

Chapter V

Investigations on microwave absorption in 1,2-dialkoxy
ethane in the liquid state

1. Introduction :

In the previous four chapters investigations were carried out on dielectric relaxation behaviour of some rotational isomeric molecules such as 1,2-dihaloethane¹, 1-chloro-2-bromoethane², 1,2-dihaloethanes, 1,2-propanedithiol³ and 1-halo-2-methylpropanes⁴ in the liquid state. It was observed that the activation energy for dielectric relaxation (ΔH_{τ}) in each case has got a close parallelism with the difference in values of electrostatic potential energy between the trans and gauche isomers in the liquid state, the latter being found to be almost equal to the amount of lowering of the energy difference between the trans and gauche rotamers from the vapour to the liquid state. The molecules of 1,2-dimethoxyethane and 1,2-diethoxyethane also have got rotational isomers. But these molecules differ from the above halo substituted ethanes and propanes in that in place of halo-substituents, the present molecule have methoxy or ethoxy group which are also capable of rotation as has been reported in anisole⁵⁻⁸, and phenetole⁹. It would be interesting to study the dielectric behaviour of these molecules to see if the observations made in the case of 1,2-dihalo substituted ethanes are also observed here or the molecular and intramolecular rotation as in the case of anisole or phenetole are present in these cases. With this object in view, complex dielectric permittivity have been made at different microwave frequencies and the results are discussed in the present paper.

2. Results :

The experimental values of dielectric permittivity (ϵ'), dielectric loss (ϵ''), dielectric constant (ϵ_0), refractive index (n) and viscosity (η) are given in Table 1.

Table 1

Values of dielectric permittivity (ϵ'), dielectric loss (ϵ''), static dielectric constant (ϵ_0), refractive index (n) and viscosity (η) at different temperatures in the liquid state

Compounds	Temp °C	$\lambda = 1.62\text{cm}$		$\lambda = 3.17\text{cm}$		$\lambda = 3.49\text{cm}$		n^2	ϵ_0	η (CP)
		ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''			
1,2- dimethoxy- ethane	10	6.29	1.83	7.01	1.30	7.07	1.20	1.92	7.80	.4483
	30	6.10	1.54	6.63	1.03	6.69	0.90	1.88	7.14	.3806
	50	5.78	1.37	6.26	0.91	6.32	0.80	1.85	6.61	.3293
	70	5.60	1.12	5.93	0.70	5.97	0.63	1.83	6.14	.2925
1,2- diethoxy- ethane	10	4.57	1.51	5.30	1.26	5.39	1.18	2.00	6.30	.6429
	30	4.44	1.40	5.11	1.09	5.18	1.04	1.96	5.86	.4878
	50	4.30	1.30	4.88	0.96	4.94	0.92	1.92	5.47	.3937
	70	4.20	1.18	4.67	0.84	4.74	0.77	1.88	5.12	.3332

The Cole-Cole arc plots Figs.(5.1 and 5.2) were drawn with the dielectric data at each temperature. The values of the distribution parameter α were obtained from the arc plots and the most probable relaxation times were calculated by the usual method. The activation energy for dielectric relaxation (ΔH_r) was obtained from the

COLE-COLE ARC PLOTS OF 1,2-DIMETHOXY ETHANE.

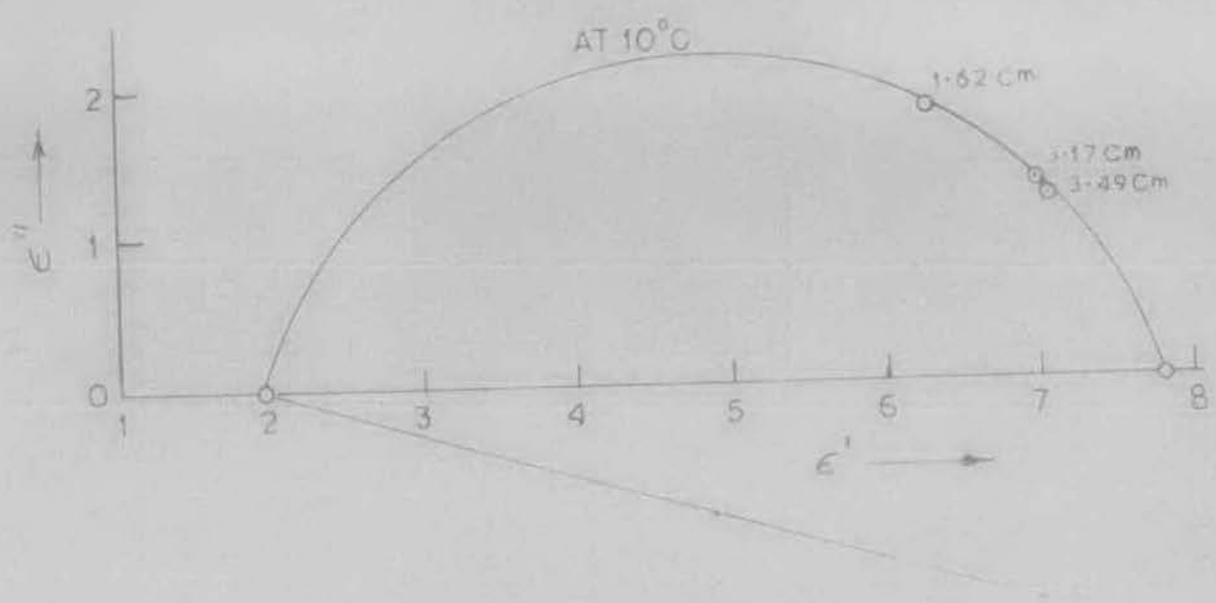


FIG. 5-1 (a)

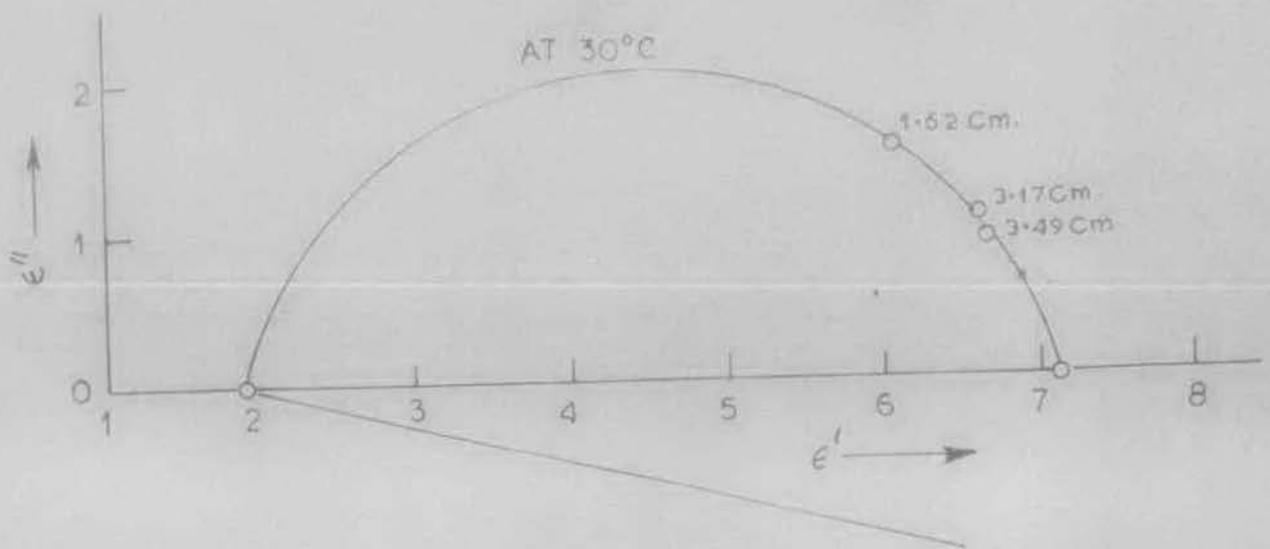


FIG. 5-1 (b)

COLE-COLE ARC PLOTS OF 1,2-DIMETHOXY ETHANE

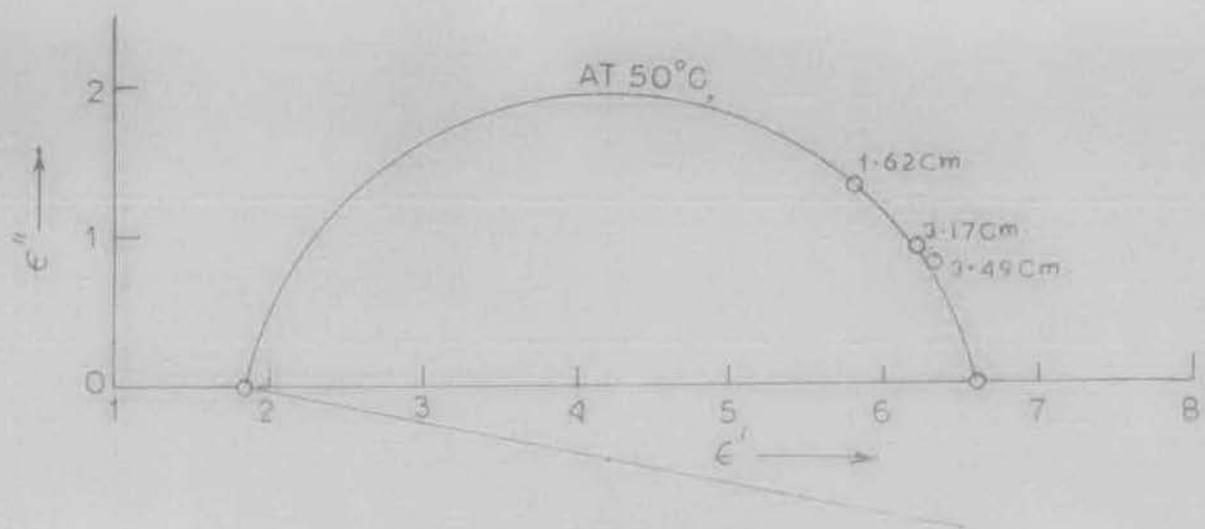


FIG. 5.1(c)

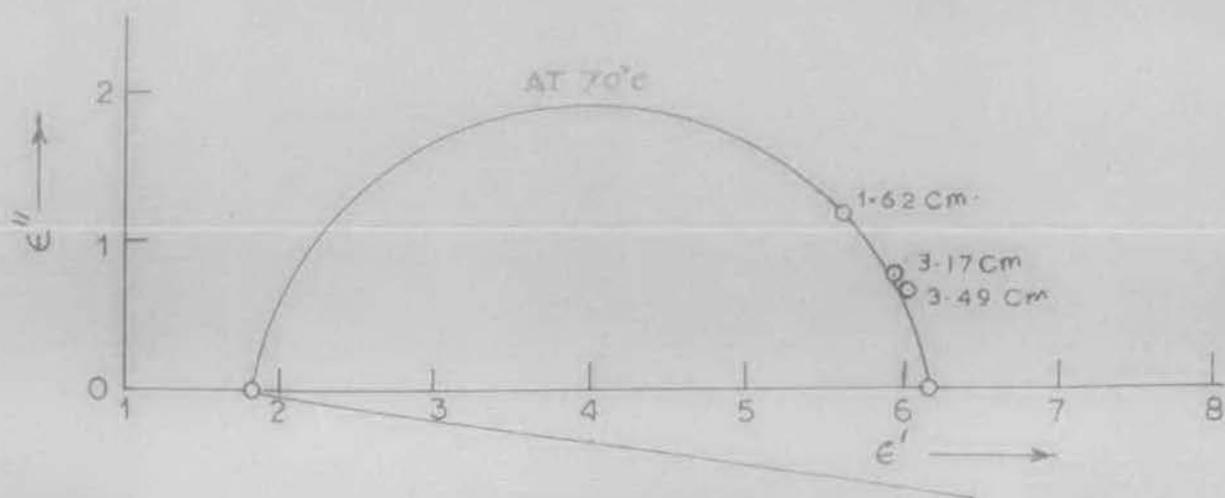


FIG. 5.1(d)

Table 2

Values of distribution parameters (α), most probable relaxation time (τ) and the activation energy for dielectric relaxation (ΔH_{τ}) and that for viscous flow (ΔH_{η}) of 1,2-dialkoxyethane at different temperatures in the liquid state

Compound	Temp °C	α	$\tau \times 10^{12}$ sec	ΔH_{τ} k.cal/ mole	ΔH_{η} k.cal/ mole
1,2- dimethoxy- ethane	10	0.19	3.64	0.526	1.30
	30	0.16	3.00		
	50	0.13	2.86		
	70	0.10	2.39		

1,2- diethoxy- ethane	10	0.20	6.23	0.254	2.30
	30	0.17	5.54		
	50	0.14	5.20		
	70	0.12	4.59		

straight line plots of $\log T\tau$ vs $1/T$ Figs (5.3 and 5.4) and the activation energy for viscous flow ΔH_{η} was obtained from the plots of $\log \eta$ vs $1/T$. The values of α , τ , ΔH_{τ} and ΔH_{η} are given in Table 2.

3. Discussion :

It can be seen from Table 2 that the distribution parameter in both the liquids are appreciable. So attempts were made to analyse

COLE-COLE ARC PLOTS OF 1,4-DIETHYL BENZENE

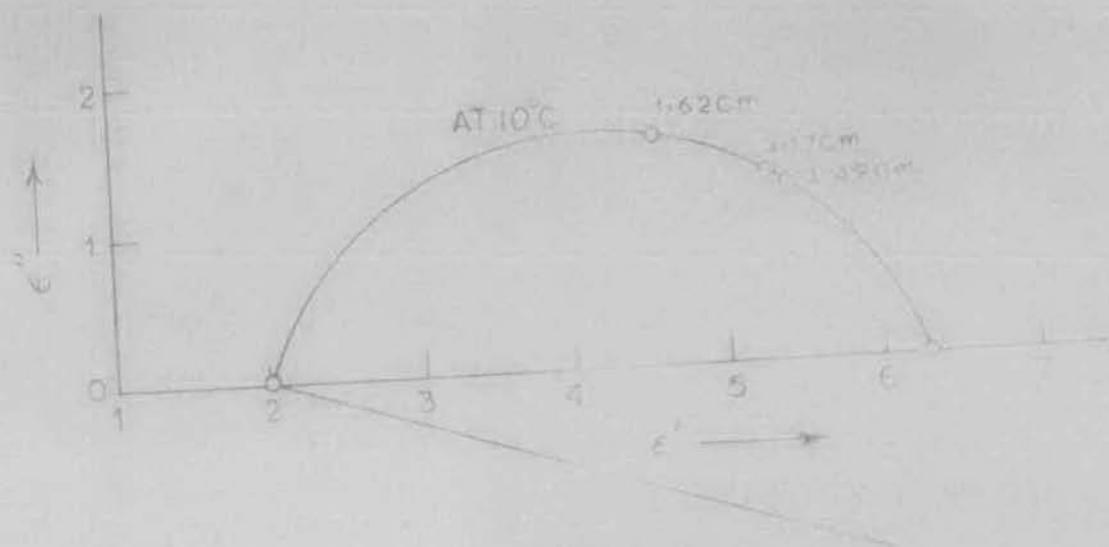


FIG 5-2(a)

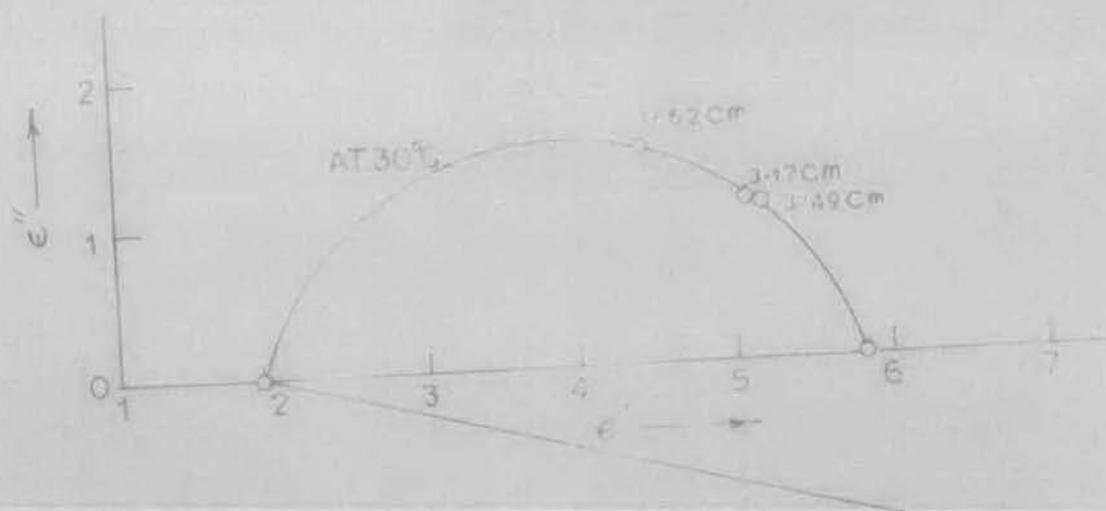


FIG 5-2(b)

COLE-COLE ARC PLOTS OF 1,2-DIETHOXY ETHANE.

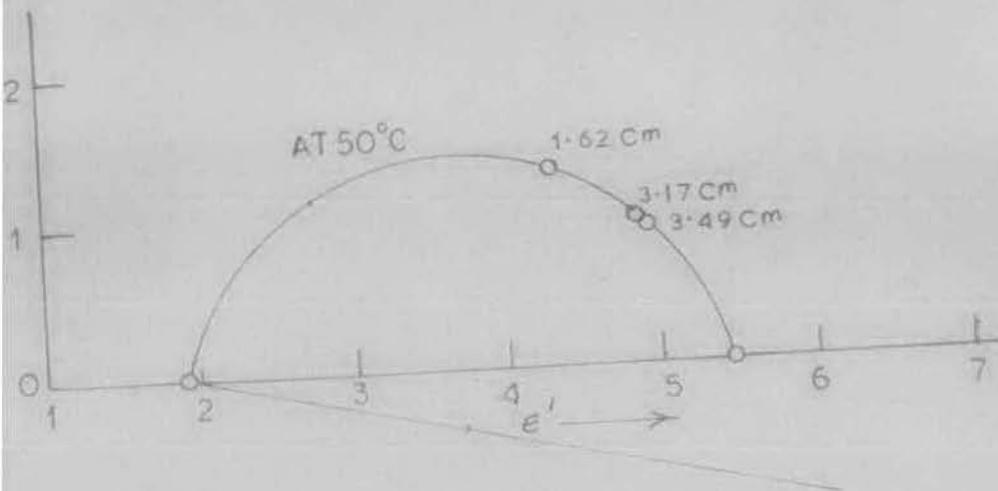


FIG. 5-2(c)

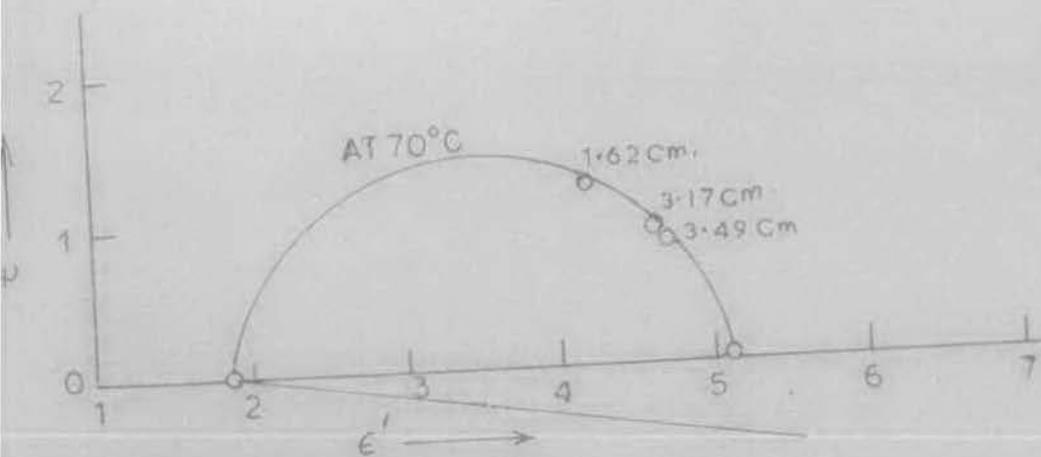
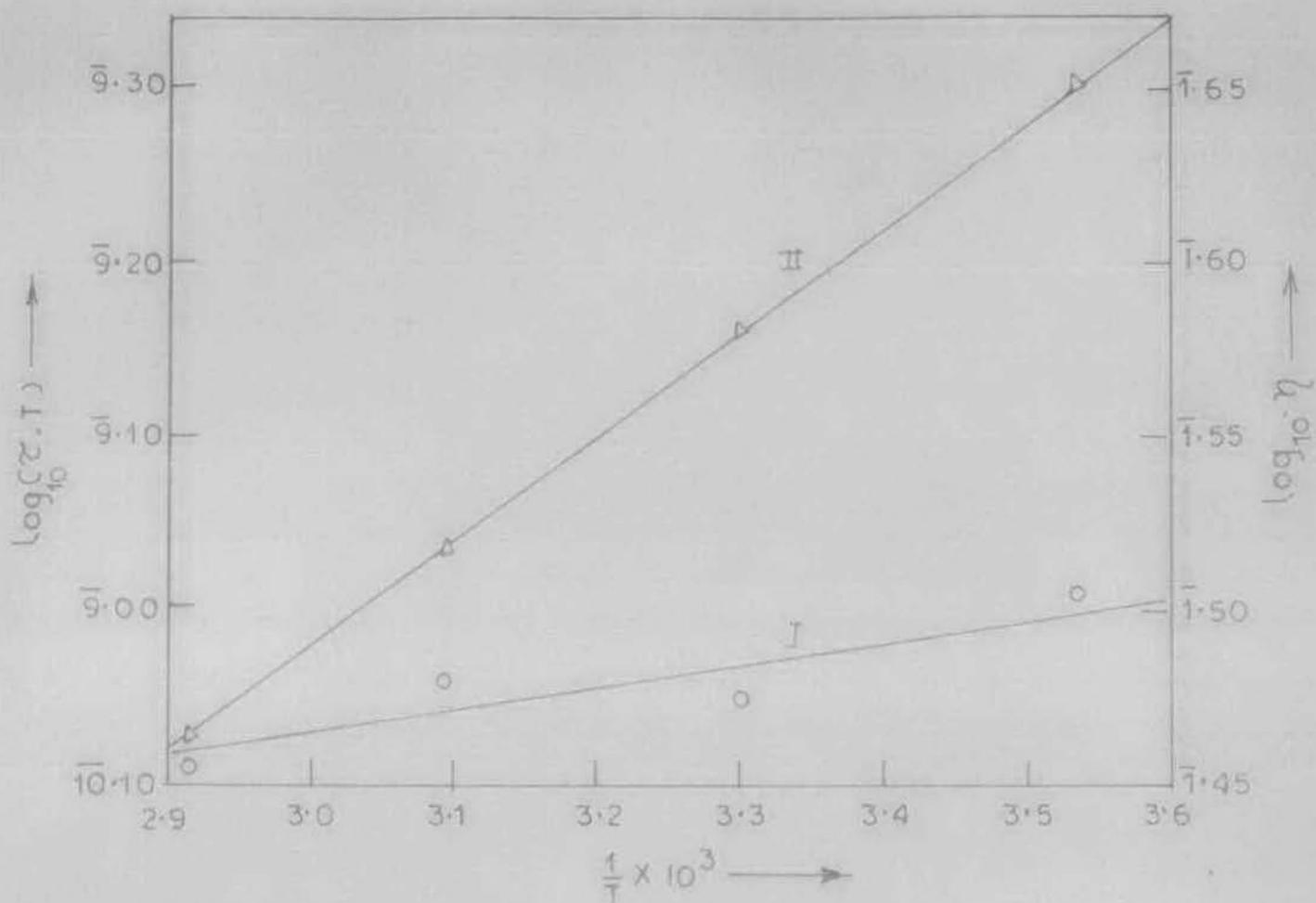


FIG. 5-2(d)

the dielectric data in terms of two relaxation processes but were not successful. In order to understand whether the τ -values in the Table 2 belong to the orientation of molecules or the groups, the following considerations will help us to clarify the mechanism of the relaxation processes involved in the present case.

The molecule of 1,2-dibromoethane is smaller in size than the molecule of 1,2-dimethoxy ethane (since CH_3 group is of the same size as the Br-atom). But the τ -value in the former is 8.6^1 at 30°C which is much larger than the value of 3.0 p.sec at 30°C obtained for the latter molecule. Evidently, the τ -value of 3.0 p.sec can not correspond to the relaxation time due to molecular orientation in 1,2-dimethoxy ethane. Moreover this τ -value of 3.0 p.sec at 30°C in this molecule compares very well with the τ -value of 3.2 p.sec at 20°C for the methoxy group rotation in anisole⁶ in the liquid state. So it is reasonably concluded that the τ -value of 3.0 p.sec is due to the methoxy group rotation in 1,2-dimethoxy ethane. That the dielectric data could not be resolved into group and molecular relaxation, may be due to the fact that the relaxation in this molecule is mostly from methoxy group rotation. In this respect the behaviour of the molecules of 1,2-dimethoxy ethane differs markedly from those of anisole in the liquid state where contribution from methoxy group rotation is only 0.2⁶. The difference in the weight factor for group rotation in anisole and 1,2-dimethoxy ethane can be understood from consideration of the respective values of dipolar activation energy (ΔH_1) The activation energy for group rotation (ΔH_2) in the former molecule

PLOTS OF $\log_{10} (\zeta T)$ AND $\log_{10} \eta$ AGAINST $\frac{1}{T}$ FOR
1,2 DIMETHOXY ETHANE.

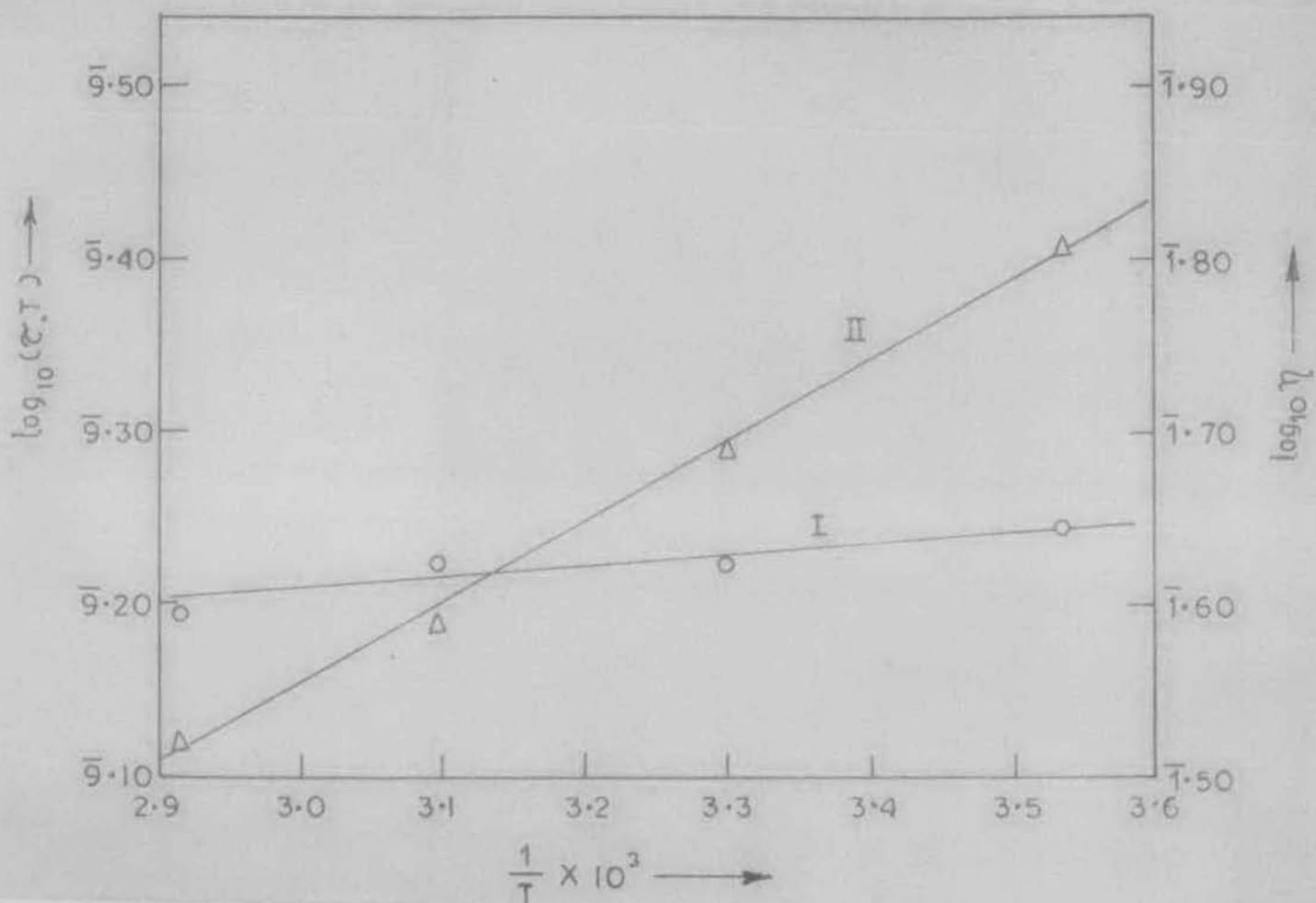


I - FOR $\log_{10} (\zeta T)$ Vs. $\frac{1}{T}$

II - FOR $\log_{10} \eta$ Vs. $\frac{1}{T}$

FIG. 5.3

PLOTS OF $\log_{10}(\alpha T)$ AND $\log_{10}\eta$ AGAINST $\frac{1}{T}$ FOR 1,2-DIETHOXY ETHANE.



I- $\log_{10}(\alpha T)$ Vs $\frac{1}{T}$
 II- $\log_{10} \eta$ Vs $\frac{1}{T}$

FIG. 5.4

is 1.5 k.cal/mole⁶ while in the latter it is only 0.53 k.cal/mole. This shows that the methoxy group is more flexible in 1,2-dimethoxy ethane than in anisole in the liquid state. The high flexibility of the methoxy group makes it possible for 1,2-dimethoxy ethane molecule to have four rotamers as is reported from spectroscopic studies¹⁰.

From similar considerations it is seen that the value of 5.5 p.sec at 30°C for τ -value in 1,2-diethoxy ethane compares fairly well with the value of about 4 p.sec at 45°C for the ethoxy group rotation in phenetole⁹ in the liquid state. So in the case of 1,2-diethoxy ethane also the relaxation is mainly due to orientation of the ethoxy group. The activation energy of dielectric relaxation (ΔH_{τ}) in this molecule can be seen from the Table 2 is about 0.250 k.cal/mole, which is even smaller than that in 1,2-dimethoxy ethane. This means that the ethoxy group in 1,2-diethoxy ethane is more flexible than the methoxy group in 1,2-dimethoxy ethane. A larger number of rotamers reported to be present in 1,2-dimethoxy ethane lends support to this. It is to be noted here that the τ -value of the methoxy group rotation at any temperature is less than that of the τ -value of the ethoxy group rotation at the same temperature which is consistent with the sizes of the groups.

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