

PART I

Dielectric studies of some rotational isomeric
molecules of 1,2-disubstituted ethanes

Introduction :

It is now well established from studies of dipole moment, Raman and infrared spectroscopy and electron diffraction that the molecules of 1,2-disubstituted ethanes co exist in rotational isomeric forms (now known as trans and gauche forms) whose structure pass from one form to another by the internal rotation about the carbon-carbon single bond as axis and that one isomeric form is more stable than the other by a certain amount of energy which depends upon the gaseous or liquid state of the molecules. The equilibrium ratio of the rotational isomers in gaseous or liquid state depends upon the temperature but in the solid state, only one form of the isomers exist in most cases.

Mizushima and his co-workers¹ have shown that the energy difference between the trans and gauche isomers in 1,2-dihaloethanes in the gaseous state is much greater than that in the liquid state. Mizushima² and later Wada³ have shown that the lowering of energy difference between the trans and gauche isomers in 1,2-dihaloethanes for a change from gaseous to liquid state is caused by inter-molecular forces in the liquid state and the amount of lowering of the energy difference is almost equal to the electrostatic potential energy of the polar isomers given by the relation

$$\Delta E = \frac{\epsilon - 1}{2\epsilon + 1} \left(\frac{\mu_g^2}{a_g^3} - \frac{\mu_t^2}{a_t^3} \right)$$

In dielectric studies, the process of molecular or group orientations requires some activation energy, sufficient to overcome the

intermolecular forces for going from one equilibrium position to another as postulated by Kauzmann⁴.

So, it is expected that the dipolar activation energy obtained from dielectric relaxation measurements and the amount of lowering of the energy difference between the trans and gauche isomer of 1,2-disubstituted ethanes from gaseous to liquid state, both of which are caused by intermolecular forces may have some relations between them.

Therefore, the objects of the present investigations were

i) To find out the relaxation times of the rotational isomeric molecules in the pure liquid state at different temperature and see how the relaxation times vary with their sizes.

ii) To determine the activation energy the dielectric relaxation of some 1,2-disubstituted ethanes in pure liquid state and to see how it compares with (a) the amount of lowering of energy difference between the trans and gauche isomers from the gaseous to the liquid state as reported in literatures from spectroscopic studies; (b) how the dipolar activation energy compares with the potential barrier for internal rotation as reported in literatures from ultrasonic studies and theoretical calculations.

iii) To see, how far the values of activation energy of dielectric relaxation agree with the electrostatic potential energy of the polar isomers given by the relation

$$\Delta E = \frac{\epsilon - 1}{2\epsilon + 1} \left(\frac{\mu_g^2}{a_g^3} - \frac{\mu_t^2}{a_t^3} \right)$$

iv) To obtain the energy difference between the trans and gauche isomers in the liquid state calculating by the method of Mizushima from the measured values of mean dipole moment at different temperature and compare with those values reported in literature obtained from the spectroscopic method.

v) To find if the internal rotation of the group $-\text{CH}_2\text{X}$ (where $\text{X} = \text{CH}_3, \text{C}_2\text{H}_5 \dots$) was detectable.

vi) To compare with the dipolar activation energy with that for viscous flow.

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Chapter I

Investigations on dielectric relaxation of 1,2-dichloroethane and 1,2-dibromoethane in the liquid state

1.1. Introduction :

It is well known that the energy differences between the trans and gauche rotational isomers of the molecules of 1,2-dichloro- and 1,2-dibromoethanes in the gaseous state are 1.27 k.cal/mol and 1.7 k.cal/mol respectively and in the liquid state this energy difference in the former molecules is almost zero while in the latter molecules about 800 cal/mol¹⁻³.

Wada⁴ explained the observed decrease in the values of energy difference in the pure liquids to be due to the electrostatic energy of the polar gauche molecules embedded in a continuous dielectric medium and the results of his calculations seem to agree with the experimental results.

Since measurements on the temperature dependence of relaxation times of the molecules of polar liquids afford a method for determining the activation energy of the molecules i.e. the potential energy of the molecules in the liquid state due to various intermolecular forces in the liquid at different temperatures by the method of microwave absorption.

The experimental results and discussion of the results are given below.

1.2. Results :

The values of ϵ' and ϵ'' determined experimentally at different temperatures and at the two microwave frequencies in the case of liquid 1,2-dichloro- and 1,2-dibromoethane are given in

Table 1. The Table 1 also contains the measured values of ϵ_0 and η at the corresponding temperatures.

Table 1

Values of ϵ' , ϵ'' , η and ϵ_0 of 1,2-dichloroethane and 1,2-dibromoethane at different temperatures

Substance	Temp °C	$\lambda = 1.62$ cm		$\lambda = 3.20$ cm		ϵ_0	η
		ϵ'	ϵ''	ϵ'	ϵ''		
1,2-dichloroethane	31.5	7.01	3.19	8.65	2.50	9.80	1.437
	50	7.11	2.74	8.31	2.23	9.35	1.428
	65	7.17	2.42	7.94	1.82	8.55	1.420
1,2-dibromoethane	30	3.44	0.802	4.01	0.815	4.67	1.533
	50	3.53	0.869	4.16	0.805	4.65	1.520
	65	3.64	0.922	4.21	0.712	4.62	1.512
	80	3.76	0.873	4.25	0.656	4.55	1.511

The values of ϵ' and ϵ'' for the two liquids at different temperatures have been fitted into the Cole-Cole arc plots, which are shown in Figs.(1.1 and 1.2). The values of τ , η and the distribution parameter α determined from these plots are shown in Table 2. The values of activation energy (ΔH_τ) for dielectric relaxation obtained from the usual plots of $\log T\tau$ vs $1/T$ (Fig.1.3 and 1.4) and the activation energy (ΔH_η) values for viscous flow obtained from the plots of $\log \eta$ vs $1/T$ are given in Table 2. The viscosity values at different temperatures are taken from standard literatures⁵.

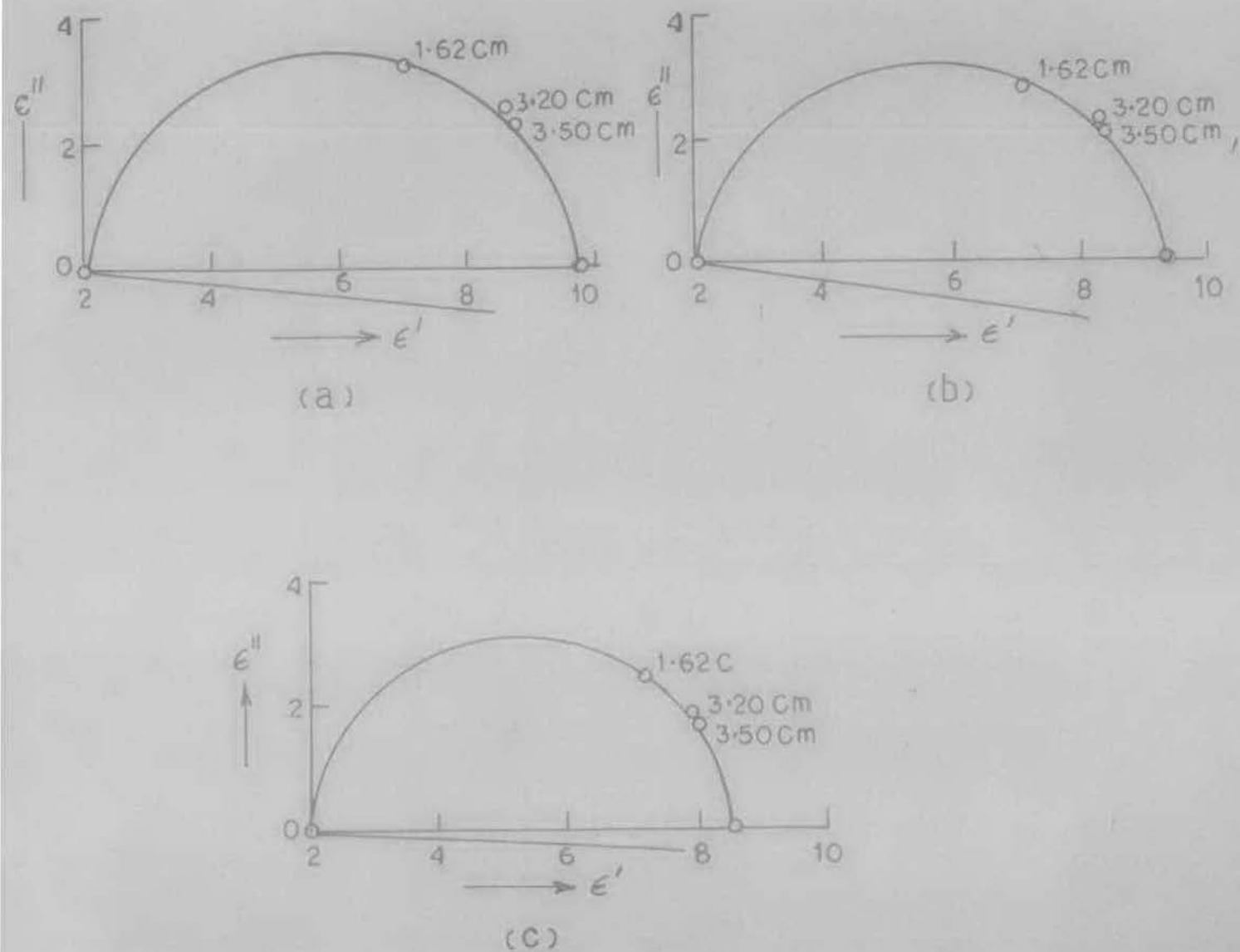
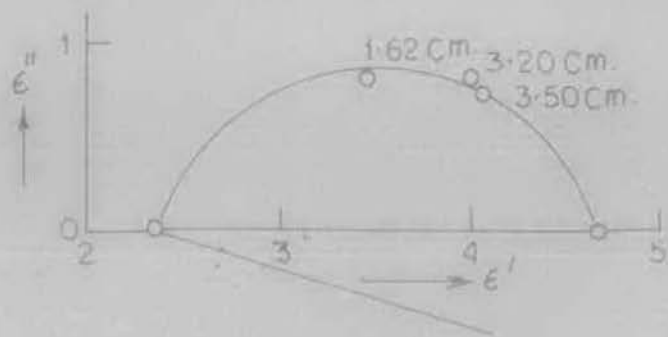
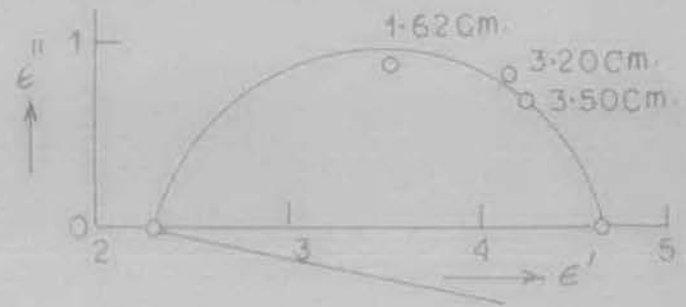


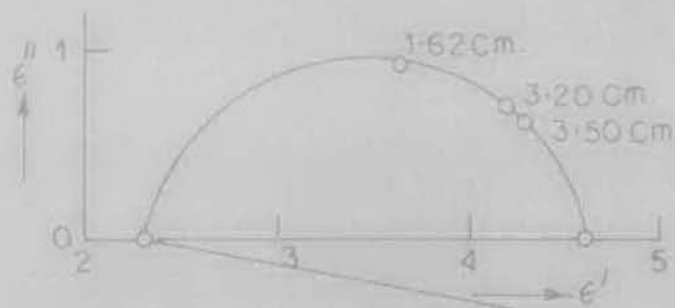
FIG. 1. COLE COLE ARC PLOT OF 1,2 DICHLORO ETHANE AT
 (a) 304.5°K (b) 323°K AND (c) 338°K



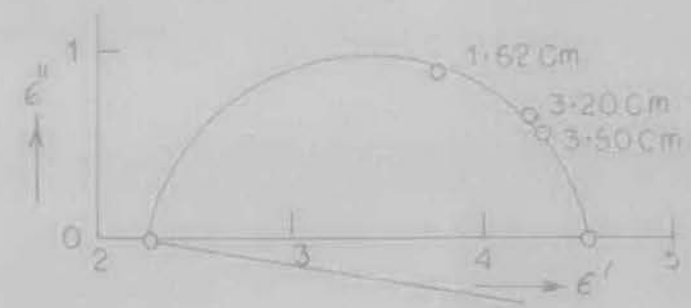
(a)



(b)



(c)



(d)

FIG. 1.2: COLE COLE ARC PLOT OF 1,2 DIBROMO ETHANE AT
 (a) 303°K (b) 323°K (c) 338°K
 AND (d) 353°K

The accuracy of the τ -values so determined is 3% in the case of 1,2-dichloroethane and in the case of 1,2-dibromoethane it is about 5%.

1.3. Discussions :

It is seen from Table 2 that the relaxation time of 1,2-dibromoethane at any temperature is larger than that of 1,2-dichloroethane which is consistent with the larger size of the former molecule. The τ -value 6.15 p.sec of 1,2-dichloroethane at 31°C

Table 2

Relaxation time (τ) Cole-Cole parameter (α) and activation energy of 1,2-dichloro- and 1,2-dibromoethanes

Substance	Temp °C	$\tau \times 10^{12}$ sec	α	E_{∞}	ΔH_2 k.cal/ mol	ΔH_1 k.cal/ mol
1,2- dichloro- ethane	31.5	6.05	0.07	2.20		
	50	5.07	0.06	2.10	1.29	2.30
	65	4.44	0.05	2.05		
1,2- dibromo- ethane	30	8.60	0.19	2.36		
	50	7.36	0.13	2.33		
	65	6.44	0.12	2.32	1.09	2.55
	80	5.63	0.10	2.29		

is compatible with the value 5.6 p.sec at 25°C for a solution of 1,2-dichloroethane in p-xylene as reported by Crossley and Walker⁶ but is somewhat larger than the value 4.53 p.sec for the same solution at 20°C given by Chitoku and Higasi⁷. However the value of

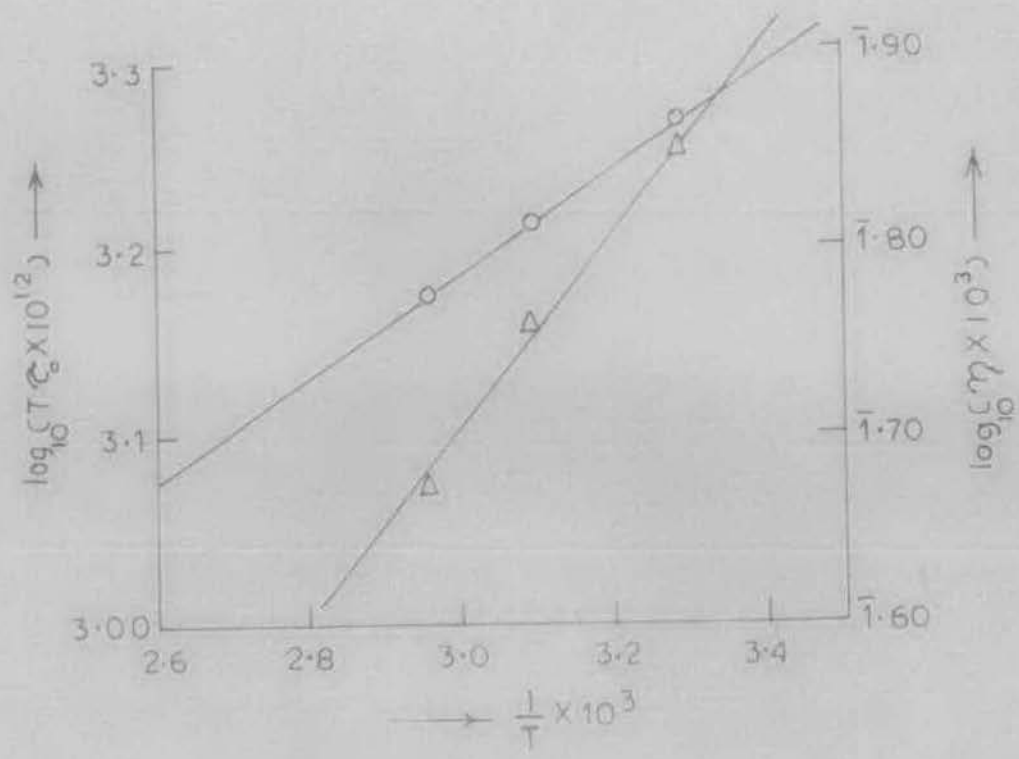


FIG. 1.3: PLOT OF $\log_{10}(T\tau)$ AND $\log_{10} \eta$ AGAINST $1/T$ FOR 1,2-DICHLOROETHANE

O - INDICATE $\log_{10} T\tau$ VS $1/T$
 Δ - $\log_{10} \eta$ VS $1/T$

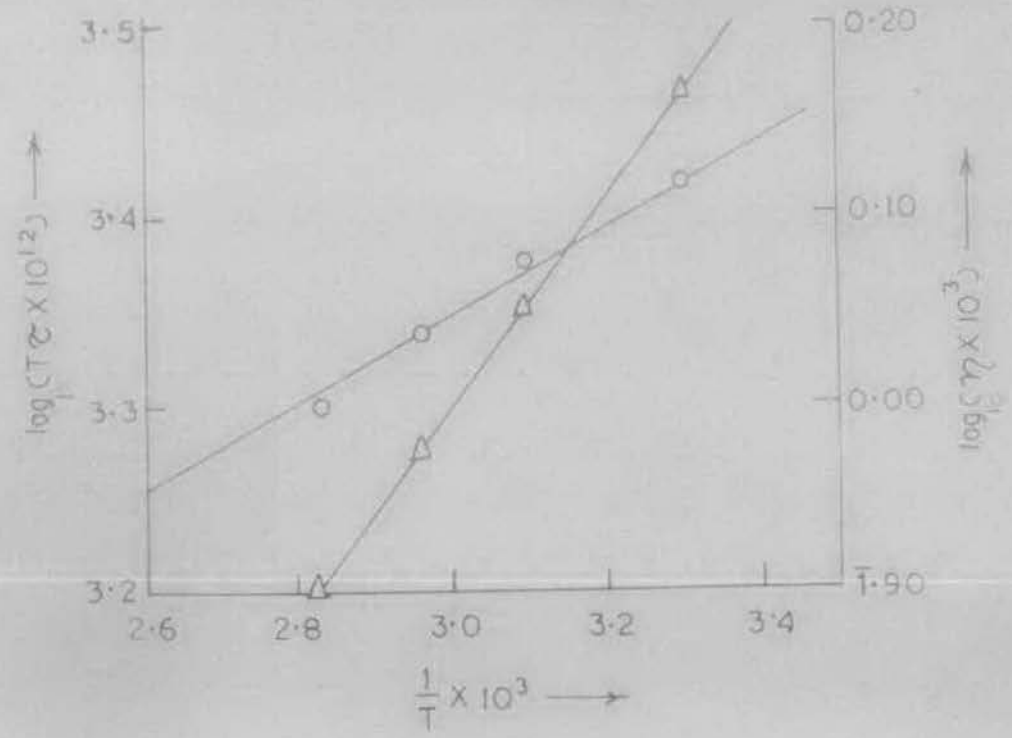


FIG. 1.4: PLOT OF $\log_{10}(T\tau)$ AND $\log_{10} \eta$ AGAINST $1/T$ FOR 1,2-DIBROMOETHANE

O - INDICATE $\log_{10} T\tau$ VS $1/T$
 Δ - $\log_{10} \eta$ VS $1/T$

relaxation time for the pure liquid has not been apparently reported in the literature. In this connection it may be noted that from the measurements of spin-lattice relaxation of a solution of 1,2-dichloroethane in 1,2-dichloroethane- d_4 Bock and Tomchuk⁸ derived a value of 8.62 p.sec for the relaxation time of 1,2-dichloroethane at 20°C. This value seems to be slightly higher than the value obtained in the present investigation.

The value of 0.07 for the distribution parameter (α) obtained in this investigation for the pure liquid at 31°C is near the value of 0.08 reported by Crossley and Walker⁶ and is much smaller than the value 0.19 obtained by Chitoku and Higasi⁷. It is seen from the Table 2 that the α -value for the pure liquid decreases with increase of temperature as is generally observed. The α -value for 1,2-dibromoethane is somewhat larger than that of 1,2-dichloroethane and also decreases with increasing temperature as in the case of 1,2-dichloroethane.

It is seen from Table 2 that the values for the activation energy for dielectric relaxation (ΔH_τ) of 1,2-dichloroethane and 1,2-dibromoethane are both smaller than the respective values of the activation energy for viscous flow (ΔH_η) for both the liquids as are generally observed with other polar liquids.

The activation energy (ΔH_τ) of 1.3 k.cal/mol in the case of 1,2-dichloroethane in liquid state as determined in the present investigation is almost equal to Wada's calculated value 1.22 k.cal/mol⁴ representing the electrostatic self energy of the

polar gauche molecule in the liquid state. In the case of 1,2-dibromoethane in the liquid state the activation energy (ΔH_{τ}) is found to be 1.09 k.cal/mol while according to Wada's calculation⁴ the electrostatic self energy in this case is about 800 cal/mol.

Thus though the observed value of (ΔH_{τ}) in the case of 1,2-dichloroethane closely agrees with the value calculated by Wada, in the case of 1,2-dibromoethane the calculated value is somewhat lower than the observed one. It need be noted that Wada considered only the electrostatic energy of the polar gauche molecules in the liquid but did not take into account other types of intermolecular forces within the liquid which will further lower the energy of gauche isomers. The small difference in (ΔH_{τ}) in the case of 1,2-dibromoethane may arise from this cause.

Considering the accuracy of the determination of the τ -values in the present investigation it may be concluded that the values of the activation energy determined experimentally are in agreement with the values calculated by Wada and that the greater part of the potential energy of the gauche isomers of the molecules of 1,2-dichloroethane and 1,2-dibromoethane in the liquid state arises from the electrostatic self energy of the polar molecules.

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