September, 1974] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (9), 2315—2318 (1974) 2315

Dielectric Studies of *ortho*- and *para*-Bromoanisoles and β-Bromophenetole in the Liquid State

Alpana Ghatak, Arati Das, and Subir Kr. Roy
Optics Department, Indian Association for the Cultivation of Science, Calcutta 32, India

(Received February 8, 1974)

Complex dielectric permittivities in *ortho*- and *para*-bromoanisoles and β-bromophenetole in the liquid state have been measured in 1.6, 3.17, and 3.49 cm microwave regions at different temperatures. The dielectric data were analysed in terms of molecular and intramolecular relaxation times. The values of methoxy group relaxation times and its contribution to total polarization obtained in the liquid bromoanisoles have been compared to the corresponding values in dilute solutions reported in literatures. Activation energy for dielectric relaxation and viscous flow in all the cases have also been obtained in all the liquids.

From studies of dielectric relaxation in anisole and dimethoxy benzenes in the liquid state Vaughan *et al.*1) reported that the relaxation time of methoxy group rotation τ_2 and its contribution C_2 to total polarization are about 3 ps at 20 °C and 0.2 respectively excepting in the case of *o*-dimethoxy benzene where $C_2=0.7$. Garg and Smyth2) extended the investigation in liquid anisole at still higher frequency region and reported the similar values of τ_2 and C_2. These values of τ_2 and C_2 in anisole and *p*-dimethoxy benzene in dilute solutions reported by different workers3–5) are found to be 7—9 ps at 20 °C and 0.7 respectively, while in *p*-bromoanisole in dilute solution though the τ_2 value is 9 ps at 20 °C, the C_2 is only 0.2 as reported by Farmer and Walker.4) So it appears that the methoxy group relaxation time and its contribution C_2 in anisole or dimethoxy benzene in dilute solution are larger than their values in pure liquids. Garg and Smyth2) suggested that the reduction in the contribution of C_2 of the methoxy group rotation from its value in solution to the liquid state might be due to some restraint in the C–O bond as a result the methoxy group rotation in anisole is not completely free but hindered.

It will be interesting to study how the methoxy group rotation τ_2 and its contribution C_2 in haloanisoles in the liquid state, compare with the corresponding values in dilute solutions published in literatures. The present paper reports the results of investigation on dielectric relaxation of *o*-bromo and *p*-bromoanisoles and β-bromophenetole in the liquid state together with a discussion of the results.

Experimental

Pure samples of *o*-bromoanisole, *p*-bromoanisole and β-bromophenetole were dried with fused calcium chloride and then subjected to fractional distillation. The proper fraction was then distilled under reduced pressure before use in the investigation. The experimental arrangement for measurement of dielectric permittivity ε', dielectric loss ε'', static dielectric constant ε_0, refractive index n_D, viscosity η, and density d at different temperatures were the same as described in an earlier paper.6) The accuracy in the measurements of ε' and ε'' were about 2 and 5% respectively.

Results

The experimentally obtained values of ε' and ε'' at different wave lengths and at different temperatures together with ε_0 at 1 MHz at different temperatures are given in Table 1 and the viscosity η, density d and refractive index n_D at different temperatures are given in Table 2. Cole-Cole arc plots (some shown in Fig. 1) were drawn with the dielectric data. The high frequency dielectric constant ε_∞ and the distribution parameter α were obtained as usual from the arc plots. The large values of distribution parameter and also the nonlinear plots of ε' *vs.* $\varepsilon''\omega$ indicated the presence of more than one relaxation mechanism in all the liquids. The dielectric data were therefore analysed in terms of two relaxation processes by a straightforward analytical method developed by Kastha7) and applied successfully by others.8–10) The values of relaxation times for

Table 1. Values of ε', ε'' and ε_0

Compound	Temp. °C	$\lambda=1.62$ cm		$\lambda=3.17$ cm		$\lambda=3.49$ cm		ε_0
		ε'	ε''	ε'	ε''	ε'	ε''	
o-Bromoanisole	30	3.27	0.97	3.68	1.41	3.91	1.62	8.96
	50	3.35	1.11	3.79	1.55	4.18	1.82	8.68
	70	3.42	1.28	3.96	1.76	4.20	1.91	8.36
	85	3.45	1.33	4.01	1.91	4.39	2.04	8.14
p-Bromoanisole	30	2.97	0.67	3.32	1.16	3.46	1.27	7.40
	50	2.99	0.89	3.35	1.43	3.47	1.53	7.12
	70	3.05	0.90	3.53	1.44	3.67	1.52	6.82
	85	3.04	0.99	3.63	1.54	3.73	1.62	6.56
β-Bromophenetole	40	3.12	0.84	3.48	1.30	3.66	1.34	7.04
	55	3.23	0.95	3.69	1.34	3.86	1.42	6.69
	70	3.32	1.04	3.88	1.40	4.00	1.45	6.28
	85	3.44	1.06	4.02	1.34	4.19	1.37	6.00

TABLE 2. VALUES OF α, η, d, n_D^2 AND ε_∞

Compound	Temp. °C	Distribution parameter α	Viscosity η (cP)	Density d (g/cm^3)	Square of refractive index n_D^2	ε_∞
o-Bromoanisole	30	0.175	1.998	1.500	2.46	2.94
	50	0.159	1.353	1.481	2.43	2.88
	70	0.140	1.002	1.455	2.40	2.84
	85	0.059	0.839	1.437	2.37	2.80
p-Bromoanisole	30	0.095	1.499	1.482	2.43	2.76
	50	0.090	1.150	1.457	2.40	2.66
	70	0.084	0.910	1.438	2.37	2.64
	85	0.080	0.769	1.421	2.35	2.56
β-Bromophenetole	40	0.126	2.420	1.409	2.39	2.82
	55	0.116	1.726	1.392	2.37	2.81
	70	0.115	1.325	1.372	2.35	2.77
	85	0.112	1.003	1.356	2.32	2.74

TABLE 3. VALUES OF τ_1, τ_2, C_1, $\Delta H\tau_1$, $\Delta H\tau_2$, $\Delta H\eta$ AND μ

Compound	Temp. °C	$\tau_1 \times 10^{12}$ (s)	$\tau_2 \times 10^{12}$ (s)	C_1	$\Delta H\tau_1$ (kcal/mol)	$\Delta H\tau_2$ (kcal/mol)	$\Delta H\eta$ (kcal/mol)	Dipole moment μ (D)
o-Bromoanisole	30	48.9	10.9	0.63	2.28	2.22	3.45	2.15
	50	37.2	8.7					
	70	28.7	7.7					
	85	22.6	6.2					
p-Bromoanisole	30	33.7	7.3	0.85	2.02	2.72	2.70	1.98
	50	24.9	5.6					
	70	23.5	4.2					
	85	19.2	3.2					
β-Bromophenetole	40	33.0	9.8	0.65	2.01	2.16	3.54	2.02
	55	28.5	8.5					
	70	22.8	7.1					
	85	20.6	5.6					

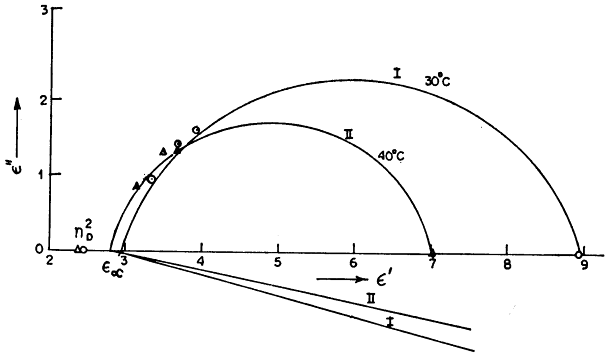

Fig. 1. Cole-Cole plot of *o*-bromoanisole at 30 °C (Curve I, ⊙) and β-bromophenetole at 40 °C (Curve II, △).

molecular orientation τ_1 and group rotation τ_2 and weight factor C_1 for molecular orientation are included in Table 3. The activation energies for dielectric relaxation by molecular orientation $\Delta H\tau_1$ and group rotation $\Delta H\tau_2$ were obtained from the slopes of the straight line plots of log $T\tau$ *vs.* $1/T$ and the activation energy for viscous flow $\Delta H\eta$ were obtained from the graphs of log η *vs.* $1/T$. The values of $\Delta H\tau_1$, $\Delta H\tau_2$, and $\Delta H\eta$ are included in Table 3.

Discussion

It can be seen from Table 3 that the molecular and intramolecular relaxation times as also the distribution parameter α in all the liquids decrease with increase of temperature as is generally observed.

The value of molecular relaxation time $\tau_1 = 49$ ps at 30 °C in *o*-bromoanisole appears much larger than the value of $\tau_1 = 33.7$ ps at the same temperature in *p*-bromoanisole. But the reduced relaxation time τ_1/η of the two molecules are of the same order (≈ 23 ps) of magnitude, showing thereby that the two isomeric molecules are of the same size.

o-Bromoanisole. A comparison of molecular relaxation time τ_1 of *o*-bromoanisole and *o*-dimethoxy benzene both in the liquid state, shows that the molecular relaxation time $\tau_1 \simeq 49$ ps at 30 °C in the former molecule obtained in the present investigation is almost the same as that of 48.5 ps at 25 °C in the latter reported by Vaughan *et al.*[1] This is consistent with the sizes of the two molecules.

The contribution of methoxy group rotation C_2 in *o*-bromoanisole in the liquid state is only about 0.37 as against the value 0.7 in the case of *o*-dimethoxy benzene in the liquid state. The former molecule having C–Br bond moment of about 1.55 D as against O–CH_3 bond moment of ≈ 1.3 D in the latter molecule, has total moment larger than the latter molecule. So the ratio of group moment component to the total moment which is a measure of C_2 is expected to be larger in the latter molecule.

The contribution of the methoxy group rotation C_2 in *o*-bromoanisole can be calculated from the consideration of total moment and methoxy group moment of the molecule. The O–CH_3 bond has a moment of about 1.3 D making an angle 55° with the direction of C–O bond in the benzene ring. The component of the O–CH_3 bond moment perpendicular to the direction of C–O bond, which is responsible for methoxy group rotation is

$$\mu_2 = 1.3\text{D} \times \sin 55° = 1.06\text{D}$$

and the total moment of the molecule μ_1 can be obtained by the vector sum of C–Br bond moment and component of O–CH_3 bond moment along the C–O axis and is given by

$$\begin{aligned}\mu_1^2 &= (1.55)^2 + (1.3\cos 55°)^2 \\ &\quad + 2 \times 1.55 \times 1.3\cos 55° \cdot \cos 60° \\ &= 3.92 \\ \mu_1 &= 1.99\text{D}\end{aligned}$$

This value of 1.99 D agrees fairly well with the experimentally obtained value of 2.15 D.

Now $$C_2 = \left(\frac{\mu_2}{\mu_1}\right)^2 = \left(\frac{1.06}{1.99}\right)^2 = 0.30$$

So theoretically calculated value of $C_2=0.30$ compares reasonably well with the experimentally obtained value of $C_2=0.37$.

p-*Bromoanisole.* The value of molecular relaxation time $\tau_1=33.7$ ps and group relaxation time $\tau_2=7.3$ ps at 30 °C as also the contribution from methoxy group rotation $C_2=0.15$ obtained in the liquid *p*-bromoanisole, agree fairly well with the values of $\tau_1=31$ ps $\tau_2=7$ ps at 25 °C and $C_2=0.2$ in *p*-bromoanisole in dilute solution of *p*-xylene reported by Farmer and Walker.[4] The similarity in dielectric behaviour of *p*-bromoanisole in pure liquid and dilute solution suggests that the dipole-dipole interaction is not very effective in the liquid state of the molecule.

Comparison of the Relaxation Time of Methoxy Group Rotation in Pure Liquid and Dilute Solution. The relaxation time of methoxy group rotation in *o*-bromo- and *p*-bromoanisole in the liquid state obtained in the present investigation are of the same order of methoxy group rotation (7—9) ps reported in anisole and substituted anisoles in dilute solutions reported by Farmer and Walker[4] and Klages and Krauss[5] but larger than the value of about 3 ps of the methoxy group rotation in anisole and dimethoxy benzenes in liquid state reported by Vaughan *et al.*[1] and Garg and Smyth.[2] So it appears that the methoxy group rotation in molecules containing only methoxy group as substituent is less hindered in the liquid state than in anisole in dilute solution or in haloanisoles either in the liquid state or in solutions. This is supported by the fact that the activation energy of methoxy group rotation in anisole in liquid state as reported by Garg and Smyth[2] is only 1.5 kcal/mol which is much smaller than the value of 2.6 kcal/mol for methoxy group rotation in anisole in dilute solution in *p*-xylene calculated from the data of Farmer and Walker[4] and also from the values of 2.2—2.6 kcal/mol (Table 3) for methoxy group rotation in the bromo-anisoles in liquid state obtained in the present investigation.

The larger value of the methoxy group rotation of anisole in benzene or *p*-xylene solution than in the pure liquid may be due to the formation of a weak bond between the π-electron of the solvent molecule and hydrogen atom of the methoxy group. Similar bond formation in 1,2-dichloroethane and benzene has been reported by Chitoku and Higasi.[11]

β-Bromophenetole. The reduced molecular relaxation time τ_1/η of β-bromophenetole at 40 °C is about 14 ps which is smaller than the value $\tau_1/\eta=23$ ps at 30 °C in bromoanisoles. Thus the β-bromophenetole molecule appears to be a little bit smaller than the molecules of bromoanisoles.

The group relaxation time $\tau_2=9.8$ ps at 40 °C in this case is larger than the methoxy group rotation in anisole in dilute solution or haloanisoles in liquid state. This value of $\tau_2=9.8$ ps at 40 °C is also larger than the relaxation time of ethoxy group rotation $\tau_2=4$ ps at 40 °C in the liquid state reported by Bhattacharyya *et al.*[8] which is consistent with their sizes.

The contribution of group rotation C_2 here is only −0.32 as against the value of $C_2=0.63$ in ethoxy group rotation in phenetole. The substitution of Br-atom in the ethoxy group might increase hindrance and thus reduces the value of C_2 in the present case.

Activation Energy. The activation energy of dielectric relaxation by molecular orientation in all the liquids are of the same order (2.1 kcal/mol) and each is smaller than the corresponding activation energy for vicous flow as usually observed.

The activation energy for molecular relaxation $\Delta H\tau_1=2.1$ kcal/mol in *p*-bromoanisole in liquid state obtained in the present investigation is about the same as the value of $\Delta H\tau_1=2.07$ kcal/mol obtained for *p*-bromoanisole in dilute solution, calculated from the data of Farmer and Walker.[4] This shows that the dipolar interaction are almost the same in the liquid *p*-bromoanisole and its solution in *p*-xylene as mentioned earlier.

The activation energy of group rotation in the liquid ($\Delta H\tau_2=2.2$ kcal/mol) and in solution ($\Delta H\tau_2=1.9$ kcal/mol) calculated from the data of Farmer and Walker[4] are also compatible.

It can be seen from Table 2 that the values of n_D^2 in all the liquids are less than the respective values of ε_∞. This indicates the presence of a high frequency absorption region as suggested by Poley.[12] This 'Poley absorption' has been generally explained as due to torsional molecular librations in potential minima of fluctuating interaction field of the neighbouring molecules.[13]

The authors wish to express their sincere thanks to Dr. S. B. Roy for his guidance and to Professor G. S. Kastha for his keen interest.

References

1) W. E. Vaughan, S. B. W. Roeder, and T. Provder, *J. Chem. Phys.*, **39**, 703 (1963).

2) S. K. Garg and C. P. Smyth, *ibid.*, **46**, 373 (1967).

3) E. Forest and C. P. Smyth, *J. Amer. Chem. Soc.*, **86**, 3474 (1964).

4) D. B. Farmer and S. Walker, *Can. J. Chem.*, **47**, 4645 (1969).

5) G. Klages and G. Krauss, *Z. Naturforsch*, **26a**, 1272 (1971).

6) A. Hasan, A. Das (nee' Pal), and A. Ghatak, This Bulletin, **44**, 322 (1971).

7) G. S. Kastha, *Ind. J. Phys.*, **42**, 223 (1968).

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

9) G. S. Kastha, B. Dutta, J. Bhattacharyya, and S. B. Roy, *Ind. J. Phys.*, **43**, 14 (1969).

10) A. Hasan, A. Das, and A. Ghatak, *ibid.*, **45**, 558 (1971).

11) K. Chitoku and K. Higasi, This Bulletin, **40**, 773 (1967).

12) J. Ph. Poley, *Appl. Sci. Res.*, **B4**, 337 (1955).

13) J. B. Birks and J. Hart, "Progress in Dielectic," Vol. 3, Heywood & Company Ltd., London (1961), p. 90.