Microwave absorption and molecular structure of polar molecules in solutions, relaxation times and activation energies of some substituted benzenes

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The present communication reports the relaxation times of 3-5 dichloronitro benzene, 2-5 dichloronitrobenzene, 2-5 dibromonitro benzene, p-bromonitrobenzene, 2-4 dinitrochlorobenzene, 1,2,4 dinitrochloro benzene in dilute solutions of benzene at wavelength 3·13 cm (9585 Mc/Sec) in the microwave region. The measurements have been made at 20°, 30° and 40°C. in order to calculate the free energies of activation for process of dipole orientation and viscous flow. It is concluded that the dipole orientation is mainly contributed by molecular rotations. From the values of ΔF_τ for the various compounds investigated inference has been drawn that energy of activation increases with the size of molecules.

1. THEORY

Relaxation time has been determined using the Concentration variation method of Gopala Krishna (1957) given by the relation as discussed in an earlier paper (1969)

$$\tau = \frac{1}{2\pi c}\left[\frac{dy}{dx}\right]. \qquad \dots \ (1)$$

Dielectric relaxation mechanism may be explained in terms of absolute rate theory (1941) by treating dipole orientation as a rate process in which the polar molecules rotate from one equilibrium position to another. This process of rotation requires as activation energy sufficient to overcome the energy barrier separating the two mean equilibrium positions and is given by

$$\tau = \left(\frac{A}{T}\right)\exp\left(-\Delta S\tau/R\right)\exp\left(\Delta H\tau/RT\right) \qquad \dots \ (2)$$

ΔH_τ is calculated from the slope of log $T\tau$ vs $1/T$ plot as shown in Fig. 1 and 2. The intercept of the plot log $T\tau$ vs $1/T$ gives the factor $A'(=Ae^{-\Delta S_\tau/R})$. $\Delta F\tau$ and $\Delta S\tau$ are calculated using the equation given in the earlier paper (1972).

The concept of viscous flow of a liquid as a rate process that involves the surmounting of a potential barrier has led to an analogous equation for viscosity of the solvent, benzene :

$$\eta = B\exp(-\Delta S\eta/R)\exp(\Delta H\eta/RT) \qquad \dots \ (3)$$

Pant, Somevanshi, Mehrotra, Saxena

$\Delta H\eta$ is obtained from the slope of plot log η against $1/T$ as shown in graph 1. B has been calculated from the intercept of the plot log η vs $1/T$. $\Delta F\eta$ and $\Delta S\eta$ are obtained from the equation given in the paper (1972)
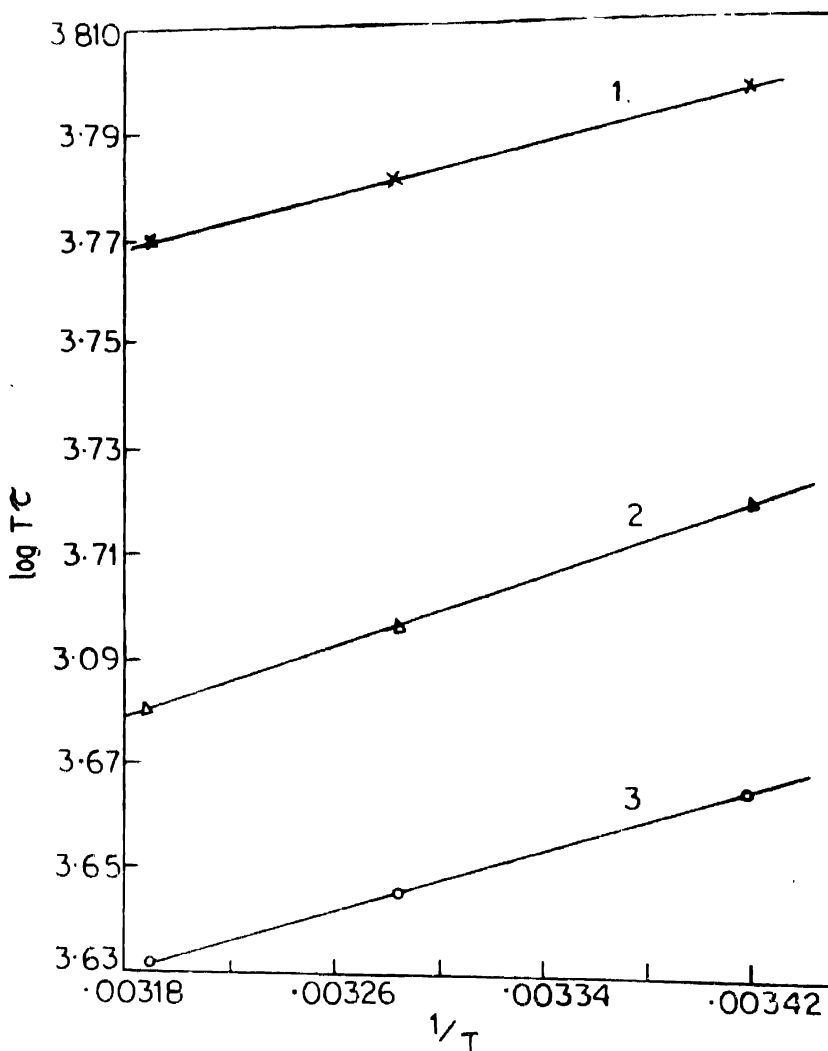

Fig. 1.

Whiffen & Thompson (1946), Gopala Krishna (1958) and Shobhandri (1960) have found energy of activation, ΔF_η for viscous flow of solvent to be always greater than ΔF_τ. Saxton (1952) and Van Eick & Poley (1957) have observed that ΔF_τ and ΔF_η are nearly equal in case of some pure liquids. Bhanumati (1963) have indicated that ΔF_τ and ΔF_η are nearly equal only in case of low

viscosity solvents. Smyth and collaborators (1948, 1960, 1961) have found ΔF_τ to increase with size of molecule.
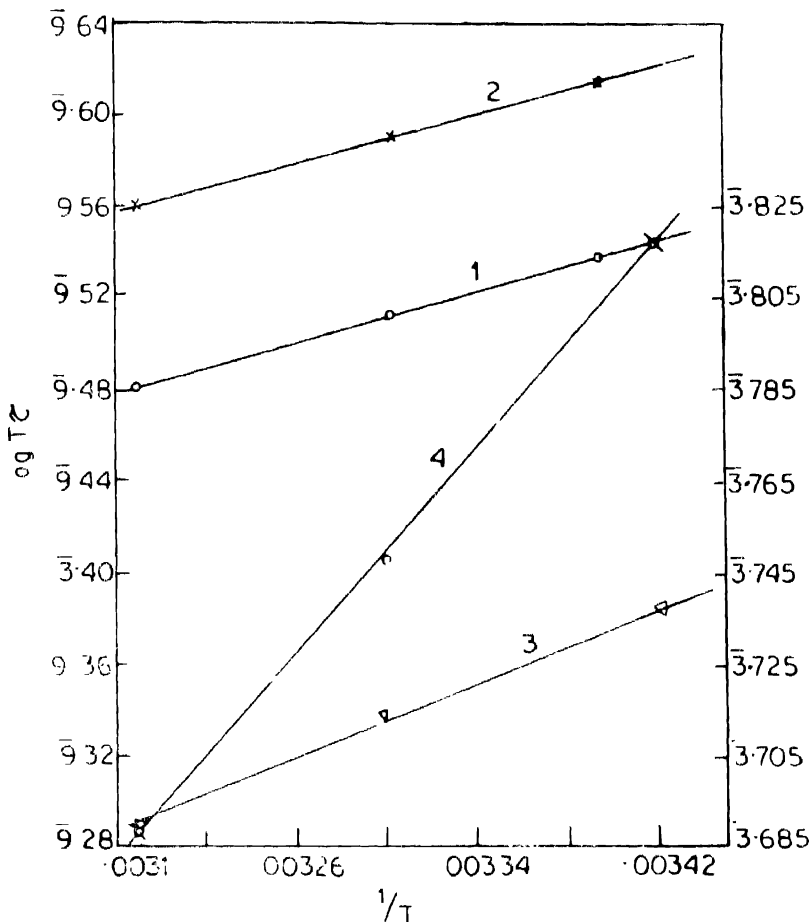

Fig. 2

A study of above results indicate that definite conclusion can not be drawn regarding the variation of energies of activation with the size, shape and nature of the molecules. The present investigation, therefore, has been undertaken to study the dielectric relaxation in relation to molecular structure and to further our knowledge about the variation of energies of activation for dielectric relaxation and viscous flow.

2. EXPERIMENTAL

Chemicals : All the compounds used are of purest quality obtained from Messrs British Drug House Ltd.. England. Purest quality Analar Benzene obtained from Messrs B. D. H. was distilled before use.

Pant, Somevanshi, Mehrotra, Saxena

A microwave bench of 3·13 cm. wavelength region has been used for measuring the dielectric constant, ϵ' and the loss factor, ϵ'', of the dilute solutions of compounds in benzene. The standing wave technique of Roberts & Von Hippel (1946) and its subsequent simplification by Dakin & Works (1947) is used for calculating values of dielectric constant and loss factor. The measurements of ϵ' are accurate to $\pm 1\%$ and those for ϵ'' to $\pm 5\%$. The relaxation times obtained by concentration variation method of Gopala Krishna (1957) are found to be accurate to $\pm 0.5\%$. The values of η of solvent benzene are 6.47×10^{-3}, 5.61×10^{-3} and 5.23×10^{-3} poise at 20°C, 30°C and 40°C respectively.

3. RESULTS

The values of dielectric constants (ϵ') and losses (ϵ'') for solutions of increasing concentrations at various temperatures are given in table 1. In table 2 the

Table 1. Experimental data for the determination of relaxation times

Compound	Concentration ω	20°C		30°C		40°C	
		ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
(1) 2-5 dichloro-nitrobenzene	.0229	2.31221	0.04771	2.32011	0.03071	2.34161	0.03101
	.0248	2.32253	0.05626	2.37215	0.06532	2.34543	0.03565
	.0281	2.34462	0.07858	2.38361	0.07468	2.36184	0.06164
	.0305	2.38364	0.09912	2.41583	0.08875	2.39002	0.06512
	.0326	2.39418	0.09987	2.41629	0.08921	2.41149	0.08690
(2) 3-5 dichloro-nitrobenzene	.0269	2.29501	0.06434	2.34221	0.10631	2.34240	0.02991
	.0281	2.29890	0.06899	2.35975	0.12119	2.34324	0.03274
	.0299	2.30521	0.07478	2.39084	0.14608	2.35915	0.05088
	.0321	2.30832	0.07803	2.42146	0.17512	2.38793	0.06329
	.0341	2.31513	0.07932	2.48913	0.23844	2.40821	0.08195
(3) 2-5 dibromo-nitrobenzene	.0231	2.28721	0.06687	2.29501	0.07794	2.32163	0.08028
	.0253	2.31933	0.11598	2.32643	0.10986	2.33984	0.11532
	.0269	2.36054	0.17322	2.35419	1.13978	2.36405	0.13981
	.0281	2.37346	0.19894	2.38322	0.18322	2.38743	0.17939
	.0298	2.37927	0.20125	2.36963	0.19951	2.40321	0.18592
(4) p-bromo-nitrobenzene	.0162	2.21001	0.02631	2.24832	0.02695	2.23941	0.03426
	.0202	2.23128	0.03018	2.26212	0.03199	2.25312	0.04512
	.0342	2.23519	0.03498	2.26698	0.03511	2.25816	0.05823
	.0375	2.24228	0.04319	2.27392	0.04412	2.26914	0.06321
	.0416	2.25398	0.04516	2.28799	0.04599	2.27893	0.07913
(5) 2-4 dinitro-chlorobenzene	.0301	2.26623	0.04962	2.28021	0.05402	2.28562	0.05832
	.0352	2.27814	0.05815	2.29841	0.06975	2.30481	0.07179
	.0391	2.32412	0.11981	2.34952	0.12143	2.35023	0.11245
	.0462	2.39650	0.18871	2.35084	0.12395	2.36124	0.11827
	.0501	2.41632	0.19923	2.36129	0.12486	2.44085	0.19421
(6) 1-2 dinitro 4-chlorobenzene	.0078	2.26621	0.04958	2.28021	0.05402	2.28399	0.05836
	.0132	2.27713	0.05861	2.29815	0.06959	2.30439	0.07129
	.0188	2.33289	0.11972	2.34929	0.11139	2.35332	0.11249
	.0241	2.39649	0.18981	2.35089	0.11998	2.35738	0.11892
	.0269	2.40128	0.19002	2.36124	0.12016	2.44089	0.19318

values of relaxation times (τ) and thermo-dynamic parameters for dipole orientation and viscous flow have been reported. The values of A' and B' alongwith Eyring's estimated values of A and B are given in table 3.

Table 2. Relaxation times and molar energy parameters

Compound	Temp. °K	$\tau \times 10^{12}$ Sec.	$\Delta F\tau$ Kcal/mol	$\Delta F\eta$ Kcal/mol	$\Delta S\tau$ Cal/mol	$\Delta S\eta$ Cal/mol	$\Delta H\tau$ Kcal/mol	$\Delta H\eta$ Kcal/mol
(1) 2,5 dichloro-nitrobenzene	293	11.87	2.48	2.90	−0.81	−1.29	2.25	2.52
	303	10.72	2.52	2.92	−0.89	−1.32	2.25	2.52
	113	9.65	2.57	2.94	−1.02	−1.31	2.25	2.52
(2) 3,5 dichloro-nitrobenzone	293	14.34	2.59	2.90	−1.03	−1.29	2.29	2.52
	303	12.97	2.64	2.92	−1.15	−1.32	2.29	2.52
	313	11.86	2.69	2.94	−1.28	−1.34	2.29	2.52
(3) 2,5 dibromo-nitrobenzene	293	21.51	2.82	2.90	−2.01	−1.29	2.23	2.52
	303	19.97	2.89	2.92	−2.17	−1.32	2.23	2.52
	313	18.86	2.97	2.94	−2.38	−1.34	2.23	2.52
(4) p-bromo-nitrobenzene	293	8.21	2.27	2.90	−1.53	−1.29	1.82	2.52
	303	7.32	2.31	2.92	−1.61	−1.32	1.82	2.52
	313	6.28	2.35	2.94	−1.69	−1.31	1.82	2.52
(5) 2,4 dinitro-chlorobenzene	293	15.42	2.63	2.90	−2.18	−1.29	1.98	2.52
	303	14.58	2.70	2.92	−2.37	−1.32	1.98	2.52
	313	13.67	2.77	2.94	−2.56	−1.34	1.98	2.52
(6) 1,2 dinitro-4-chlorobenzene	293	17.53	2.71	2.90	−1.77	−1.29	2.19	2.52
	303	16.46	2.78	2.92	−1.94	−1.32	2.19	2.52
	313	15.39	2.85	2.94	−2.14	−1.34	2.19	2.52

Table 3. Relaxation Times and Factors A', B', A and B

Compound	Temp. °K	$\tau \times 10^{12}$ Sec.	$A'(=Ae^{\Delta S\tau/R}) \times 10^{11}$	$B'(=I\,e^{\Delta S_\eta/R}) \times 10^{5}$	$A(=h/K) \times 10^{11}$	$B(=hN/V) \times 10^{5}$
(1) 2,5 dichloro-nitrobenzene	293	11.87	5.54	8.57	4.80	4.49
	303	10.72	4.84	8.58	8.80	4.44
	313	9.65	4.56	8.60	4.80	4.38
(2) 3,5 dichloro-nitrobenzene	293	14.34	6.99	8.57	4.80	4.49
	303	12.97	6.43	8.58	4.80	4.44
	313	11.86	5.96	8.60	4.80	4.38
(3) 2,5 dibromo-nitrobenzene	293	21.51	11.91	8.57	4.80	4.49
	303	19.97	11.22	8.58	4.80	4.44
	313	18.86	10.64	8.60	4.80	4.38
(4) p-bromo-nitrobenzene	293	8.21	11.35	8.57	.30	4.49
	303	7.32	11.19	8.58	.80	4.44
	313	6.28	12.01	8.60	.80	4.38
(5) 2,4 dinitro-chlorobenzene	293	15.42	7.67	8.57	.80	4.49
	303	14.58	7.46	8.58	.80	4.44
	313	13.67	7.18	8.60	.80	4.38
(6) 1,2 dinitro-4-chlorobenzene	293	17.53	8.35	4.57	.80	4.49
	303	16.46	8.85	8.58	.80	4.44
	313	15.39	8.29	8.60	4.80	4.38

4. DISCUSSION

The relaxation time of 3,5 dichloronitrobenzene is larger than that of 2,5 dichloronitro benzene, though the size of the both molecules is same. This can be explained by considering the fact that in 2,5 dichloronitrobenzene both chlorine atoms are at para positions to each other hence the dipole formed is weak, while in 3,5 dichloronitro benzene both chlorine atoms are at meta position to the nitro group which due to negative mesomeric effect produces greater steric hindrance to the rotation of the molecule resulting in higher value of relaxation time. 2-5 dibromonitro benzene exhibits higher relaxation time than other compounds of the series which is due to the larger size of the molecule and strong polarity of the bromo group. *p*-bromonitro benzene possesses the lowest relaxation time which can be explained not only due to the smallest size of the molecule but also due to the fact that both the substituted groups i.e nitro and bromo groups are at para position with crespect of each other.

It is observed from the table that the dielectric relaxation time of 2,4 dinitrochlorobenzene is larger than that of 2,5 dichloronitrobenzene which is due to the larger size of former molecule and the strong polarity of the nitro groups. 1,2 dinitro 4-chlorobenzene exhibits higher relaxation time than that of 2,4 dinitro chlorobenzene. This can not be explained on the basis of Debye's (1929) Conception, as the size of both the molecules is same. This can be attributed to the larger volume swept out for dipole orientation by the former molecule.

Thermodynamic parameters

The free energies of activation for both the process of dielectric relaxation and viscous flow increases with increasing temperature while the relaxation time decreases. This is due to the fact that at higher temperature the molecular collision rate increases with the result that energy required to bring molecules into activated state will also increase. Similar results have also been obtained by Mehrotra and Collaborators in case of some substituted anilines and anisoles (1972). 2-5 dibromonitrobenzene molecule has the highest value for the free energy of activation for dielectric relaxation and the *p*-bromonitrobenzene exhibits the lowest value. This can be attributed to the fact that the former molecule experiences the maximum resistance in dipolar rotation, whereas the latter experiences the least hindrance. It has been observed from table 2 that activation energy for dipole orientation increases with size and shape of molecules which in accordance with the results obtained by Smyth and collaborator (1948, 1960, 1961)

It has been found that the free energy of activation for viscous flow process is always greater than that for the dielectric relaxation process in all cases investigated. This is due to the fact that the process of viscous flow involves both rotation and translation, while the process of dipole orientation involves

only the rotation of the molecule. Similar results have earlier been observed by Petro & Smyth (1957). Krishnaji (1965) and two of the authors (1969) Further the ratio of ΔF_τ and ΔF_η approaches unity for some of the compounds investigated, which suggests that the moving units participating in two process are identical and that activation takes place in some degree of freedom because the same bonds have to be broken before either motion is possible.

The most probable enthalpies of activation are less than the corresponding free energies so that most probably entropies of activation are negative. According to Branin & Smyth (1952) a negative entropy of activation indicates that there are fewer configurations possible in the activated states and for these configurations activated state is more ordered than the normal state because in activated state dipoles try to align in the direction of applied field which should obviously be more ordered. This indicates the existence of cooperative orientations of the molecules resulting from steric forces. Similar results have been obtained by Man Singh (1961), Fong & Smyth (1963) and by one of the authors (1969).

The values of A' ($= A e^{-\Delta S_\tau/R}$) given in table 3 are found to vary little with temperature for one solution but are different for solutions having different polar molecules varying from 4.56 to 12.01×10^{-11}. This indicates that the observed values of this factor differ widely from theoretical value $\frac{h}{k} e^{-\Delta S_\tau/R} = 4.8 \times 10^{-11}$, where A is equal to h/k as shown by Eyring and the exponential factor has been taken to be nearly equal to 1 as ΔS_τ is a very small quantity.

As given in table 3, factor B' ($= B e^{-\Delta S_\eta/R}$) which is very nearly equal to B, varies little within the observed range of temperature and is nearly twice the Eyring's estimated values of hN/V for the frequency factor B. It may therefore be concluded that frequency factors A and B are not constants and are better represented by A' and B', the new factors one of which A' is appreciably influenced by the nature of the molecule and temperature and is always greater than the Eyring's value A ($= h/k$). The factor B' differs from factor B but does not vary appreciably with temperature or the nature of the molecules. Similar results were obtained by Shukla and workers in case of benzaldehydes (1968).

312 Pant, Somevanshi, Mehrotra, Saxena

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