

CHAPTER 3

RELAXATION MECHANISMS IN HALOTHIOPHENOLS IN THE LIQUID STATE

3.1 Introduction

Studies on intramolecular rotation in various polar groups in aromatic molecules in dilute solution and in polar liquids were reported by many workers¹⁻³. Such studies on intramolecular rotation of the SH group in organic molecules are rather few. Fong and Smyth⁴ reported the intramolecular rotation of the SH group in naphthalenethiol in dilute benzene solution. Recently Hasan et al.⁵ reported that the SH group rotation is the major relaxation process in benzenethiol and benzylthiol in the liquid state. From a comparison of the values of SH group relaxation time τ_2 and its weight factor C_2 in benzene- and benzylthiols with the corresponding τ_2 and C_2 values for OH group rotation in phenols and substituted phenols reported by Aihara and Davies⁶, Hasan et al.⁵ concluded that the intermolecular hydrogen bonding S-H...S are negligible in the thiophenols even in the liquid state.

The object of the present investigation was ^{to} extend ~~to~~ similar studies in p-halothiophenols in the liquid state and compare the results with the corresponding halophenols. The results in the case of 4-chlorothiophenol, 4-chloro- α -toluol thiol and 4-bromo-3-methylthiophenol are presented and discussed in this chapter.

3.2 Results

The experimental values of dielectric permittivity ϵ' and dielectric loss ϵ'' at different microwave frequencies together with the values of static dielectric constants ϵ_0 at different temperatures are presented in Tables 3.1 - 3.3. These data were then fitted in Cole-Cole arc plots (Fig.3.1). The high frequency dielectric constant ϵ_∞ and the distribution parameter α were obtained as usual from the arc plots. The values of α were found appreciably high at all temperatures, indicating the presence of more than one relaxation process. The dielectric data were, therefore, analysed in terms of two relaxation processes by the method of least squares as described below.

Method of analysis

Bergmann's⁷ equation for the two relaxation processes are

$$a = \frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{c_1}{1 + (\omega\tau_1)^2} + \frac{c_2}{1 + (\omega\tau_2)^2} \quad (3.1)$$

and

$$b = \frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = \frac{c_1 \omega\tau_1}{1 + (\omega\tau_1)^2} + \frac{c_2 \omega\tau_2}{1 + (\omega\tau_2)^2} \quad (3.2)$$

and the simplified equation⁸ obtained from eqns.(3.1) and (3.2) is

$$\frac{1-a}{b\omega} = \tau_1 + \tau_2 - \frac{a\omega}{b} \tau_1 \tau_2 \quad (3.3)$$

the eqn.(3.3) with the dielectric data at several microwave frequencies can be written in the form

$$\sum_{i=1}^n Sx_i - Py_i - 1 = 0 \quad (3.4)$$

where $S = c_1 + c_2$, $p = c_1 c_2$, $x = \frac{b\omega}{1-a}$ and $y = \frac{a\omega^2}{1-a}$

This is a linear equation and was solved by the method of least squares (Noy et al.⁹). From the principle of least square it can be easily shown from eqn.(3.4) that

$$S = \frac{\sum_{i=1}^n y_i \sum_{i=1}^n x_i y_i - \sum_{i=1}^n x_i \sum_{i=1}^n y_i^2}{\left(\sum_{i=1}^n x_i y_i\right)^2 - \sum_{i=1}^n x_i^2 \sum_{i=1}^n y_i^2} \quad (3.5)$$

$$p = \frac{\sum_{i=1}^n y_i \sum_{i=1}^n x_i^2 - \sum_{i=1}^n x_i \sum_{i=1}^n x_i y_i}{\left(\sum_{i=1}^n x_i y_i\right)^2 - \sum_{i=1}^n x_i^2 \sum_{i=1}^n y_i^2} \quad (3.6)$$

Solving eqns. (3.5) and (3.6), c_1 and c_2 can be concluded. The value c_1 is then obtained from the eqns.(3.1) and (3.2) by applying the least squares principle.

$$c_1 = \frac{\sum_{i=1}^n a_i f_i + \sum_{i=1}^n b_i g_i - \sum_{i=1}^n f_i f'_i - \sum_{i=1}^n g_i g'_i}{\sum_{i=1}^n f_i^2 + \sum_{i=1}^n g_i^2} \quad (3.7)$$

where $f_i = (f_i - f')$, $f_1 = \frac{1}{1 + \omega^2 c_1^2}$, $f' = \frac{1}{1 + \omega^2 c_2^2}$
 $g_i = (g_i - g')$, $g_1 = \frac{\omega c_1}{1 + \omega^2 c_1^2}$, $g' = \frac{\omega c_2}{1 + \omega^2 c_2^2}$

The value of ϵ_{∞} as obtained from Cole-Cole plot may not coincide with the actual value in eqns.(3.1) and (3.2), but it will be between the n_D^2 -value and ϵ' -value obtained at the highest microwave frequency used. So, to start with, any value for ϵ_{∞} within the above limit is assumed and τ_1, τ_2 and C_1 values are determined. With these values of τ_1, τ_2 and C_1 the values of ϵ' and ϵ'' are calculated from eqns.(3.1) and (3.2). The value of ϵ_{∞} is then varied and the process is repeated till the mean square deviation A from the relation

$$A = \sum (\epsilon''_{obs} - \epsilon''_{cal})^2 + \left(\frac{\epsilon'_{obs} - \epsilon'_{cal}}{n} \right)^2$$

is found to be minimum. The 'n' is a scaling factor to reduce the error in ϵ' to the same magnitude of the error in ϵ'' . A value of $n = 3$ is used in the present case.

Table 3.1

Observed and calculated values of dielectric permittivity and dielectric loss

4-chlorothiophenol										
T°C	f = 1 MHz		f = 8.6 GHz		f = 18.5 GHz		f = 24.03 GHz		f = 35.13 GHz	
	ϵ_0	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{cal}	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{cal}	
65	3.59	3.43	3.40	0.20	0.22	3.27	3.27	0.21	0.21	
85	3.52	3.40	3.39	0.18	0.18	3.26	3.27	0.20	0.20	
65	3.59	3.22	3.23	0.20	0.20	3.16	3.18	0.18	0.18	
85	3.52	3.23	3.23	0.19	0.19	3.18	3.18	0.18	0.18	

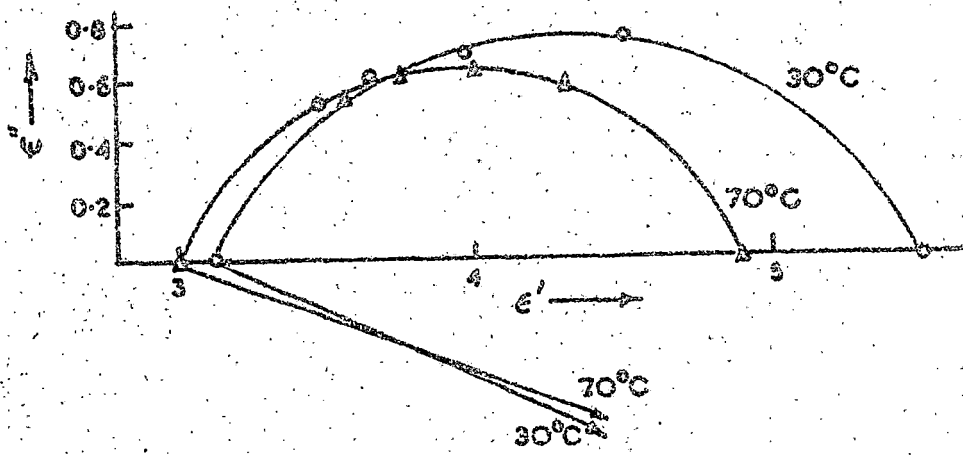
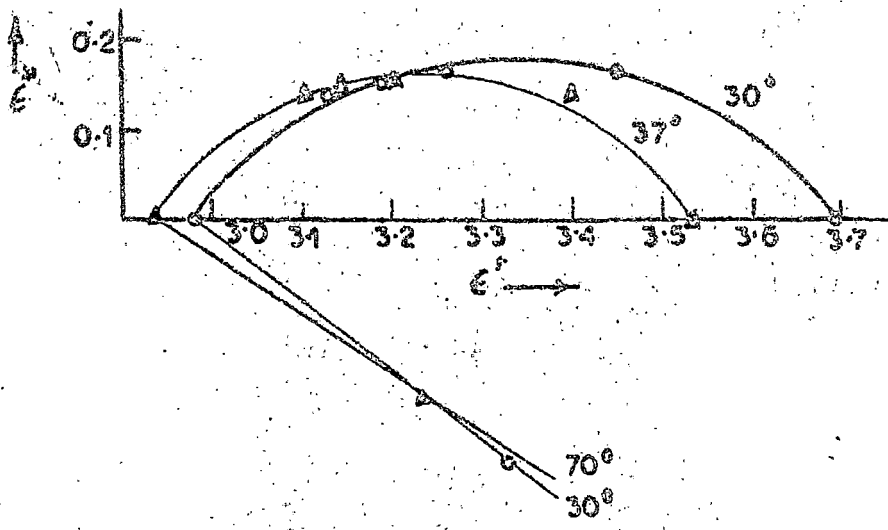
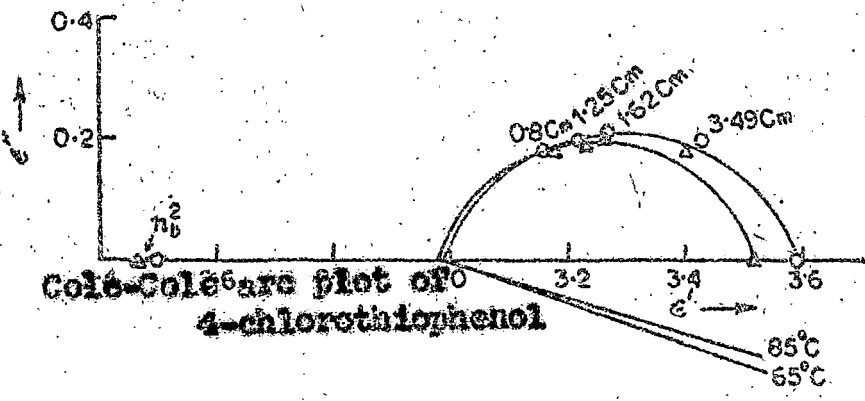


Fig. 3-1

The values of n_D^2 , ϵ_∞ , α , τ_1 , τ_2 , τ and C_1 are given in Table 3.4. All the calculations were carried out on the IBM computer 1130. The calculated values of ϵ' and ϵ'' are also included in Tables 3.1 - 3.3 for comparison. The activation

Table 3.2

Observed and calculated values of dielectric permittivity and dielectric loss

4-bromo-3-methylthiophenol									
T°C	f = 1 MHz		f = 8.6 GHz			f = 18.3 GHz			
	ϵ_0	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{cal}	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{cal}
30	3.70	3.45	3.33	0.16	0.19	3.26	3.26	0.16	0.16
50	3.61	3.42	3.31	0.15	0.19	3.23	3.24	0.16	0.16
70	3.53	3.40	3.30	0.14	0.19	3.20	3.21	0.16	0.16
f = 24.4 GHz					f = 35.14 GHz				
30	3.70	3.19	3.24	0.15	0.16	3.14	3.20	0.14	0.17
50	3.61	3.17	3.21	0.15	0.16	3.12	3.18	0.14	0.16
70	3.53	3.15	3.18	0.15	0.16	3.10	3.15	0.14	0.15

energies for dielectric relaxation and viscous flow were obtained from the straight line plots of $\log(\tau\epsilon)$ vs $1/T$ and $\log \tau$ vs $1/T$ (Figs. 3.2 - 3.3) respectively. The dipole moments were calculated using Onsager Equation. The dipole moment

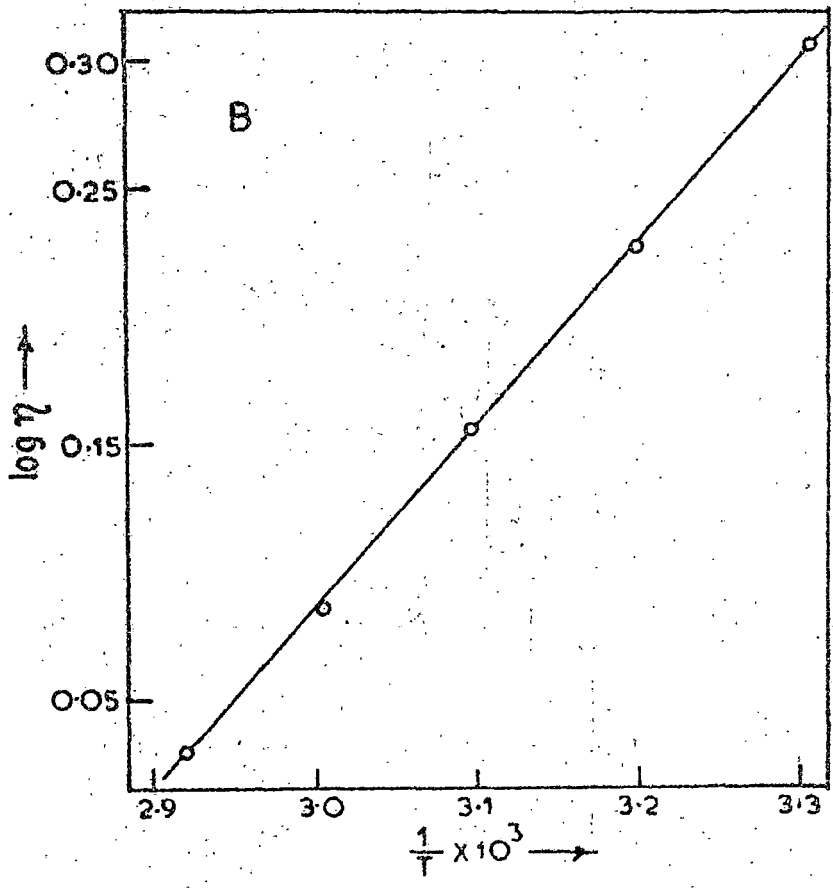
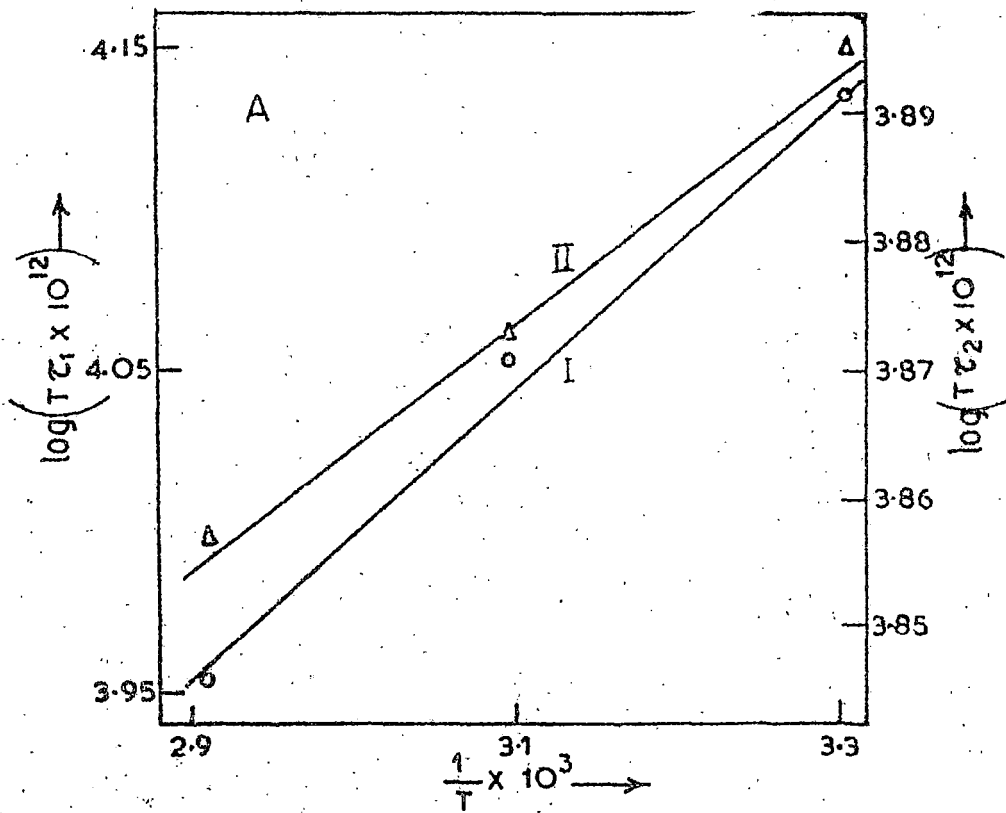


FIG. 3-2

- A. I. Plot of $\log (\tau c_1)$ vs. $1/T$ for 4-bromo-3-methylthiophenol
- II. Plot of $\log (\tau c_2)$ vs. $1/T$ for 4-bromo-3-methylthiophenol
- B. Plot of $\log \eta$ vs. $1/T$ for 4-bromo-3-methylthiophenol

of 4-chlorothiophenol could not be calculated as the density values in this case could not be measured. The viscosity values also could not be measured in this case.

The values of ΔH_{c_1} , ΔH_{c_2} , ΔH_{c_3} and the dipole moment μ_D which is independent of temperature are included in Table 3.5.

Table 3.3

Observed and calculated values of dielectric permittivity and dielectric loss

4-chloro- α -toluolthiol										
T°C	f = 1 MHz		f = 9.6 GHz				f = 18.1 GHz			
	ϵ_0	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{cal}	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{cal}	
30	5.50	4.50	4.24	0.75	0.81	3.96	3.93	0.70	0.70	
50	5.22	4.40	4.23	0.70	0.75	3.96	3.92	0.66	0.65	
70	4.90	4.32	4.24	0.58	0.64	4.00	3.93	0.64	0.63	
f = 24.20 GHz										
f = 36.15 GHz										
30	5.50	3.66	3.81	0.62	0.66	3.48	3.63	0.56	0.61	
50	5.22	3.72	3.81	0.60	0.62	3.54	3.65	0.53	0.58	
70	4.90	3.76	3.82	0.62	0.62	3.56	3.65	0.55	0.59	

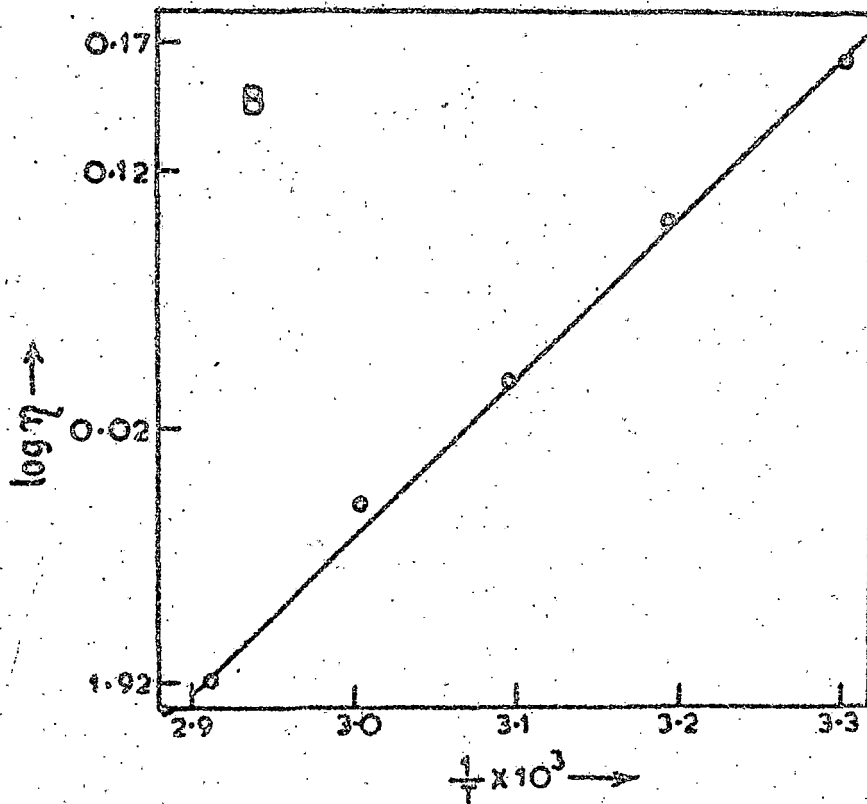
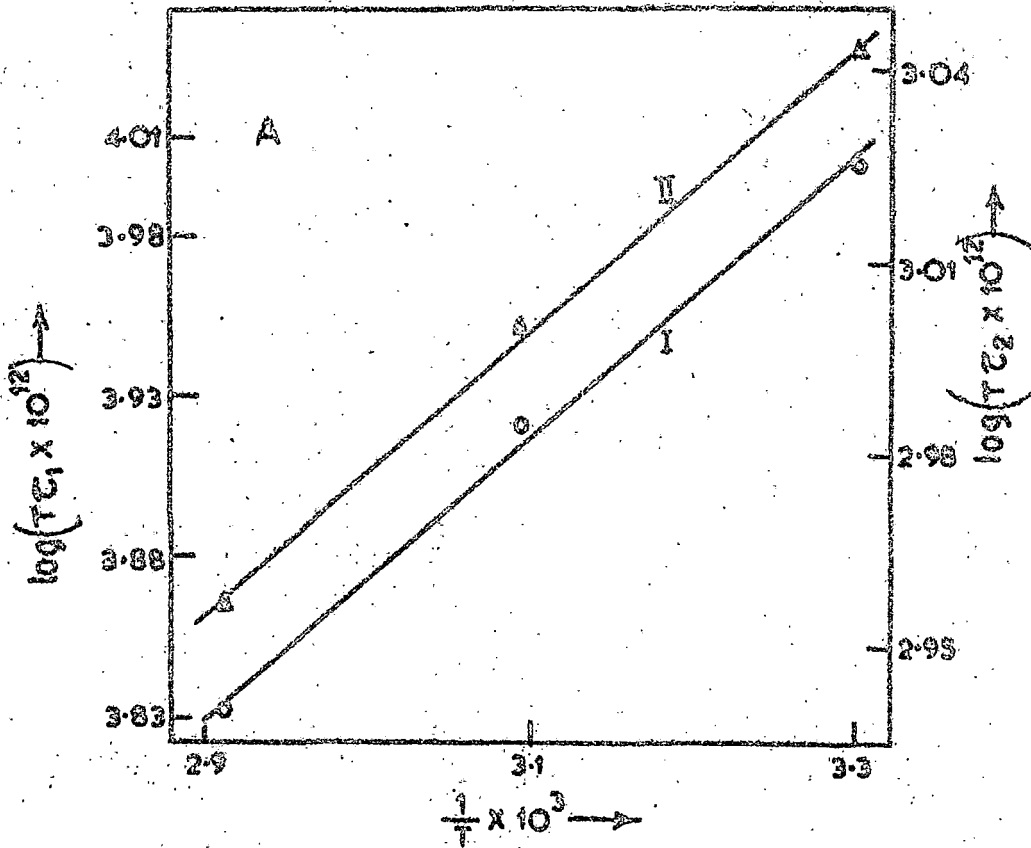


FIG. 3-3

- A. I. Plot of $\log(TC_1)$ vs. $1/T$ for 4-chloro- α -toluolthiol
 II. Plot of $\log(TC_2)$ vs. $1/T$ for 4-chloro- α -toluolthiol
 B. Plot of $\log \eta$ vs. $1/T$ for 4-chloro- α -toluolthiol

3.3 Discussion

It can be seen from the Table 3.4 that the molecular relaxation time (τ_1) and intramolecular relaxation time (τ_2) in the halosubstituted thiophenols in the liquid state as also the distribution parameter α decrease with increase in temperature as is generally observed in polar liquids.

The reduced relaxation time (τ_1/η) of 4-bromo-3-methylthiophenol and 4-chloro- α -toluolthiol at 30°C are about 22 and 24 p.sec respectively, showing thereby that the two molecules are of similar sizes. The intramolecular relaxation times τ_2 for SH group rotation in the 4-chlorothiophenol and 4-bromo-3-methylthiophenol in the liquid state are also nearly equal (2.4 - 2.8 p.sec) and compare well with SH group relaxation time of 2.5 p.sec in naphthalenethiol⁴ in dilute solution in benzene. Thus it is found that the SH group relaxation time in pure liquid as also in dilute solution are almost the same. This shows the intermolecular hydrogen bonding S-H...S, of the type hydroxyl hydrogen bonding O-H...O observed in phenols and substituted phenols reported earlier¹⁰ are negligible in halothiophenols even in the pure liquid state. The CH₂SH group relaxation time of 3.6 p.sec at 30°C in 4-chloro- α -toluolthiol compares well with the CH₂SH group relaxation time of 3.1 p.sec in benzylthiol⁵ in the liquid state at 30°C.

Table 3.4

Values of n_D^2 , ϵ_α , τ_1 , τ_2 , C_1 and η

$T^\circ C$	n_D^2	ϵ_α	α	$\tau_1 \times 10^{12}$ Sec	$\tau_2 \times 10^{12}$ Sec	C_1	η
4-chlorothiophenol							
65	2.50	3.00	0.21	17.7	2.8	0.63	
85	2.47	2.99	0.19	14.2	2.4	0.62	
4-bromo-3-methylthiophenol							
30	2.60	2.93	0.49	44.44	2.60	0.60	2.05
50	2.56	2.95	0.46	35.67	2.30	0.58	1.43
70	2.52	2.94	0.43	26.10	2.10	0.53	1.09
4-chloro-α-toluolthiol							
30	2.51	3.12	0.29	32.00	3.65	0.66	1.45
50	2.48	3.10	0.27	25.80	3.10	0.64	1.08
70	2.45	3.00	0.24	19.90	2.65	0.57	0.84

It would be interesting to compare the τ_1 and τ_2 values of the halothiophenols with those of halophenols in dilute solution in p-xylene¹⁰. The molecular relaxation time τ_1 of 39 p.sec at 25°C in 4-chlorophenol⁸ in dilute solution is only slightly less than the τ_1 of 44 p.sec in 4-bromo-3-methylthiophenol and slightly larger than the τ_1 of 32 p.sec in 4-chloro- α -toluolthiol, at 30°C both in the liquid state. But the OH group relaxation time τ_2 of 8.4 p.sec in 4-chlorophenol is much larger than the relaxation time of the SH (2.6 p.sec) or CH₂SH (3.6 p.sec) group in the present halothiophenols. The unusual lengthening of the OH group relaxation time in 4-halophenols was attributed by Magee and Walker¹⁰ to association among the solute molecules in addition to the effects of solvents. It may be noted here that the free hydroxyl relaxation time in naphthol in benzene⁴ and 2,6-dimethylphenol in benzene¹¹ is reported to be about 3.4 p.sec which compares well with the SH group relaxation time observed in the present case.

Weight factors

It can be seen from the Table 3.4 that the weight factor for the molecular reorientation in the three liquids is about 0.6 which shows that the molecular reorientation is the major relaxation mechanisms in all the liquids. An estimate for the weight factor for SH group rotation may be made from bond moment considerations. The SH group having a moment .7 D is

inclined at an angle 135° ¹² to the C-S bond in 4-bromo 3 methyl thiophenol and 4-chlorothiophenol. The moment component responsible for the SH group rotation in both is $.7 \sin 45 = .5D$. The observed moment of 4-bromo-3 methylthiophenol is $.95 D$. So the weight factor

$$C_2 = \frac{\mu_2^2}{\mu^2} = .28$$

∴ $C_1 = .72$

Assuming the bond moments $\mu_{C-S} = 0.9D$, $\mu_{H-S} = .70 D$, $\mu_{C-Cl} = 1.5D$ the moment component μ_1 responsible for the molecular reorientation in 4-chlorothiophenol is $1.1D$.

So
$$C_2/C_1 = \frac{\mu_2^2}{\mu_1^2} = \left(\frac{.5}{1.1}\right)^2$$

hence $C_1 = .73$

Thus the theoretical C_1 values is slightly larger than the experimentally observed values of 0.6 in each case and this may be due to mesomeric change shift across the molecules¹³.

Table 3.5

Compounds	$\Delta H\eta$ KCal/mole	$\Delta H\epsilon_1$ KCal/mole	$\Delta H\epsilon_2$ KCal/mole	μ Debye
4-chlorothiophenol				1.4
4-bromo-3-methyl thiophenol	3.29	2.00	0.5	0.99
4-chloro- thiol -toluol	2.95	1.80	0.80	1.54

Potential barriers to molecular, intramolecular rotation and viscous flow (ΔH_{c_1} , ΔH_{c_2} , ΔH_{η})

It can be seen from the Table 3.5 that the potential barrier for molecular reorientation (ΔH_{c_1}) in 4-bromo-3 methyl thiophenol is about 2 Kcal/mole is, as usual, less than the corresponding activation energy (ΔH_{η}) of 3.3 Kcal/mole for viscous flow. This is also true in the case of 4-chloro- α - toluolthiol. The energy barrier to group rotations are about 0.5 and 0.8 Kcal/mole respectively in 4-bromo-3 methylthiophenol and 4-chloro- α -toluolthiol. These values are much smaller than the corresponding potential barriers for molecular orientation. The groups are therefore more flexible to rotate than the molecules in the present cases.

Dipole moments

The observed values of dipole moments (Table 3.5) in 4-bromo-3 methylthiophenol and 4-chloro- α -toluolthiol are 0.95 and 1.54 D respectively. These values compare well with the moment values of 1.2 and 1.5 D, calculated from bond moments and bond angles calculation in the two molecules.

In all the thiophenols the values of ϵ_{α} is appreciably larger than the corresponding n_D^2 values. This indicates the presence of a third dispersion region of 'Foley type' in the submillimeter region.

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