March, 1976]   BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(3), 663—665 (1976)   663

Dielectric Relaxation in *p*-Substituted Thiophenols in the Liquid State

Subir K. Roy, Kamalendu Sengupta, and S. B. Roy
Optics Department, Indian Association for the Cultivation of Science, Calcutta-32, India

(Received April 21, 1975)

The dielectric absorption in 4-methylthiophenol and 4-chlorothiophenol in the liquid state has been studied in 0.8, 1.25, 1.62 and 3.49 cm microwave regions. Molecular and intramolecular relaxation times, their relative weight factors and the heats of activation have been determined. The results have been discussed and compared with other related molecules.

Intramolecular rotation of various polar groups in aromatic molecules[1–3] in dilute solutions and in pure liquids has been studied extensively. Such studies of intramolecular rotation of SH group in organic molecules are rather few. Fong and Smyth[4] reported the intramolecular rotation of SH group in naphthalenethiol in dilute benzene solution. Recently, Hasan *et al.*,[5] from studies of dielectric relaxation in benzenethiol and benzylthiol in the liquid state reported that intramolecular rotation of the SH group was the main relaxation process in both the thiophenols. From a comparison of the values of SH group relaxation time τ_2 and its weight factor C_2 in the thiophenols, with the corresponding τ_2 and C_2 values for OH group rotation in phenols and substituted phenols reported by Aihara and Davies,[6] 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 investigations was to extend similar studies in the case of *p*-substituted thiophenols in the liquid state and compare the results with the corresponding *p*-substituted phenols. The results obtained in the case of 4-methylthiophenol and 4-chlorothiophenol are presented and discussed in this paper.

Experimental

The apparatus for the measurements of dielectric permittivity ε', dielectric loss ε'' in the region 0.8, 1.25, 1.62 and 3.49 cm microwaves were described earlier.[7] The static dielectric constant ε_0 was measured at 1 MHz, the refractive index n_D was determined with an Abbe refractometer, the viscosity η was measured with an Ostwald viscometer and the density d with a pycnometer. The temperature in each experiment was kept constant within ±1 °C by means of a thermostat. The estimated errors in ε' and ε'' are about 2% and 4% respectively.

Results

The experimental values of ε' and ε'' at different microwave frequencies together with the values of ε_0 at different temperatures are given in Table 1. These data were then fitted in Cole-Cole arc plots (Fig. 1). The high frequency dielectric constant ε_∞ and the distribution parameter α were obtained as usual from the arc plots. The values of ε_∞ in each case was found much higher than that of $n_D{}^2$. The values of the distribution parameter were appreciably high at all temperatures, indicating the presence of more than one relaxation process. This was confirmed by the non linear plots of ε' vs $\varepsilon''\omega$. The dielectric data were then analysed in terms of two relaxation processes following the equations of Bergmann *et al.*[8] and as simplified by Bhattacharyya *et al.*[9] for straightforward calculations.

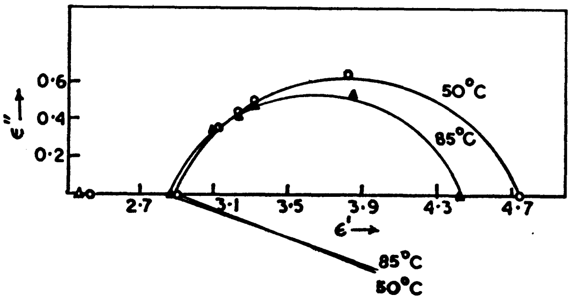

Fig. 1. Cole-Cole arc plot of 4-thiocresol.

Bergmann's equations are

$$a = \frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{C_1}{1+\omega^2\tau_1{}^2} + \frac{(1-C_1)}{1+\omega^2\tau_2{}^2} \tag{1}$$

and

$$b = \frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \frac{C_1\omega\tau_1}{1+\omega^2\tau_1{}^2} + \frac{(1-C_1)\omega\tau_2}{1+\omega^2\tau_2{}^2} \tag{2}$$

The simplified equation[9] is

$$\frac{1-a}{b\omega} = \tau_1 + \tau_2 - \frac{a\omega}{b}\tau_1\tau_2 \tag{3}$$

which can be written in the form

$$\sum_{i=1}^{n} Sx_i - Py_i - 1 = 0 \tag{4}$$

where

$$S = \tau_1 + \tau_2,\ P = \tau_1\tau_2,\ x = \frac{b\omega}{1-a} \text{ and } y = \frac{a\omega^2}{1-a}$$

Eq. (4) is a linear equation and can be solved by the method of least squares. From the principle of least square, it can be easily shown from Eq. (4) that

$$S = \frac{\sum_{i=1}^{n} y_i \sum_{i=1}^{n} x_i y_i - \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i{}^2}{\left(\sum_{i=1}^{n} x_i y_i\right)^2 - \sum_{i=1}^{n} x_i{}^2 \sum_{i=1}^{n} y_i{}^2} \tag{5}$$

$$P = \frac{\sum_{i=1}^{n} y_i \sum_{i=1}^{n} x_i{}^2 - \sum_{i=1}^{n} x_i \sum_{i=1}^{n} x_i y_i}{\left(\sum_{i=1}^{n} x_i y_i\right)^2 - \sum_{i=1}^{n} x_i{}^2 \sum_{i=1}^{n} y_i{}^2}\,. \tag{6}$$

Solving Eqs. (5) and (6), τ_1 and τ_2 can be calculated. The value of C_1 is then determined from the equation given below, obtained from Eqs. (1) and (2) by applying the least square principle.

Table 1. Observed and calculated values of dielectric permittivity ε' and dielectric loss ε''

T °C	Freq. = 8.60 GHz				Freq. = 18.50 GHz				Freq. = 24.03 GHz				Freq. = 35.13 GHz				1MHz
	$\varepsilon'_{\text{obsd}}$	$\varepsilon'_{\text{calcd}}$	$\varepsilon''_{\text{obsd}}$	$\varepsilon''_{\text{calcd}}$	$\varepsilon'_{\text{obsd}}$	$\varepsilon'_{\text{calcd}}$	$\varepsilon''_{\text{obsd}}$	$\varepsilon''_{\text{calcd}}$	$\varepsilon'_{\text{obsd}}$	$\varepsilon'_{\text{calcd}}$	$\varepsilon''_{\text{obsd}}$	$\varepsilon''_{\text{calcd}}$	$\varepsilon'_{\text{obsd}}$	$\varepsilon'_{\text{calcd}}$	$\varepsilon''_{\text{obsd}}$	$\varepsilon''_{\text{calcd}}$	ε_0
								4-Methylthiophenol									
50	3.83	3.68	0.66	0.70	3.32	3.35	0.50	0.51	3.24	3.28	0.44	0.45	3.13	3.20	0.36	0.39	4.74
70	3.85	3.68	0.59	0.66	3.31	3.34	0.48	0.50	3.23	3.27	0.42	0.43	3.12	3.19	0.34	0.36	4.56
85	3.85	3.70	0.54	0.63	3.32	3.37	0.47	0.47	3.24	3.25	0.41	0.41	3.09	3.19	0.32	0.33	4.43
								4-Chlorothiophenol									
65	3.43	3.40	0.20	0.22	3.27	3.27	0.21	0.21	3.22	3.23	0.20	0.20	3.16	3.18	0.18	0.18	3.59
85	3.40	3.39	0.18	0.18	3.26	3.27	0.20	0.20	3.23	3.23	0.19	0.19	3.18	3.18	0.18	0.18	3.52

Table 2. Values of α, ε_∞, τ_1, τ_2, $\Delta H\tau_1$, $\Delta H\eta$ and μ

T °C	α	$n_D{}^2$	ε_∞	$\tau_1\times 10^{12}$ s	$\tau_2\times 10^{12}$ s	C_1	$\Delta H\tau_1$ kcal/mol	$\Delta H\eta$ kcal/mol	μ_D
				4-methylthiophenol					
50	0.23	2.43	2.91	29.7	3.1	0.79	1.31	2.03	1.4
70	0.22	2.40	2.92	25.8	2.6	0.79			
85	0.22	2.38	2.92	22.2	1.9	0.82			
				4-Chlorothiophenol					
65	0.21	2.50	3.00	17.7	2.8	0.63	2.00	—	—
85	0.19	2.47	2.99	14.2	2.4	0.62			

$$C_1 = \frac{\sum_{i=1}^{n} a_i f_i + \sum_{i=1}^{n} b_i g_i - \sum_{i=1}^{n} f_i f_i' - \sum_{i=1}^{n} g_i g_i'}{\sum_{i=1}^{n} f_i^2 + \sum_{i=1}^{n} g_i^2} \tag{7}$$

where

$$f_i = (f_1 - f'),\ f_1 = \frac{1}{1+\omega^2\tau_1{}^2},\ f' = \frac{1}{1+\omega^2\tau_2{}^2}$$

$$g_i = (g_1 - g'),\ g_1 = \frac{\omega\tau_1}{1+\omega^2\tau_1{}^2},\ g' = \frac{\omega\tau_2}{1+\omega^2\tau_2{}^2}.$$

The value of ε_∞ as obtained from Cole-Cole plot may not coincide with the actual value in Eqs. (1) and (2), but it will lie 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 Eqs. (1) and (2). The value of ε_∞ is then varied and the process is repeated till the mean square deviation A, from the relation

$$A = \sum (\varepsilon''_{\text{obsd}} - \varepsilon''_{\text{calcd}})^2 + \left\{\frac{\varepsilon'_{\text{obsd}} - \varepsilon'_{\text{calcd}}}{n}\right\}^2,$$

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. The values of ε_∞, τ_1, τ_2 and C_1 are given in Table 2. All the calculations were carried on the IBM Computer 1130. The calculated values of ε' and ε'' are included in Table 1.

The activation energies for dielectric relaxation and viscous flow were obtained from the straight line plots of log τT *vs.* $1/T$ and log η *vs.* $1/T$ respectively. The dipole moment in the case of 4-methylthiophenol was calculated from ε_0 and density d using Onsager's equation. The values of α, $n_D{}^2$, $\Delta H\tau_1$, $\Delta H\eta$ and μ are included in Table 2.

Discussion

It can be seen from Table 2 that the molecular and intramolecular relaxation times in both the *para* substituted thiophenols, decrease with increase in temperature as is generally observed in polar liquids, so also the distribution parameter α decreases with increase of temperature.

The intramolecular relaxation time τ_2 for SH group rotation in both the liquids are of the same order ($\approx$3ps) and compares well with the τ_2-values in thiophenol (2.6 ps) and in benzylthiol (3.1 ps) in the liquid state reported earlier[5] as also in naphthalenethiol (2.5 ps) in dilute solution in benzene reported by Fong and Smyth.[4] Thus it is found that the SH group relaxation times in pure liquids as also in dilute benzene solution are almost the same, showing thereby that the intermolecular hydrogen bondings S–H···S of the type hydroxyl hydrogen bonding, observed in phenol and substituted phenols,[10] are negligible in the thiophenols even in the liquid state.

It would be interesting to compare the τ_1 and τ_2 values of the present liquids, with those of *p*-substituted phenols reported by Magee and Walker.[10] Though the molecular relaxation time τ_1 of 29.7 ps at 50 °C in 4-methylthiophenol compares well with the value of $\tau_1=32$ ps at 25 °C in 4-methylphenol in *p*-xylene solution, the SH group relaxation time of 2.85 ps in the former, is definitely much smaller than the OH group relaxation time $\tau_2=8.4$ ps in the latter. The molecular relaxation time $\tau_1=17.7$ ps at 65 °C in 4-chlorothiophenol in the liquid state is almost half the value of $\tau_1=39$ ps in 4-chlorophenol in *p*-xylene solution and the τ_2-value of 2.8 ps for SH group rotation in the former is about our fourth the τ_2-value of 12.7 ps for OH group rotation in the latter. The unusual lengthing of the OH group relaxation of *p*-substituted phenols in *p*-xylene solution was attributed by Magee and Walker[10] to association among the solute molecules, in addition to the effects of solvents. The lengthing of molecular relaxation time (τ_1=39 ps) in 4-chlorophenol in dilute *p*-xylene solution to double the τ_1-value of 17.7 ps in 4-chlorothiophenol, seems to suggest that a dimer has been formed in *p*-chlorophenol molecule by association with other solute molecule probably through H–Cl hydrogen bond. Similar bond formation is not observed in 4-methylphenol in the *p*-xylene solution.

Weight factors: It is seen from Table 2 that the weight factor C_1 for 4-methylthiophenol and 4-chlorothiophenol are about 0.79 and 0.63 respectively. An estimate for the weight factors for both the thiophenols can be made from consideration of bond moments. Assuming the moments of $\mu_{CH_3}=0.37D$, $\mu_{C-S}=0.9D$, $\mu_{H-S}=0.7D$, $\mu_{C-Cl}=1.5D$ and $\angle CSH=135°$,[11] and remembering that the CH_3 group moment is directed towards the benzene ring, the moment components responsible for SH group rotation are $\mu_2=0.49D$ in both the molecules, while the moment components responsible for molecular reorientations are $\mu_1=0.8\,D$ in methyl thiophenol and $\mu_1=1.1D$ in 4-chlorothiophenol. From the above values of μ_1 and μ_2, the ratio of the weight factors in the two cases are,

$$\frac{C_2}{C_1}=\left(\frac{0.49}{0.8}\right)^2=\frac{0.24}{0.64} \quad \text{or} \quad C_1 = 0.73$$

in 4-methylthiophenol and

$$\frac{C_2}{C_1}=\left(\frac{0.49}{1.1}\right)^2=\frac{0.24}{1.21} \quad \text{or} \quad C_1 = 0.83$$

in 4-chlorothiophenol. Thus the weight factors C_1 for molecular reorientation in both the liquids are larger than that for group rotation. The is in conformity with the values obtained experimentally. It may be noted here that some uncertainty may arise in the calculated value of the dipole moment in 4-chlorothiophenol, due to appreciable mesomeric charge shift occurring across the molecule.[12]

The activation energy $\Delta H\tau_1$ for molecular relaxation in 4-methylthiophenol is about 1.3 kcal/mol which, as usual, is less than the corresponding activation energy of $\Delta H\eta=2$ kcal/mol for viscous flow. In the case of 4-chlorothiophenol, the dielectric data could be taken only for two temperatures and therefore activation energy $\Delta H\tau_1$ may not be reliable in this case.

The values of ε_∞ in both the *p*-substituted thiophenols are appreciably larger than the value of $n_D{}^2$ at all temperatures. This indicates the presence of a third dispersion region of the 'Poley type' in the high frequency region.

The dipole moment of 4-methylthiophenol has been determined from ε_0 and density *d*, using Onsager's equation and is found to be 1.4D, which agrees well with the value of 1.46D obtained from bond moment calculation of the CH_3 group in the *para* postition of thiophenol (μ=1.22D).

The authors express their sincere thanks to Professor G. S. Kastha for helpful discussions and to Mr. D. Bhowmic for his help in making the computer programme.

References

1) C. P. Smyth, "Molecular Relaxation processes," Academic Press, London (1966), p. 1.

2) K. H. Illinger, "Progress in Dielectrics," (Ed. Birk and Hart), Vol 4, (1962).

3) K. Higasi, "Dielectric Relaxation and Molecular Structurer," Res. Inst. Appl. Electricity, Tokyo, Japan (1961).

4) K. F. Fong and C. P. Smyth, *J. Phys. Chem.*, **67**, 226 (1963).

5) A. Hasan, A. Das and A. Ghatak. *Indian J. Phys.*, **48**, 246 (1974).

6) A. Aihara and M. Daries, *J. Colloid Sci.*, **11**, 671 (1956).

7) A. Das, A. Chatak, and A. Hasan, This Bulletin, **46**, 1354 (1973).

8) K. Bergmann, D. Roberti, and C. P. Smyth *J. Phys. Chem.*, **64**, 665 (1960).

9) J. Bhattacharyya, A. Hasan, S. B. Roy, and G. S. Kastha, *J. Phys. Soc. Japan*, **28**, 204 (1970).

10) M. D. Magee and S. Walker, *J. Phys. Chem.*, **74**, 2378 (1970).

11) V. I. Minkin, O. A. Osipov, and Y. Zhdanov, "Dipole Moments in Organic Chemistry," Plenum Press, New York (1970).

12) J. W. Smith, "Electric Dipole Moments," Butterworth & Co., London (1955).