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Intramolecular Rotations in 1,2-Dialkoxyethanes in the Liquid State

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Dielectric measurements have been made in 1,2-dimethoxy- and 1,2-diethoxyethane in the liquid state in 1.62, 3.17, and 3.49 cm microwave region. Both the molecules are found to relax mostly by methoxy/ethoxy group rotations.

The methoxy group rotation has been reported in anisole both in pure liquid[1,2] and in dilute solutions[3,4] in non polar solvents. It was observed that while the weight factor C_2 for methoxy group rotation in anisole in dilute solution is about 0.8,[3,4] it is only about 0.2[2] in the pure liquid state. The decrease in the value of C_2 from dilute solution to the pure liquid was explained by Garg and Smyth[2] to be due to some restraint in the C–O bond resulting the methoxy group rotation not completely free but hindered.

Similar rotation of the methoxy group has not been reported in aliphatic molecules. In order to study how the methoxy or ethoxy group behave to dipolar relaxation in aliphatic molecules, dielectric studies have been made in the case of 1,2-dimethoxy- and 1,2-diethoxyethane in pure liquid state in 1.62, 3.17, and 3.49 cm microwave region. The results are presented and discussed in the paper.

Experimental

Pure samples of 1,2-dimethoxy- and 1,2-diethoxyethane procured from Schuchardt (Germany) were first dried and fractionated. The proper fraction was distilled under reduced pressure before use in the investigations. The experimental arrangements for measuring the complex dielectric permittivity (ε' and ε''), static dielectric constant ε_0 refractive index n_D and viscosity η were the same as described earlier.[5] The temperature of the experiment was kept constant within ±1 °C by means of a thermostat. The accuracy in the measurements of ε' and ε'' are about 3 and 5% respectively.

Results

The experimental values of ε', ε'', ε_0, $n_D{}^2$ and η are given in Table 1. Cole-Cole arc plots (Fig. 1) were

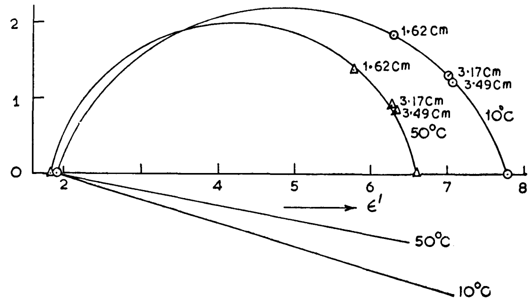

Fig. 1a.

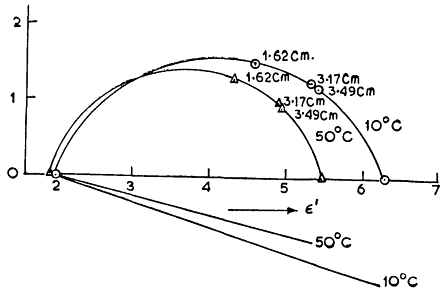

Fig. 1b.

Fig. 1. Cole arc plots of (a) 1,2-dimethoxyethane, (b) 1,2-diethoxyethane.

Table 1. Values of $n_D{}^2$, ε', ε'', ε_0 and η

T°C	$n^2{}_D$	$\lambda=1.62$		$\lambda=3.17$		$\lambda=3.49$		ε_0	η (cp)
		ε'	ε''	ε'	ε''	ε'	ε''		
1,2-Dimethoxyethane									
10	1.92	6.29	1.83	7.01	1.30	7.07	1.20	7.80	0.4483
30	1.88	6.10	1.54	6.63	1.03	6.69	0.09	7.14	0.3806
50	1.85	5.78	1.37	6.26	0.91	6.32	0.08	6.61	0.3293
70	1.83	5.60	1.12	5.93	0.70	5.97	0.63	6.14	0.2925
1,2-Diethoxyethane									
10	2.00	4.57	1.51	5.30	1.26	5.39	1.18	6.30	0.6424
30	1.96	4.44	1.40	5.11	1.09	5.18	1.04	5.86	0.4878
50	1.92	4.30	1.30	4.88	0.96	4.94	0.92	5.47	0.3937
70	1.88	4.20	1.18	4.67	0.84	4.74	0.77	5.12	0.3332

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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 $\Delta H\tau$ was obtained from the straight line plots of $\log \tau T$ *vs.* $1/T$ (Fig. 2) and the activation energy for viscous flow $\Delta H\eta$ was obtained from the plots of $\log \eta$ *vs.* $1/T$. The values of α, τ, $\Delta H\tau$, and $\Delta H\eta$ are given in Table 2.

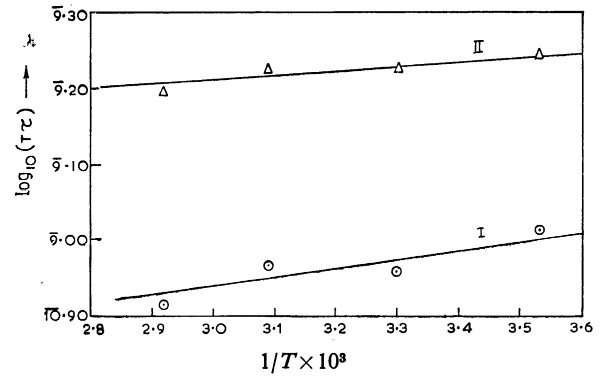

Fig. 2. Plots of $\log \tau T$ *vs.* $1/T$. (I) 1,2-dimethoxyethane (II) 1,2-diethoxyethane

TABLE 2. VALUES OF α, τ, $\Delta H\tau$ AND $\Delta H\eta$

T°C	α	$\tau \times 10^{12}$ s	$\Delta H\tau$ kcal/mol	$\Delta H\eta$ kcal/mol
		1,2-Dimethoxyethane		
10	0.19	3.64	0.520	1.30
30	0.16	3.00		
50	0.13	2.86		
70	0.10	2.39		
		1,2-Diethoxyethane		
10	0.20	6.23	0.254	2.30
30	0.17	5.54		
50	0.14	5.20		
70	0.12	4.59		

Discussion

It can be seen from Table 2 that the distribution parameter in both the liquids are appreciable. So attempts were made to analyse the 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 orientation of molecules or the groups, the following consideration 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-dimethoxyethane (since CH_3 group is of the same size as the Br-atom). But the τ-value in the former is 8.6 ps[5] at 30 °C which is much larger than the value of 3.0 ps at 30 °C obtained for the latter molecule. Evidently, the τ-value of 3.0 ps can not correspond to the relaxation time due to molecular orientation in 1,2-dimethoxyethane. Moreover, this τ-value of 3.0 ps at 30 °C in this molecule compares very well with the τ-value of 3.2 ps at 20 °C for the methoxy group rotation in anisole[2] in the liquid state. So it is reasonably concluded that the τ-value of 3.0 ps is due to the methoxy group rotation in 1,2-dimethoxyethane. 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 molecules of 1,2-dimethoxyethane differs markedly from that of anisole in the liquid state where contribution from methoxy group rotation is only 0.2.[2] The difference in the weight factor for group rotation in anisole and in 1,2-dimethoxyethane can be understood from consideration of the respective values of dipolar activation energy $\Delta H\tau$. The activation energy for group rotation ($\Delta H\tau_2$) in the former molecule is 1.5 kcal[2] while in the latter it is only 0.53 kcal/mol. This shows that the methoxy group is more flexible in 1,2-dimethoxyethane than in anisole in the liquid state. The high flexibility of the methoxy group makes it possible for 1,2-dimethoxyethane molecule to have four rotational isomers as is reported from spectroscopic studies.[6]

From similar considerations, it is seen that the value of 5.5 ps at 30 °C for τ-value in 1,2-diethoxyethane compares fairly well with the value of about 4 ps at 20 °C in the ethoxy group rotation in phenetole[7] in the liquid state. So in the case of 1,2-diethoxyethane also the relaxation is mainly due to orientation of the ethoxy group. The activation energy of dielectric relaxation in this molecule as can be seen from Table 2 is about 0.25 kcal/mol, which is even smaller than that in 1,2-dimethoxyethane. This means that the ethoxy group in 1,2-dimethoxyethane is more flexible than the methoxy group in 1,2-dimethoxyethane. A larger number of rotamers reported to be present in 1,2-diethoxyethane[6] lends support to this. It is to be noted here that the τ-value of 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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