxy benzene in dilute solution are larger than their values in pure liquids. Garg and Smyth² suggested that the reduction in the weight factor C_2 for methoxy group rotation from its value in solution to the liquid state might be due to some restraint in the C-O bond, as a result the methoxy group rotation in anisole is not completely free

but hindered.

It will be interesting to study how the methoxy group rotation τ_2 and its contribution C_2 in halobenzenes in the liquid state, compare with the corresponding values in dilute solutions published in literature. The results of investigation on dielectric dispersion in o-bromobenzene, para-bromobenzene and β -bromophenol in the liquid state are presented and discussed in this chapter.

4.2 Results

The experimentally obtained values of ϵ' and ϵ'' at different microwave frequencies and at different temperatures, together with the values of static dielectric constant ϵ_0 (at 1 MHz) at different temperatures are given in Table 4.1. Cole-Cole arc plots (Fig.4.1) were drawn with the dielectric data. The high frequency dielectric constant ϵ_∞ and the distribution parameter α were obtained as usual from the arc plots. The large value of distribution parameter and the non-linear plot of $\epsilon' \text{ vs } \epsilon''/\omega$ indicated the presence of more than one relaxation process in all the liquids. The dielectric data were therefore analysed in terms of two relaxation processes by a straight forward analytical method⁶. The values of $\tau_1, \tau_2, \tau_D^2, \epsilon_\infty, \alpha$ density (d) and viscosity (η) are included in Table 4.2.

Table 4.1

Observed values of dielectric permittivity and dielectric loss

T°C	f = 1 MHz	f = 3.6 GHz		f = 9.46 GHz		f = 13.5 GHz	
	ϵ_0	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
o-Bromanisole							
30	8.96	3.91	1.62	3.63	1.41	3.27	0.97
50	8.63	4.13	1.82	3.79	1.55	3.35	1.11
70	8.36	4.20	1.91	3.96	1.76	3.42	1.23
85	8.14	4.33	2.04	4.01	1.91	3.45	1.33
p-Bromanisole							
30	7.40	3.46	1.27	3.32	1.16	2.97	0.67
50	7.12	3.47	1.53	3.35	1.43	2.93	0.89
70	6.82	3.67	1.52	3.53	1.44	3.05	0.90
85	6.56	3.73	1.62	3.63	1.64	3.04	0.93
β-Bromophenetole							
40	7.04	3.66	1.34	3.48	1.30	3.12	0.84
55	6.69	3.86	1.42	3.69	1.34	3.23	0.95
70	6.23	4.00	1.45	3.83	1.40	3.32	1.04
85	6.00	4.19	1.37	4.02	1.34	3.44	1.06

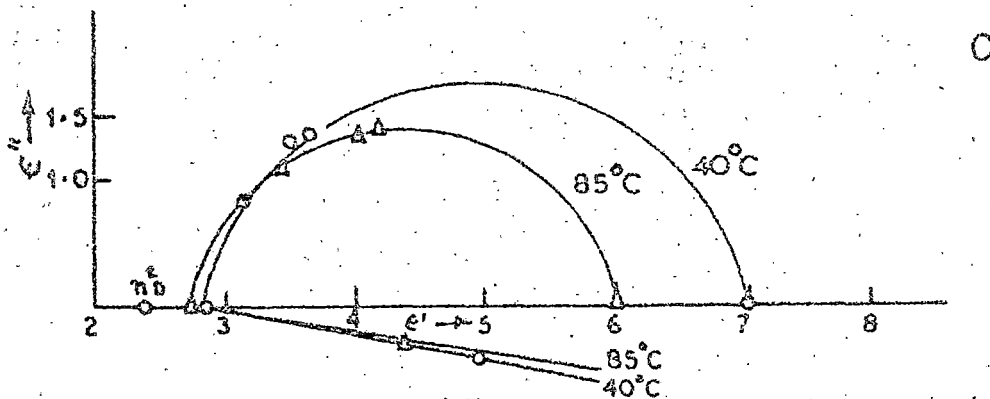
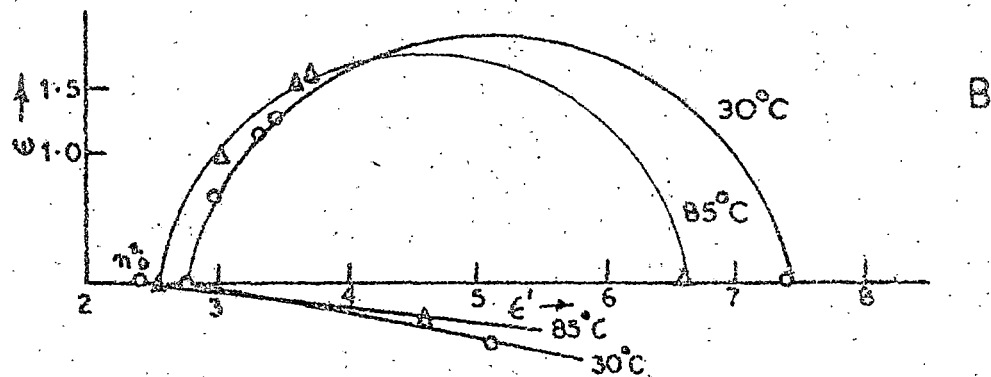
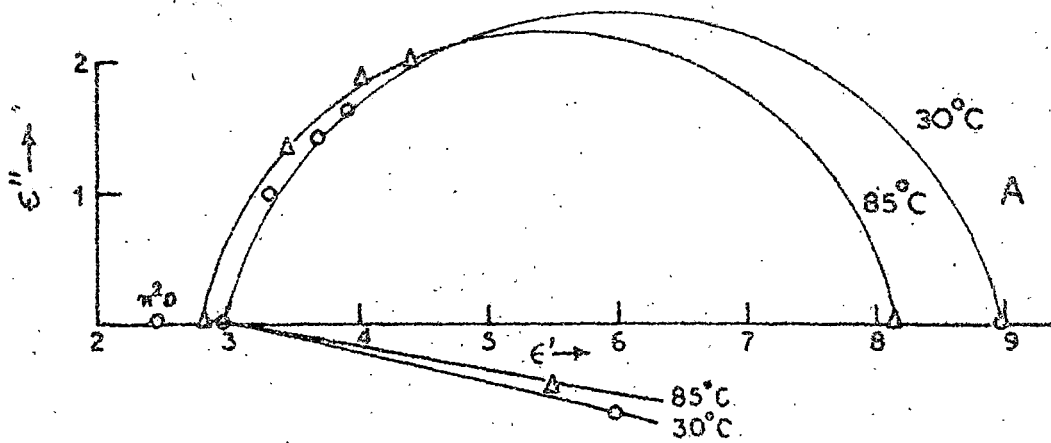


FIG 4-1

- A. Cole-Cole arc plot of ortho bromoanisole
- B. Cole-Cole arc plot of para bromoanisole
- C. Cole-Cole arc plot of β -bromophenethole

The values of activation energies for molecular orientation ΔHc_1 and group rotation ΔHc_2 and for viscous flow $\Delta H\eta$ determined as usual, from straight line plots of $\log(\tau c)$ vs $1/T$ and $\log \eta$ vs $1/T$ respectively. The values of weight factor C_1 and the dipole moment μ_D for both the liquids are given in Table 4.3 and the values of activation energies are also included in the same table. The plots of $\log(\tau c)$ vs $1/T$ and $\log \eta$ vs $1/T$ are shown in Figs.(4.2 - 4.4).

4.3 Discussion

It can be seen from Table 4.2 that the molecular and intramolecular relaxation times as also the distribution parameter α in all the liquids decrease with increase of temperature as are generally observed. The value of molecular relaxation time $\tau_1 = 49$ p.sec at 30°C in o-bromoanisole appears much larger than the value of $\tau_1 = 33.7$ p.sec at the same temperature in p-bromoanisole. But the reduced relaxation time τ_1/η of the two molecules are of the same order showing thereby that the two isomeric molecules are of similar sizes.

o-Bromoanisole

A comparison of molecular relaxation time τ_1 of o-bromoanisole and o-dimethoxy benzene both in the liquid state, shows that the molecular relaxation time $\tau_1 = 49$ p.sec at 30°C

in the former molecule obtained in the present investigations is almost the same as that of 48.5 p.sec at 25°C in the latter reported by Vaughan et al.¹ This is consistent with the sizes of the two molecules.

The contribution of ~~one~~ methoxy group rotation C_2 in ortho bromoanisole in the liquid state is only about .37 as against the value 0.7 in the case of o-dimethoxy benzene in the liquid state. The former molecule having C-Br bond moment of about 1.55 D as against -O-CH₃ bond moment of 1.3 D in the latter molecule has total moment larger than the latter molecule. So the ratio of the group moment component to the total moment which is the measure of C_2 is expected to be larger in the latter molecule. The contribution of methoxy group rotation in o-bromoanisole can be calculated from the consideration of total moment and the methoxy group moment of the molecule. The O-CH₃ bond has a moment of about 1.3 D making an angle 55° with the direction of the C-O bond in the benzene ring. The component of the O-CH₃ bond moment perpendicular to the direction of C-O bond, which is responsible for methoxy group rotation is

$$\mu_2 = 1.3 \sin 55^\circ = 1.06 \text{ D.}$$

and the total moment of the molecule μ can be obtained by the vector sum of C-Br bond moment and the component of O-CH₃ bond moment along the C-O axis and is given by

$$\mu^2 = (1.55)^2 + (1.3 \cos 55^\circ)^2 + 2 \times 1.55 \times 1.3 \cos 55^\circ \cos 60^\circ$$

or $\mu = 1.99 \text{ D.}$

This value of 1.99 D agrees fairly well with the experimentally obtained value of 2.15 D.

Now,
$$C_2 = \frac{\mu_2^2}{\mu^2} = .30$$

So, theoretically calculated value of $C_2 = 0.30$ compares reasonably well with the experimentally obtained value of $C_2 = .37$.

p-Bromoisole

The value of molecular relaxation time $\tau_1 = 33.7$ p.sec and the group relaxation time $\tau_2 = 7.3$ p.sec at 50°C as also the contribution from methoxy group rotation $C_2 = .15$ obtained in the liquid p-bromoisole agree fairly well with the values of $\tau_1 = 31$ p.sec, $\tau_2 = 7$ p.sec at 25°C and $C_2 = 0.2$ in para bromoisole in dilute solution of p-xylene reported by Farmer and Walker⁵. The similarity of dielectric behaviour of p-bromoisole in pure liquid and dilute solution suggests that the dipole-dipole interaction is not very effective in the liquid state of the molecule.

Comparison of the relaxation time of methoxy group rotation in pure liquid and dilute solution

The relaxation time of methoxy group rotation in ortho-bromo and para bromoisoles in the liquid state obtained in the present investigations are of the same order of methoxy group rotation (7 - 9 p.sec) in anisole and substituted anisole in dilute solutions reported by Farmer and Walker⁴ and Klages

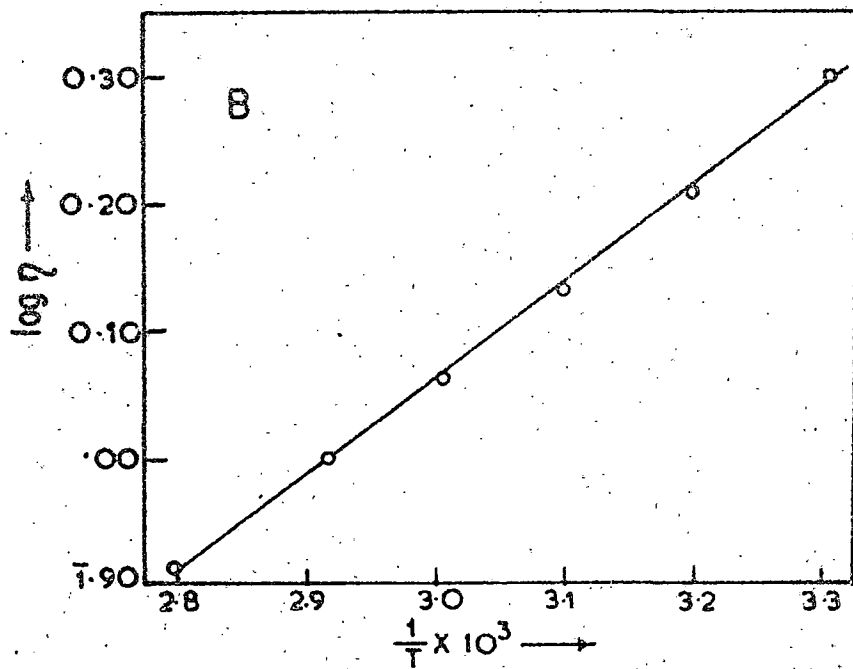
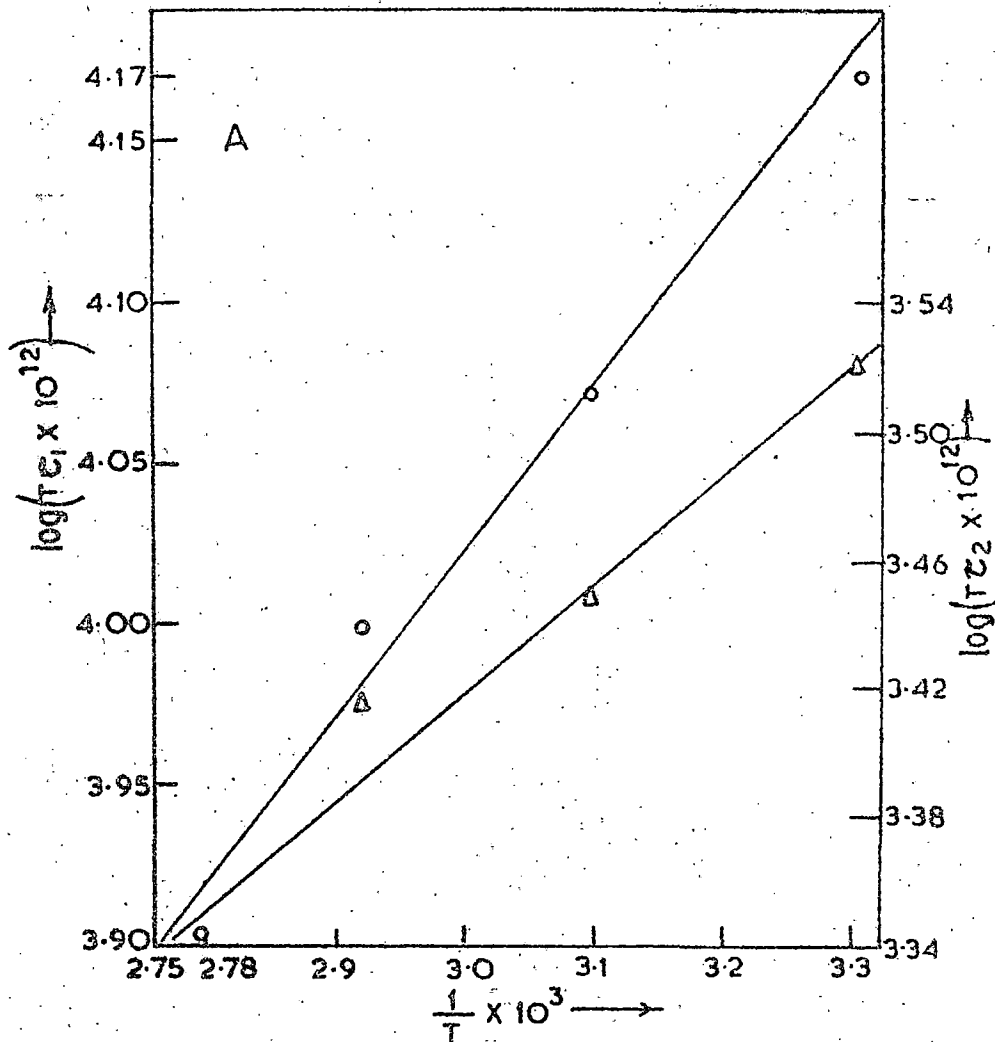


FIG. 4.2

- A. I. Plot of log (τc₁) vs. 1/T of ortho bromoanisole
 II. Plot of log (τc₂) vs. 1/T of ortho bromoanisole
 B. Plot of log η vs. 1/T of ortho bromoanisole

Table 4.2

Values of ϵ_α , n_D^2 , α , τ_1 , τ_2 density (d) and viscosity (η)

TOC	ϵ_α	α	$\tau_1 \times 10^{12}$ sec	$\tau_2 \times 10^{12}$ sec	n_D^2	d gm/cc	η c.P
o-bromoanisole							
30	2.94	.18	48.9	10.9	2.46	1.50	2.00
50	2.88	.16	37.2	8.7	2.43	1.48	1.35
70	2.84	.14	28.7	7.7	2.40	1.46	1.00
85	2.80	.06	22.6	6.2	2.37	1.43	0.84
p-bromoanisole							
30	2.76	.10	33.7	7.3	2.43	1.48	1.50
50	2.68	.09	24.9	5.6	2.40	1.46	1.15
70	2.64	.08	23.5	4.2	2.37	1.44	0.91
85	2.56	.08	19.2	3.2	2.35	1.42	0.77
β-bromophenstole							
40	2.82	.13	33.0	9.8	2.39	1.41	2.42
55	2.81	.12	28.5	8.5	2.37	1.39	1.73
70	2.77	.11	22.8	7.1	2.35	1.37	1.33
85	2.74	.11	20.6	5.6	2.32	1.36	1.00

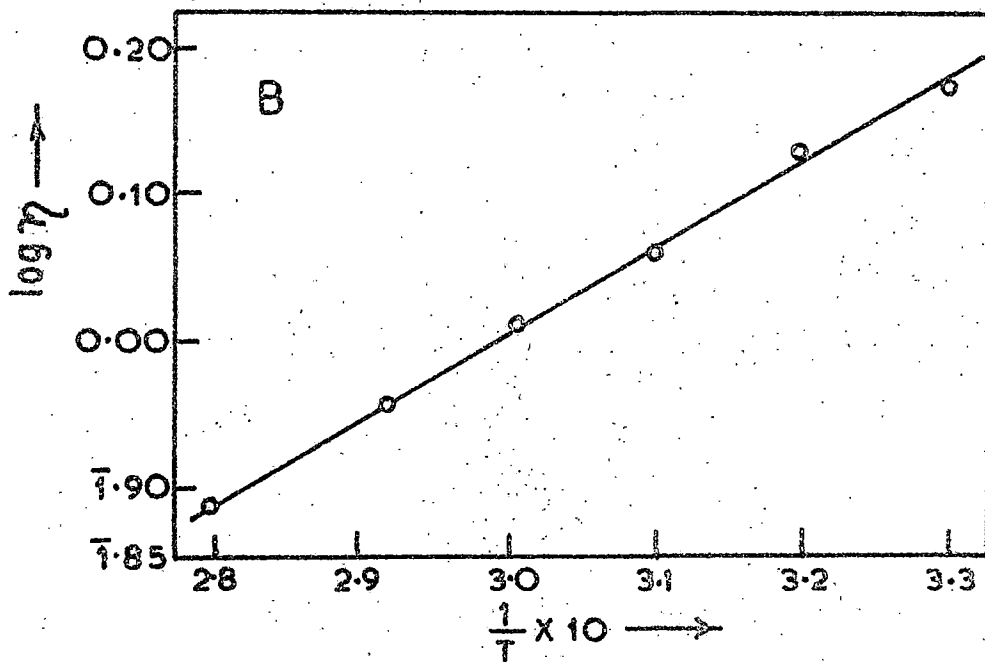
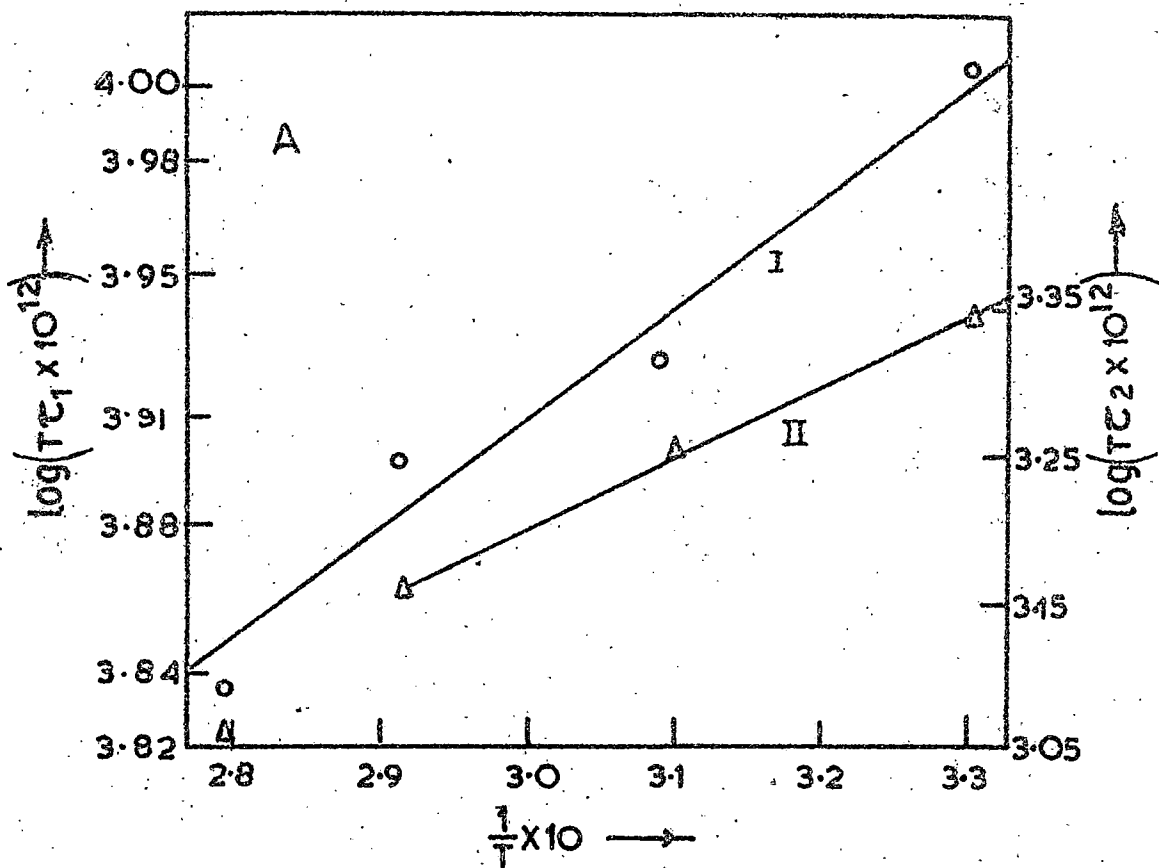


FIG. 4.3

- A. I. Plot of $\log(\tau c_1)$ vs. $1/T$ for para bromoanisole
 II. Plot of $\log(\tau c_2)$ vs. $1/T$ for para bromoanisole
 B. Plot of $\log \eta$ vs. $1/T$ for para bromoanisole

and Krauss⁵ but larger than the value of the methoxy group rotation (3 p.sec) in anisole and dimethoxy benzene in the liquid state reported by Vaughan et al.¹ and Garg and Smyth².

The larger value of methoxy group rotation of anisole in benzene or p-xylene solution than in the pure liquid may be due to the formation of a weak bond between the π -electron of the solvent molecule and hydrogen atom of the methoxy group. Similar bond formation in 1,2-dichloroethane and benzene has been reported by Chitoku and Higasi⁷.

β -bromophenetole

The reduced molecular relaxation time $\tau_{1/2}$ of β -bromophenetole at 40°C is about 14 p.sec which is smaller than the value of $\tau_{1/2} = 23$ p.sec at 30°C in bromoanisoles. Thus the β -bromophenetole molecule appears to be little bit smaller than the molecule of bromoanisoles.

The group relaxation time $\tau_2 = 9.8$ p.sec at 49°C in this case is larger than the methoxy group rotation in anisole in dilute solution or haloanisoles in liquid state. This value of $\tau_2 = 9.8$ p.sec at 40°C is also larger than the relaxation time of ethoxy group rotation $\tau_2 = 4$ p.sec at 40°C in the liquid state reported by Bhattacharyya et al.⁶ which is consistent with their sizes.

The contribution of group rotation C_2 here is only 0.32 as against the value of $C_2 = 0.63$ in ethoxy group rotation in phenetole. The substitution of Br-atom in the ethoxy group might increase hindrance and thus reduces the value of C_2 in the present case.

Table 4.3

Values of C_1 , $\Delta H\eta$, ΔHc_1 , ΔHc_2 and dipole moment (μ)

	C_1	ΔHc_1 Kcal/mole	ΔHc_2 Kcal/mole	$\Delta H\eta$ Kcal/mole	
o-Bromoanisole	0.68	2.28	2.22	3.45	2.15
p-Bromoanisole	0.35	2.02	2.72	2.70	1.98
m-Bromophenetole	0.65	2.01	2.16	3.54	2.02

Potential barriers to molecular and intramolecular rotation and viscous flow (ΔHc_1 , ΔHc_2 , $\Delta H\eta$)

The potential barriers for molecular orientation ΔHc_1 in all the liquids are of the same order (2.1 Kcal/mole) and each is smaller than the corresponding energy barrier $\Delta H\eta$ for viscous flow as usually observed in other polar liquids.

The energy barrier for molecular orientation $\Delta Hc_1 = 2.1$ Kcal/mole in p-bromoanisole in the liquid state obtained in the present investigation is about the same as the value of $\Delta Hc_1 = 2.07$ Kcal/mole obtained for p-bromoanisole in dilute solution, calculated from

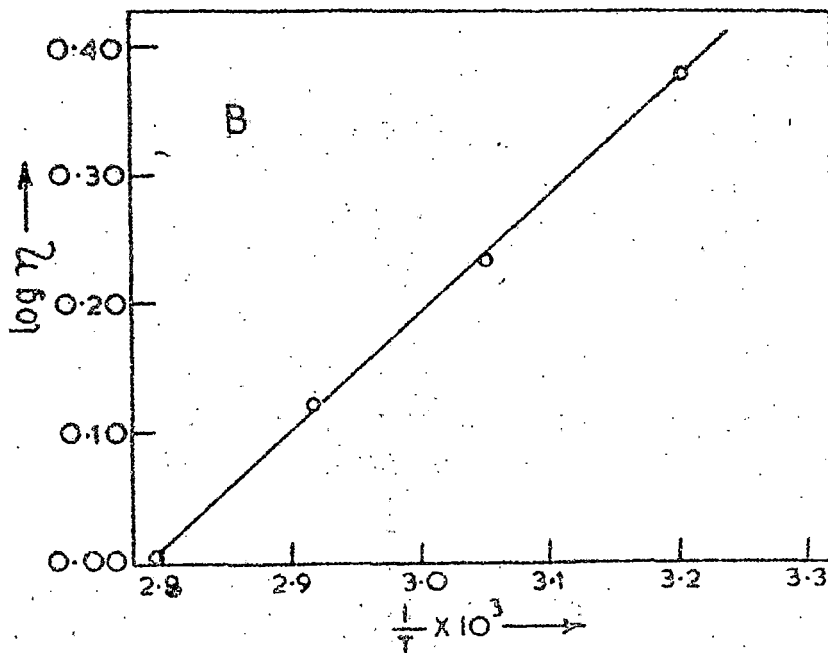
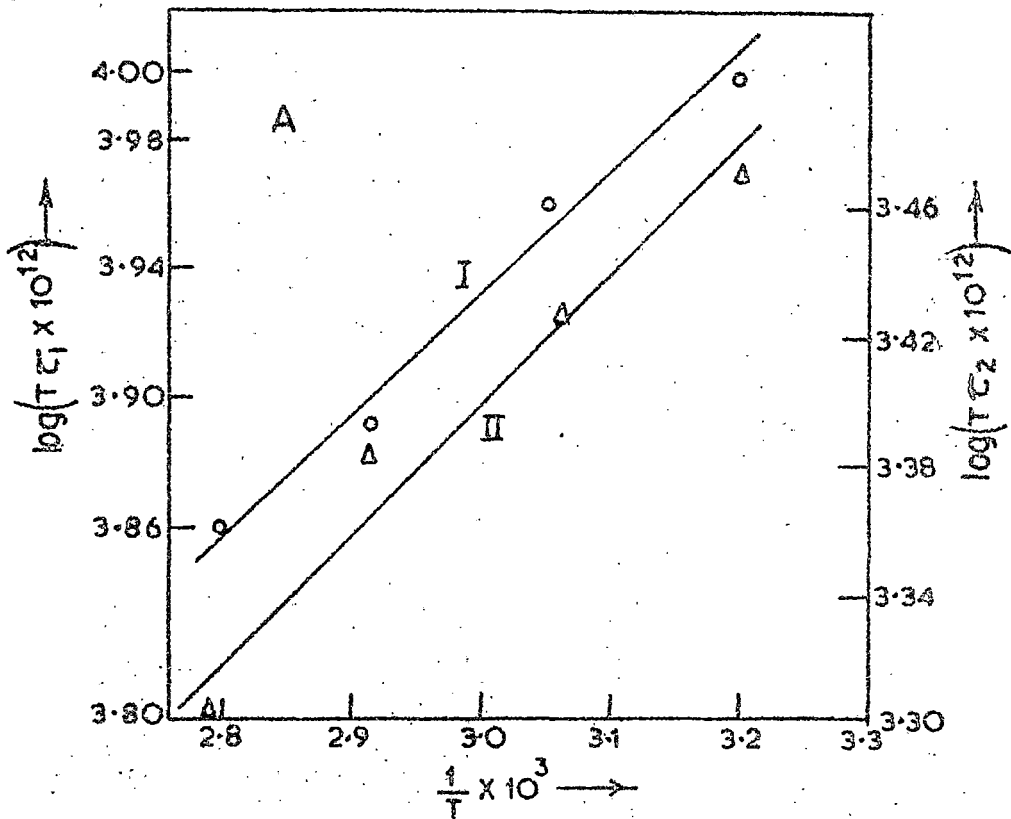


FIG. 4-4

- A. I. Plot of $\log (TC_1)$ vs. $1/T$ for β -bromophenetole
 II. Plot of $\log (TC_2)$ vs. $1/T$ for β -bromophenetole
 B. Plot of $\log \eta$ vs. $1/T$ for β -bromophenetole

the data of Farmer and Walker⁴. This shows that the dipolar interaction are almost the same in the liquid p-bromoanisole and its solution in p-xylene as mentioned earlier.

The energy barrier ΔH_{c_2} to methoxy group rotation in anisole in the liquid state as reported by Garg and Smyth² is only 1.5 Kcal/mole which is much smaller than the value of 2.6 Kcal/mole for methoxy group rotation in anisole in dilute solution in p-xylene calculated from the data of Farmer and Walker⁴ and also from the values 2.2 - 2.6 Kcal/mole (Table 3.3) for methoxy group rotation in the bromoanisoles in the liquid state. This indicates the methoxy group rotation in molecules containing only methoxy group as substituent is less hindered in the liquid state than in anisole in dilute solution or in haloanisoles either in the liquid state or in solution. The larger value of OCH_3 group relaxation time (7 - 9 p.sec) in anisole or dimethoxy benzene in benzene solution and in haloanisoles both in liquid state and in solution as mentioned earlier only lends supports to this.

It can also be seen from the Table 3.2 that the values of n_D^2 in all the liquids are less than that the respective values of ϵ_∞ . This indicates the presence of a high frequency absorption region as suggested by Polcy³.

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