

CHAPTER 5

MICROWAVE ABSORPTION AND RELAXATION PROCESSES IN THIOANISOLE IN THE LIQUID STATE

5.1 Introduction

In Chapters 3 and 4, the dielectric behaviour of aromatic molecules with groups $-SH$, $-CH_2SH$, $-OCH_3$ and $-OC_2H_5$ were discussed. In this chapter the results of dielectric absorption in thioanisole in the liquid state is presented and discussed.

Molecular and intramolecular relaxations have been reported in anisole^{1,2} and thiophenol³ both in the liquid state. It was reported that, whereas molecular reorientation is the major relaxation mechanism in anisole^{1,2} in the liquid state, in the thiophenol³ in the liquid state, intramolecular rotation is the major relaxation process. The $S-CH_3$ group in thioanisole has got similarity with $O-CH_3$ group in anisole and $-SH$ group in thiophenol. It will be interesting to compare the dielectric behaviour of thioanisole in the liquid state with those of anisole and thiophenol in the liquid state reported earlier¹⁻³.

5.2 Results

The values of ϵ' and ϵ'' obtained at different microwave frequencies at different temperatures, together with the values of ϵ_0 at different temperatures are given in Table.5.1. The Cole-Cole arc plots (Fig.5.1A) 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 ϵ''/ω indicated the presence of more than one relaxation mechanisms.

So the dielectric data were analysed in terms of two relaxation processes by a straight forward calculation using equations due to Kasha⁴ and used successfully by others⁵⁻⁷. The values of $\tau_1, \tau_2, \alpha, \epsilon_{\infty}, \tau_D^2$ density (d) and viscosity (η) are given in Table 5.2. 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 $\log(\tau\tau_1)$ vs $1/T$ and $\log(\tau\tau_2)$ vs $1/T$ respectively (Fig.5.2.).

Table 5.1

Observed values of dielectric permittivity and dielectric loss of Jhioanisole

T ^o C	f = 1MHz	f = 86 GHz		f = 9.5 GHz		f = 18.4 GHz	
	ϵ_0	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
30	4.88	4.41	0.57	4.39	0.53	3.83	0.64
50	4.65	4.30	0.51	4.28	0.52	3.80	0.61
70	4.53	4.20	0.50	4.17	0.51	3.80	0.58
		f = 24.00 GHz		f = 36.1 GHz			
30	4.88	3.63	0.61			3.37	0.53
50	4.65	3.65	0.60			3.38	0.53
70	4.53	3.67	0.57			3.40	0.51

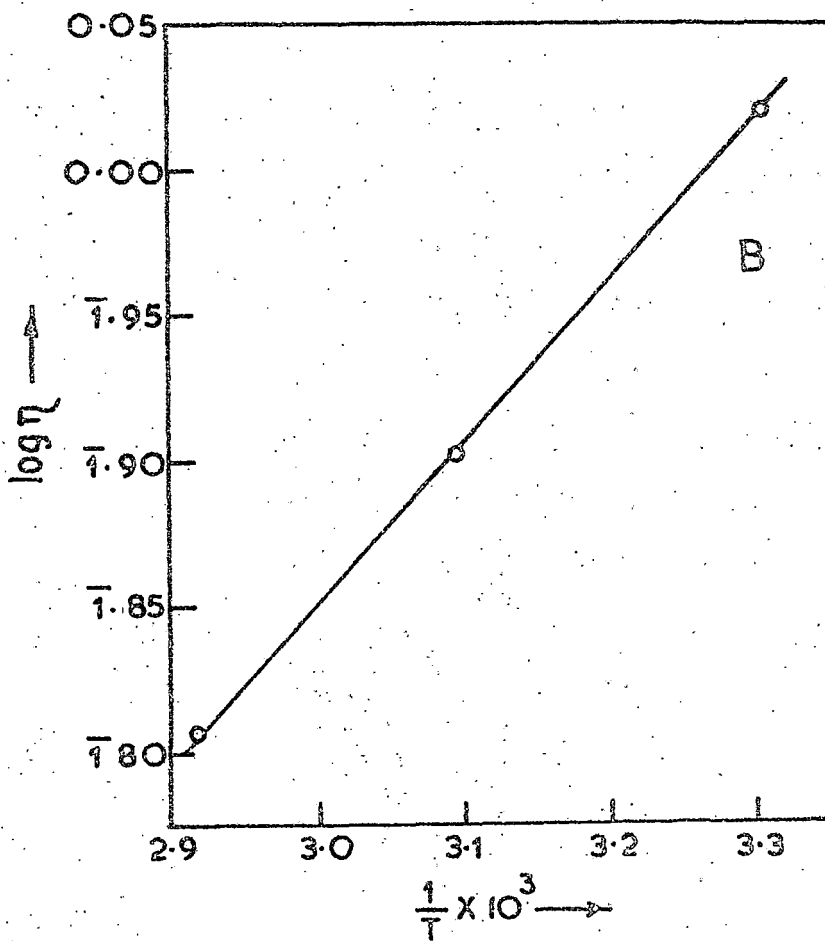
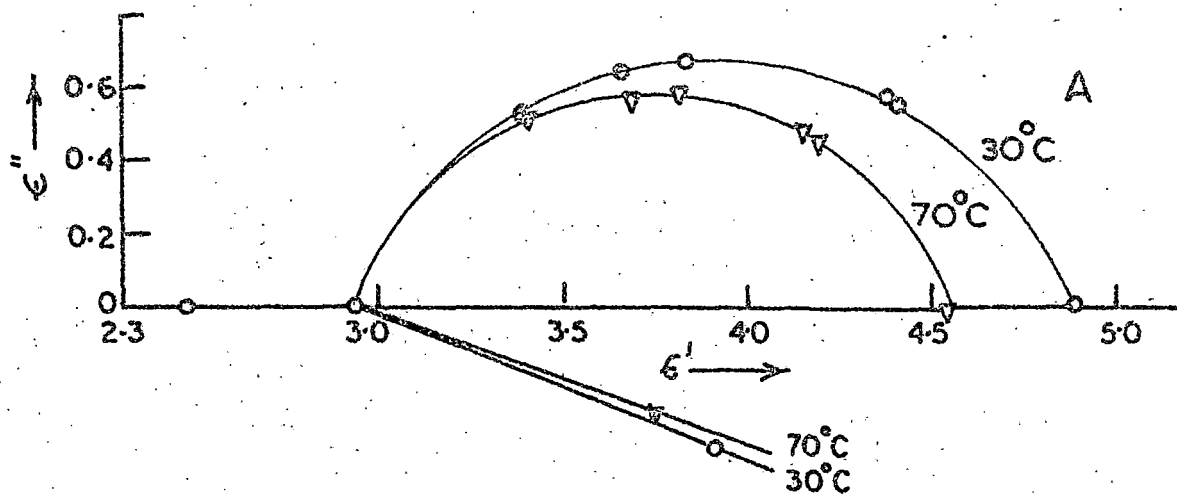


FIG. 5.1

- A. Cole-Cole arc plot of thioanisole
 B. Plot of $\log \eta$ vs. $1/T$ of thioanisole

The activation energy for viscous flow $\Delta H\eta$ was obtained from the plots of $\log \eta$ vs $1/T$ (Fig. 5.18). The values of ΔHc_1 , ΔHc_2 , $\Delta H\eta$, C_1 and dipole moment μ_D are included in Table 5.3.

5.3 Discussion

From Table 5.2 it can be seen that both the molecular and intramolecular relaxation times decrease with the increase of temperature as are 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 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 (Table 5.2) is comparable with molecular relaxation time

$\tau_1 = 23$ p.sec at 30°C in thiophenol³ in the liquid state but larger than the value of $\tau_1 = 15$ p.sec at 20°C either in liquid anisole^{1,2} or its solution in benzene (14 p.sec at 25°C)⁸⁻¹⁰. This is consistent with the sizes of the molecules.

Table 5.2

Values of density (d), viscosity (η) $\propto \tau_D^2$, ϵ_∞
 τ_1 and τ_2

T°C	d gm/cc	η c.p	α	τ_D^2	ϵ_∞	$\tau_1 \times 10^{12}$ Sec	$\tau_2 \times 10^{12}$ Sec
30	1.05	1.05	.24	2.50	2.91	22.7	3.00
50	1.03	0.80	.23	2.46	2.95	16.7	2.70
70	1.01	0.54	.22	2.43	2.91	13.1	2.20

The S-CH₃ group relaxation time τ_2 of 3 p.sec at 30°C in the present case compares well with the OCH₃ group relaxation time of 3 p.sec at 20°C in the anisole^{1,2} and -SH group relaxation time of 2.7 p.sec in thiophenol³ both in the liquid state. It is interesting to note that the weight factor $C_2 = .63$ for the -SCH₃ group rotation in the liquid thioanisole (Table 5.3) agrees well with the $C_2 \approx .7$ in thiophenol³ in the liquid state, but it is much larger than the value of $C_2 \approx .2$ for the O-CH₃ group rotation in liquid anisole^{1,2}. The reduction in the C_2 value of the O-CH₃ group rotation in the liquid anisole^{1,2} from its value of $C_2 \approx .7$ in benzene solution⁸⁻¹⁰ was attributed by Garg and Smyth¹ to some hindrances of the OCH₃ group rotation in the liquid anisole. Such hindrance of the SCH₃ group rotation in thioanisole or the SH group rotation in thiophenol in the liquid state is almost absent.

Table 5.3

Values of C_2 , μ , ΔHc_1 , ΔHc_2 and $\Delta H\tau$.

C_2	μ Debye	ΔHc_1 Kcal/mole	ΔHc_2 Kcal/mole	$\Delta H\tau$ Kcal/mole
0.63	1.32	2.01	0.77	2.54

The weight factor C_2 for the group rotation in thioanisole can be estimated from the dipole moment considerations. The dipole

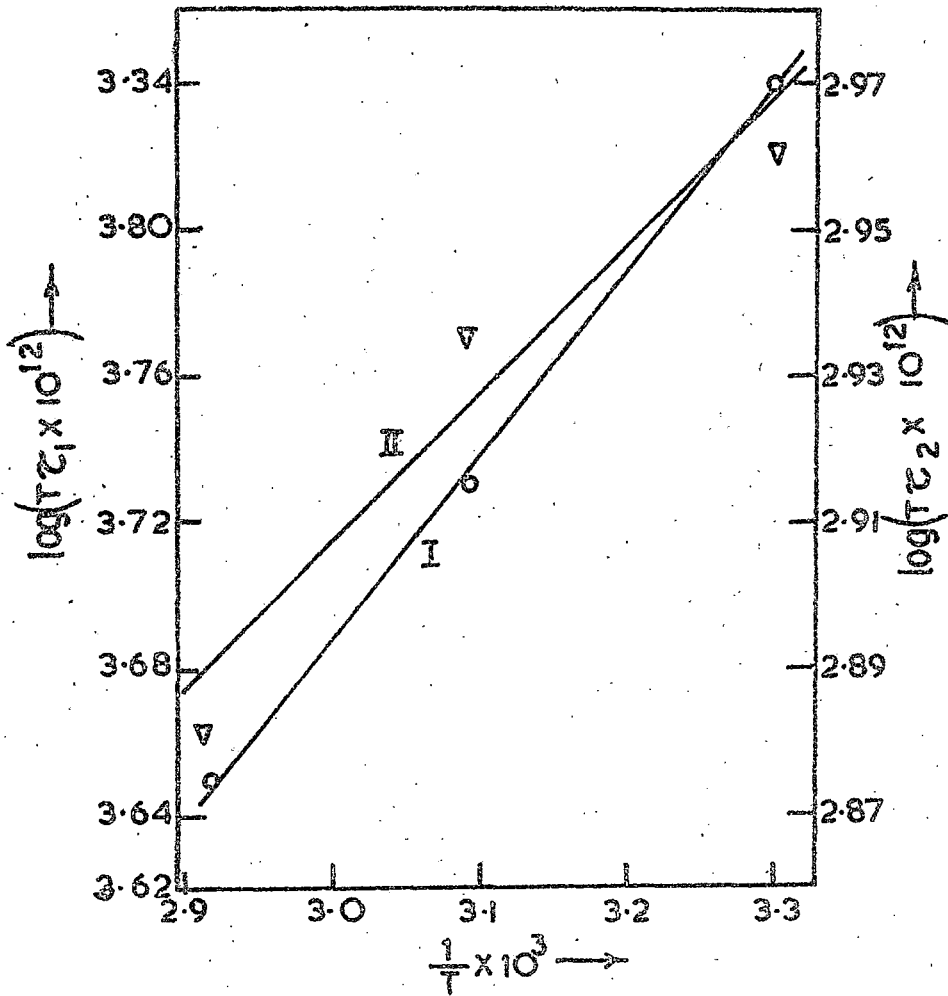


FIG. 5.2

- I. Plot of $\log(\tau c_1)$ vs. $1/T$ for thioanisole
 II. Plot of $\log(\tau c_2)$ vs. $1/T$ for thioanisole

moment in the liquid thioanisole (Table 5.3) is found to be 1.32 D, which compares well with the literature value of 1.27D¹¹. 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.

$$C_2 = \frac{(1.32 \sin 57^\circ)^2}{(1.32)^2} = .70$$

where the angle made by the group moment with the C-S axis is 57° reported by Smyth¹¹.

Thus the theoretical value of $C_2 = .7$ for the S-CH₃ group rotation agrees fairly well with the experimental value of .63.

This supports the earlier conclusion that the S-CH₃ group rotation in the liquid thioanisole is more or less free unlike the case of O-CH₃ group rotation in anisole in the liquid state.

This is also supported by the fact that the potential energy barrier ($\Delta H_{C_2} = 1.5$ Kcal/mole) for O-CH₃ group in the liquid anisole¹ is much larger than the corresponding energy barriers to group rotation in thiophenol ($\Delta H_{C_2} = .81$ Kcal/mole) or in thioanisole ($\Delta H_{C_2} = .77$ Kcal/mole) both in the liquid state. The appreciable difference between the values of ϵ_∞ and n_D^2 (Table 5.2) indicates the presence of a third absorption region in the submillimeter wavelength region of the type of Poley absorption¹².

References

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