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Dielectric Relaxation of 1,2-Dichloroethane and 1,2-Dibromoethane in the Liquid State

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The activation energies for dielectric relaxation (ΔH_τ) of the gauche rotational isomers of 1,2-dichloroethane and 1,2-dibromoethane in the liquid state have been determined from the dielectric relaxation data obtained from the absorption in 1.62 cm and 3.20 cm microwave regions at different temperatures. The activation energies (ΔH_τ) in both the liquids obtained in the present investigation agree fairly well with the values of electrostatic self energy of the polar isomers in the liquid state calculated theoretically by Wada.

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 kcal/mol and 1.7 kcal/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/mol.[1-3]

Wada[4] 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 the various intermolecular forces in the liquid, it was intended to study the relaxation times of 1,2-dichloroethane and 1,2-dibromoethane molecules in the liquid state at different temperatures by the method of microwave absorption.

The experimental results and discussions of the results are presented in this paper.

Experimental

Chemically pure samples of 1,2-dichloroethane and 1,2-dibromoethane obtained from E. Merck were first dehydrated with fused calcium chloride and then fractionated. The proper fractions were then distilled under reduced pressure and used in the experiment.

The dielectric constant (ε') and dielectric loss (ε'') values of the two liquids at different temperature were measured by

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[1] Y. Morino, I. Watanabe, and S. Mizushima, *Sc. paper J.P.C.R.* (Tokyo), **39**, 396 (1941).

[2] D. H. Rank, R. E. Kagrise, and D. W. E. Axford, *J. Chem. Phys.*, **17**, 1354 (1949).

[3] N. Sheppard, *Advan. in Spectry.*, **1**, 298 (1959).

[4] A. Wada, *J. Chem. Phys.*, **22**, 198 (1954).

Surber's method[5] at 1.62-cm and by Poley's method[6] at 3.2-cm microwaves. The values of the static dielectric constants (ε_0) were determined at 1 MHz while the refractive indices (n) were measured with an Abbe Refractometer. The temperature in all the measurements were kept constant within $\pm 1/2$°C by means of a thermostat.

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-dichloroethane and 1,2-dibromoethane are given in Tables 1 and 2. Each of the tables also contains the measured values of ε_0 and n at the corresponding temperatures.

TABLE 1. VALUES OF ε', ε'', ε_0, AND n OF 1,2-DICHLOROETHANE AT DIFFERENT TEMPERATURES

Temp. °C	λ=1.62 cm		λ=3.20 cm		ε_0	n
	ε'	ε''	ε'	ε''		
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

TABLE 2. VALUES OF ε', ε'', ε_0, AND n OF 1,2-DIBROMOETHANE AT DIFFERENT TEMPERATURES

Temp. °C	λ=1.62 cm		λ=3.20 cm		ε_0	n
	ε'	ε''	ε'	ε''		
30	3.44	0.802	4.01	0.185	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, some of which are shown in Figs. 1 and 2. The values of τ, ε_∞ and the distribution parameters α determined from these plots are shown in Tables 3 and 4. The values of activation energy (ΔH_τ) for dielectric relaxation obtained from the usual plots of $\log(T\tau)$ *vs.* $1/T$ (Fig. 3) and the activation energy (ΔH_η)-values for viscous flow obtained from the plots of $\log(T\tau)$ *vs.* $1/T$ are given in Tables 3 and 4 respectively. The viscosity values at different temperatures are taken from standard literatures.[7]

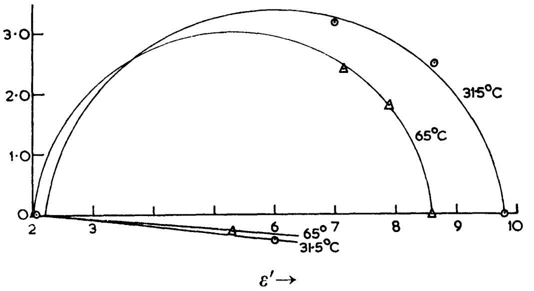

Fig. 1. Cole-Cole arc plot of 1,2-dichloroethane at 31.5°C and 65°C.

TABLE 3. RELAXTION TIME τ, Cole-Cole PARAMETER α, ε_∞, AND ACTIVATION ENERGIES OF 1,2-DICHLOROETHANE

Temp. °C	$\tau\times10^{12}$ sec	α	ε_∞	ΔH_τ kcal/mol	ΔH_η kcal/mol
31.5	6.05	0.07	2.20	1.29	2.30
50	5.07	0.06	2.10		
65	4.44	0.05	2.05		

TABLE 4. RELAXATION TIME τ, Cole-Cole PARAMETER α, ε_∞, AND ACTIVATION ENERGIES OF 1,2-DIBROMOETHANE

Temp. °C	$\tau\times10^{12}$ sec	α	ε_∞	ΔH_τ kcal/mol	ΔH_η kcal/mol
30	8.60	0.19	2.36	1.09	2.55
50	7.36	0.13	2.33		
65	6.44	0.12	2.32		
80	5.63	0.10	2.29		

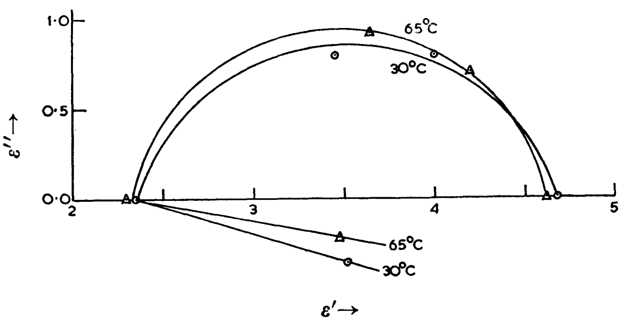

Fig. 2. Cole-Cole arc plot of 1,2-dibromoethane at 30°C and 65°C.

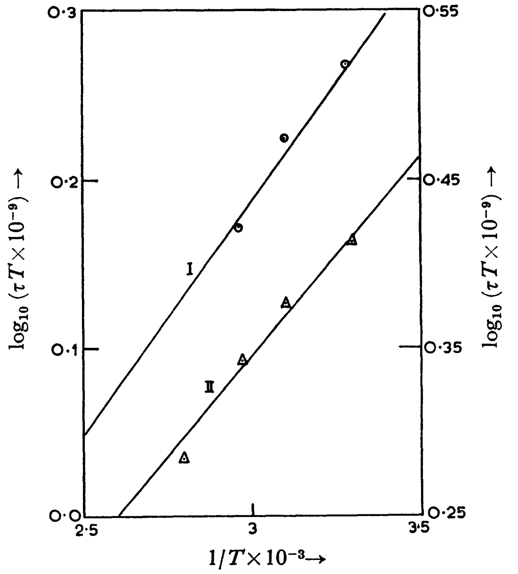

Fig. 3. Plot of log ($T\tau$) versus $1/T$
Curve I: 1,2-dichloroethane Ordinate to the left.
Curve II: 1,2-dibromoethane Ordinate to the right.

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%.

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[5] W. H. Surber, Jr., *J. Appl. Phys.*, **10**, 534 (1948).

[6] J. Ph. Poley, *Appl. Sci. Res.*, **B4**, 337 (1955).

[7] *Int. Critical Tables*, **7**, 213 (1930).

Discussions

It is seen from Tables 3 and 4 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 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 Walker[8] but is somewhat larger than the value 4.53 p·sec for the same solution at 20°C given by Chitoku and Higasi.[9] However the value of 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 Tomchuk[10] 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 Walker[8] and is much smaller than the value 0.19 obtained by Chitoku and Higasi.[9] It is seen from Table 3 that the α-values for the pure liquid decreases with the increase of temperature as is generally observed. The α value for 1,2-dibromoethane (Table 4) 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 Tables 3 and 4 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 kcal/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 kcal/mol[4] 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 kcal/mol while according to Wada's calculation[4] 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 the 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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[8] J. Crossley and S. Walker, *J. Chem. Phys.*, **48**, 4742 (1968).

[9] K. Chitoku and K. Higasi, This Bulletin, **40**, 773 (1967).

[10] E. Bock and E. Tomchuk, *Can. J. Chem.*, **47**, 4635 (1969).