

Microwave absorption and relaxation processes in thioanisole in the liquid state

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Complex dielectric permittivities in thioanisole in the liquid state have been measured at different microwave frequency regions. The dielectric data have been analysed in terms of molecular and intramolecular relaxation processes.

1. INTRODUCTION

Molecular and intramolecular relaxation have been reported in the case of anisole in the liquid state (Vaughan *et al* 1963, Garg & Smyth 1967) as well as in dilute solution in benzene (Forest & Smyth 1964, Farmer & Walker 1969, Klages & Krauss 1971). Though the molecular relaxation time τ_1 in the pure liquid and in dilute solution are almost the same ($\tau_1 = 15$ p.sec. at 20°C), the methoxy group relaxation time $\tau_2 = 3$ p.sec at 20°C and its contribution $C_2(0.2)$ to total polarization in the liquid state differs considerably from the values of $\tau_2 = 7$ p.sec at 20°C and $C_2 = 0.8$ in dilute benzene solution. The drastic reduction of the weight factor $C_2(0.2)$ for methoxy group rotation in the liquid anisole from its value ($C_2 = 0.8$) in the dilute benzene solution has been attributed by Garg & Smyth (1967) to some restraint in the C-O bond as a result the methoxy group rotation is not completely free but hindered. The increase in the methoxy group relaxation time ($\tau_2 = 7$ p.sec) in dilute benzene solution was suggested by Ghatak *et al* (1974) as due to the formation of weak bond between π -electron of the ring and hydrogen atom of the methoxy group.

The -S-CH₃ group in thioanisole is similar to the -O-CH₃ group in anisole. It will be interesting to compare the dielectric behaviour of the two molecules in the pure liquid state. With this object in view, investigations on microwave absorption in thioanisole in the liquid state were carried out in the wavelength regions 3.49 cm., 3.17 cm., 1.62 cm., 1.25 cm. and 8 mm. The results are presented and discussed in the present communication.

Chemical : A pure sample of thioanisole was obtained from EGA Chemie (West Germany). It was distilled under reduced pressure before use in the investigations.

2. EXPERIMENTAL

The dielectric permittivity ϵ' and dielectric loss ϵ'' at different microwave frequencies were measured by Suber's (1948) method.

The static dielectric constant ϵ_0 was measured at 1 MHz/sec obtained from an crystal controlled oscillator, the refractive index n_D was determined with an Abbe refractometer and the viscosity η and density d were measured with an Ostwald viscometer and a picnometer respectively.

All the dielectric data were obtained at temperatures 30, 50 and 70°C. The temperature of each experiment was controlled within $\pm 1^\circ\text{C}$ by a thermostat.

3. RESULTS

The values of ϵ' and ϵ'' obtained at different microwave regions and at different temperatures together with the values of ϵ_0 and viscosity (η) and density (d) at different temperatures are given in table 1.

Table 1. Values of ϵ_0 , ϵ' , ϵ'' , η and d for thioanisole at different temperatures

λcm	3.49		3.17		1.626		1.249		0.83		η	d gm/cc	
	ϵ_0	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'			ϵ''
30	4.88	4.41	0.57	4.39	0.58	3.83	0.64	3.63	0.61	3.37	0.53	1.05	1.05
50	4.65	4.30	0.51	4.28	0.52	3.80	0.61	3.65	0.60	3.38	0.53	0.80	1.03
70	4.53	4.20	0.50	4.17	0.51	3.80	0.58	3.67	0.57	3.40	0.51	0.54	1.01

The Cole-Cole arc plots (shown in figure 1) were drawn in the complex plane and the high frequency dielectric constant ϵ_∞ and the distribution parameter α were obtained from the arc plots as usual. Appreciable value of the distribution parameter at all temperatures as also the curvature in the plot of ϵ' vs $\epsilon''w$ indicated the presence of more than one relaxation mechanism.

So the dielectric data were analysed in terms of two relaxation processes by straight forward calculations using equations due to Kasta (1968) and used successfully by others (Ghatak *et al* 1974, Bhattacharyya *et al* 1970, Kasta *et al* 1969, Hasan *et al* 1971). The values of τ_1 and τ_2 at different temperatures together with the weight factor C_2 are given in table 2. The activation energies for dielectric relaxation for the molecular orientation $\Delta H\tau_1$ and for group rotation $\Delta H\tau_2$ were obtained from the straight line plots of $\log \tau_1 T$ vs $1/T$ and $\log \tau_2 T$ vs $1/T$ respectively. The activation energy for viscous flow $\Delta H\eta$ was obtained

from the plots of $\log \eta$ vs $1/T$. The values of $\Delta H\tau_1$, $\Delta H\tau_2$, $\Delta H\eta$, α , n_D^2 and dipole moment (m) are included in table 2.

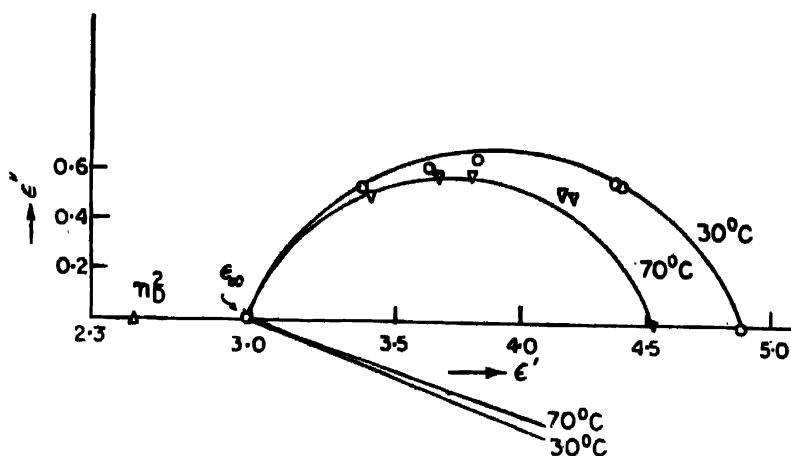


Fig. 1. Cole-Cole are plot of thioanisole

4. DISCUSSIONS

From table 2 it can be seen that both the molecular and intramolecular relaxation times decrease with the increase of temperature as is generally observed. The intramolecular relaxation time τ_2 is found to be much less dependent on temperature and consequently on viscosity than the molecular relaxation time. This shows that the groups are well shielded from the influence of neighbouring molecules. The molecular relaxation time τ_1 of about 22 p.sec at 30°C in the liquid thioanisole obtained in the present investigations is larger than the value of $\tau_1 = 15$ p.sec at 20°C either in the liquid anisole (Garg & Smyth 1967) or its solution in benzene (Forest & Smyth 1964, Farmer & Walker 1969, Klages & Krauss 1971). This is consistent with the sizes of the molecules. The $-S-CH_3$ group relaxation time $\tau_2 = 3$ p.sec at 30°C in the present case compares well with the $-O-CH_3$ group relaxation time of 3 p.sec at 20°C in the liquid anisole.

Table 2. Values of α , ϵ_∞ , n_D^2 , τ_1 , τ_2 , $\Delta H\tau_1$, $\Delta H\tau_2$, $\Delta H\eta$ and moment m

Temp °C	α	n_D^2	$\tau_1 \times 10^{12}$ in sec.	$\tau_2 \times 10^{12}$ in sec.	C_2	$\Delta H\tau_1$ in k.cal/mole	$\Delta H\tau_2$ in k.cal/mole	$\Delta H\tau_n$ in k.cal/mole	Mean moment m in D
30	0.24	2.91	2.50	22.7					
50	0.23	2.90	2.46	16.7	0.63	2.01	0.77	2.54	1.32
70	0.22	2.91	2.43	13.1					

It is interesting to note that the weight factor C_2 for group rotation in thioanisole (table 2) is about 0.63 which is much larger than the $C_2 = 0.2$ in the case of liquid anisole. So it appears that the $-S-CH_3$ group rotation in thioanisole in the liquid state is much less hindered than the $-O-CH_3$ group rotation in anisole in the liquid state.

This is also supported by the fact that the activation energy for $-O-CH_3$ group rotation in the liquid anisole is about 1.5 k.cal/mole (Garg & Smyth 1967) which is much larger compared to the $\Delta H\tau_2 = 0.770$ k.cal./mole for $-S-CH_3$ group rotation in thioanisole in the liquid state. The weight factor C_2 for group rotation in thioanisole can be estimated from dipole moment considerations. For this purpose the dipole moment of thioanisole in the liquid state was calculated by using Onsager equation (Smyth 1955) from the measured values of static dielectric constant ϵ_0 , refractive index n_D and density (d) of the liquid. It is found to be 1.32 D , which compares well with the literature value (Smyth 1955) of 1.27 D . The weight factor C_2 is given by the ratio of the square of dipole moment component perpendicular to the axis of rotation (C-S axis) to the square of the total moment of the molecule i.e.,

$$C_2 = \frac{(1.32 \sin 57^\circ)^2}{(1.32)^2} = 0.70,$$

where 57° (Smyth 1955) is the angle made by the group moment with the C-S axis.

Thus the theoretical values of $C_2 = 0.7$ for $-S-CH_3$ group rotation agrees well with the experimentally obtained value of 0.63.

This supports the earlier conclusion that the $-S-CH_3$ group rotation in the liquid thioanisole is more or less free unlike the case of $-O-CH_3$ group rotation in anisole in the liquid state.

The appreciable difference between the values of ϵ_∞ and n_D^2 (table 2) indicates the presence of a third absorption region in mm. wavelength region of the type of *Poley absorption* (Poley 1955).

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