9

STUDIES ON THE DIELECTRIC LOSS AT 7.7 MM. MICROWAVES OF SOME SUBSTITUTED BENZENE AND NAPHTHALENE COMPOUNDS

(MISS) B. SINHA, S. B. ROY AND G. S. KASTHA
OPTICS DEPARTMENT,
INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE,
CALCUTTA-32.

(*Received January* 10, 1966)

ABSTRACT. The times of relaxation (τ) of a number of halo-substituted benzene and naphthalene compounds in solutions in different non-polar solvents at different temperatures have been determined. The results have been compared with the various expressions for the time of relaxation proposed by Hill and Chau *et al* and it has been pointed out that neither of these expressions for τ is in aggrement with the experimental results. Further, the value of internal viscosity (η_{int}) obtained from the equation for τ derived by Perrin in case of ellipsoidal molecules, has been found to be related with the macroscopic viscosities (η) of the solutions by the relation $\eta_{int} = \text{const.}\ \eta^{\gamma}$, where γ is the ratio of molar heats of activation of dielectric relaxation and viscous flow.

INTRODUCTION

It is well known that the macroscopic viscosity of a medium does not adequately describe the internal friction, opposing the orientation of a polar molecule in that medium under the action of an externally applied R.F. field. Several expression have since been developed relating the internal friction (η_{int}) with macroscopic viscosity (η) (Fischer, 1949, Wirtz, 1954, Hill 1954; Hase, 1953, Chau *et al*, 1957). Fischer (1949) suggested that internal friction $\eta_{int} = C\eta$ where C is an adjustable fraction. Hill (1954), from a consideration of the transference of linear and angular momenta at the time of collisions between the solute and the solvent molecules in dilute solutions, concluded that the mutual viscosity between the solvent and the solute molecules should be a better representation of internal friction. Chau *et al* (1957), on the other hand developed an empirical expression for the time of relaxation in terms of the molecular parameters of the solute and physical properties of the solvent. Though all these expressions were found to be of limited applicability either in a particular solvent or at a particular temperature, these were not tested at different temperature regions (where τ, η_{int} and η are expected to vary simultaneously) for want of sufficient data. Recently, Sinha *et al* (1965) have suggested that in the case of dilute solutions of polar molecules in non-polar solvents of viscosity η, η^{γ} may represent fairly the internal viscosity of the medium. The value of γ is given by the ratio of the molar heats of activation for dielectric relaxation and viscous flow. The object of the present investigation is to find out how far the values of τ obtained experimentally in the case of solutions of some polar compounds having molecules with rigid dipoles in various non-polar solvents at different temperatures are in agreement with various expressions of τ and η_{in} as stated aove. The results have been discussed in the following paragraphs.

EXPERIMENTAL

The liquids fluoro-, chloro-, bromo- orthodichloro-, metadichlorobenzene and α-chloronaphthalene studied in the present investigation were of chemically pure quality. These were first fractionated and the proper fractions were repeatedly distilled under reduced pressure and dried before being used in the investigation. The solvents carbon tetrachloride, benzene *n*-hexane and medicinal paraffin were carefully dried by usual methods The dried solvents showed slight losses in the frequency region of 7 7 mm. which were properly taken into account in determining the overall losses due to various solutions. The experimental arrangements and the method of calculation of loss tangent (tan δ) were the same as described earlier (Bhattacharyya *et al*, 1964). The viscosities of paraffin and some of the solutions in carbon tetrachloride and benzene at different temperatures were determined experimentally. The viscosities of the other mixtures and the solvents were taken from the standard literatures.

RESULTS AND DISCUSSION

The values of time of relaxation (τ) for the various molecules in solution in non-polar solvents at different temperatures (T) were calculated from the experimental tan δ values with the help of the following equation

$$\tan\delta = \frac{(\epsilon'+2)^2}{\epsilon'}\cdot\frac{4\pi Nc\mu^2}{27kT}\cdot\frac{\omega\tau}{1+\omega^2\tau^2} \qquad \ldots \quad (1)$$

where the various symbols have their usual significance. The values of dipole moments (μ) of various compounds excepting in a few cases were taken from the standard literatures. The μ-values in the case of *m*-dichlorobenzene in benzene and in *n*-haxane and of bromobenzene in *n*-hexane were calculated from the experimental results. The values of ϵ' were taken to be equal to the static dielectric constants of the pure solvents taken from the published literature values. The values of tan δ, τ and $\tau\cdot T/\eta^{\gamma}$ at different temperatures for different solutions for the various compounds are given in Tables I—VI.

The values of molar heats of activation $\Delta H\tau$ for dielectric relaxation and $\Delta H\eta$ for viscous flow have been determined respectively from the plots of log ($T\cdot\tau$) and log η against $1/T$. Some of the plots are shown in Figures 1a, 1b and

1c. The values of ΔH_T, ΔH_η and their ratio (γ) for different compounds are given at the foot of respective Tables.

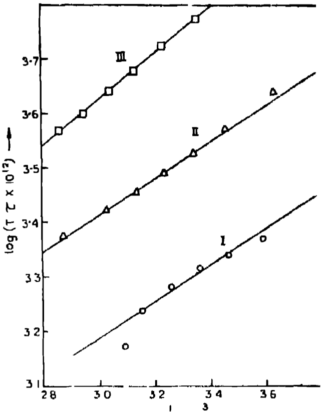

Fig. 1a Plots of log (τ T) vs 1/T Curve I Solution of bromobenzene in hexane Curve II Solution of bromobenzene in benzene Curve III Solution of bromobenzene in paraffin

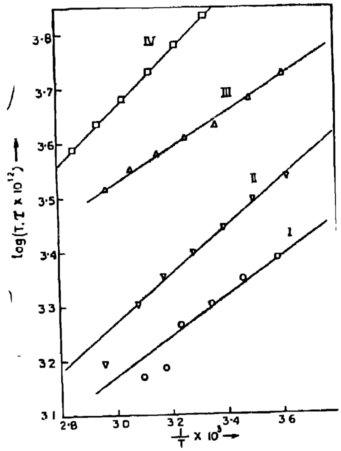

Fig. 1b. Plots of log (τ.T) vs 1/T Curve I Solution of metadichlorobenzene in hexane Curve II Solution of metadichlorobenzene in benzene Curve III Solution of metadichlorobenzene in carbon tetrachloride Curve IV Solution of metadichlorobenzene in paraffin

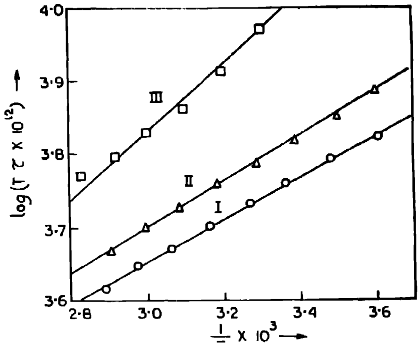

Fig. 1c Plots of log (τ T) vs 1/T Curve I Solution of α-chloronaphthalene in benzene
Curve II Solution of α-chloronaphthalene in carbon tetrachloride
Curve III Solution of α-chloronaphthalene in paraffin

a) *Comparison of Hill's equation for τ with the experimental values*

For very dilute solutions of polar molecules in non-polar solvents Hill (1954) deduced the relations,

$$2\tau kT = \zeta = 6g^2\eta_{AB}\sigma_{AB} \text{ with } g^2 = \frac{I_{AB}\cdot I_B}{I_{AB}+I_B}\cdot\frac{m_A+m_B}{m_A\cdot m_B} \tag{2}$$

and

$$\eta_m = f_A{}^2\eta_A\frac{\sigma_A}{\sigma_m}+f_B{}^2\eta_B\frac{\sigma_B}{\sigma_m}+2f_Af_B\eta_{AB}\frac{\sigma_{AB}}{\sigma_m} \quad \ldots \tag{3}$$

η_{AB} is the mutual viscosity between the molecules of the solvent (A) and the solute (B) and the other symbols have the meanings given in Hill's paper. The value of viscosity of the mixtures (η_m) at different concentrations and temperatures were obtained in the case of chlorobenzene +benzene and bromobenzene+ benzene systems from International Critical Tables and in other cases they were determined experimentally. The values of $\sigma_A = \left(\frac{M_A}{Nd_A}\right)^{1/3}$, $\sigma_B = \left(\frac{M_B}{Nd_B}\right)^{1/3}$ and $\sigma_m = \left[\frac{[f_AM_A+f_BM_B]}{Nd_m}\right]^{1/3}$ at different temperatures were calculated from the molecular weights M_A, M_B of the solvent and the solute respectively and the density d_A of the solvent, the density d_B of the solute and the density d_m of the solution. The values of η_{AB} were obtained for two different concentrations and the mean value was used.

TABLE Ia

$f = 38\ 8$ K Mc/s — Chlorobenzene — $f = 38.8$ K.MC/s

2.93×10^{-4} mole/cc in Hexane				2.93×10^{-4} mole/cc in benzene			
T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta^\gamma} \times 10^7$	T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta^\gamma} \times 10^7$
276	1 71	8 53	14 82	277	12.0	14 13	16.90
287	1.73	7 81	14 66	289	12 8	12 35	16 75
298	1 75	7 10	14 43	299	13 5	11 10	16.54
308	1 78	6 42	13 95	311	14 0	10.10	16 64
321	1 73	6 19	14 63	325	14 3	9 00	16 69
329	1 71	6 01	14 89	336	14 5	8 41	16 76
				348	14 7	7 73	16 93

$\Delta H_\tau = 0\ 63$ K Cal/Mole
$\Delta H_\eta = 1\ 84$ K Cal/Mole
$\gamma = 0\ 34$

$\Delta H_\tau = 0\ 99$ K.Cal/Mole
$\Delta H_\eta = 2\ 53$ K Cal/Mole
$\gamma = 0\ 39$

TABLE Ib

$f = 37\ 9$ K.Mc/s — $f = 38.8$ K.Mc/s

$2\ 92\ 10^{-4}$ mole/cc in CCl				$2\ 95 \times 10^{-4}$ mole/cc in Paraffin			
T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta^\gamma} \times 10^7$	T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta^\gamma} \times 10^7$
278	11 9	14 27	15 68	297	9 8	16 59	-
290	12 3	13 02	16 14	309	10 0	14 73	11.39
298	12 7	12 07	16 03	319	11 0	13 20	11 72
305	12 9	11 18	16 16	329	11.7	11 83	11 93
315	13 3	10 51	16 03	339	12.3	10.51	11 92
325	13 7	9 66	15 81	339	13.0	9 46	11 41
335	14.1	8 82	15.52				
345	14 3	8 21	15 55				

$\Delta H_\tau = 0\ 90$ K Cal/Mole
$\Delta H_\eta = 2\ 11$ K.Cal/Mole
$\gamma = 0\ 37$

$\Delta H_\tau = 1.84$ K.Cal/-Mole
$\Delta H_\eta = 6.33$ K. Cal/Mole
$\gamma = 0\ 29$

TABLE IIa

Bromobenzene

$f = 38.8$ K.Mc/s				$f = 38.8$ K.Mc/s			
2.85×10^{-4} mole/cc in hexane				2.84×10^{-4} mole/cc in benzene			
T°K	$\tan\delta \times 10^{3}$	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta\gamma} \times 10^{7}$	T°K	$\tan\delta \times 10^{3}$	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta\gamma} \times 10^{7}$
278	15.0	8.50	7.83	275	9.8	15.81	11.63
288	15.5	7.60	7.93	289	11.1	12.90	11.50
297	16.0	6.96	8.09	299	12.0	11.25	11.37
307	15.9	6.25	8.14	309	12.6	10.03	11.32
317	16.1	5.45	7.99	319	13.3	8.90	11.26
323	16.4	4.62	7.18	330	13.7	8.02	11.34
332	15.9	4.66		318	14.1	6.83	11.57

2.85 × 10⁻⁴ mole/cc in hexane	2.84 × 10⁻⁴ mole/cc in benzene
$\Delta H_\tau = 1.54$ K.Cal/Mole	$\Delta H_\tau = 1.51$ K.Cal/Mole
$\Delta H_\eta = 1.81$ K.Cal/Mole	$\Delta H_\eta = 2.53$ K.Cal/Mole
$\gamma = 0.84$	$\gamma = 0.61$

TABLE IIb

$f = 37.9$ K.Mc/s				$f = 38.8$ K.Mc/s			
2.83×10^{-4} mole/cc in CCl_4				2.84×10^{-4} mole/cc in Paraffin			
T°K	$\tan\delta \times 10^{3}$	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta\gamma} \times 10^{7}$	T°K	$\tan\delta \times 10^{3}$	$\tau \times 10$ sec	$\frac{\tau T}{\eta\gamma} \times 10^{7}$
276	7.97	19.75	11.82	298	7.15	19.96	—
286	8.78	16.99	11.70	309	7.79	17.14	12.11
296	9.60	14.74	11.55	319	8.45	15.09	12.31
304	10.20	13.25	11.33	329	9.10	13.33	12.46
314	10.60	12.13	11.61	339	9.75	11.79	12.37
321	11.10	11.08	11.73	349	10.20	10.67	12.47
334	11.40	10.11	11.81				
343	11.85	9.21	11.83				

2.83 × 10⁻⁴ mole/cc in CCl₄	2.84 × 10⁻⁴ mole/cc in Paraffin
$\Delta H_\tau = 1.46$ K.Cal/Mole	$\Delta H_\tau = 1.96$ K.Cal/Mole
$\Delta H_\eta = 2.44$ K.Cal/Mole	$\Delta H_\eta = 6.33$ K.Cal/Mole
$\gamma = 0.60$	$\gamma = 0.31$

TABLE IIIa

m-Dichlorobenzene

$f = 38.8$ K.Mc/s $f = 37.9$ K.Mc/s

2.62×10^{-4} Mole/cc in hexane				2.61×10^{-4} Mole/cc in benzene			
T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta^\gamma} \times 10^{12}$	T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta^\gamma} \times 10^7$
279	12.00	8.73	7.31	276	10.0	12.51	6.32
289	12.46	7.73	7.38	286	11.0	10.70	6.35
299	12.90	6.73	7.38	295	11.6	9.13	6.50
309	13.14	5.94	7.36	305	12.0	8.20	6.46
315	13.60	4.87	6.50	315	12.7	7.23	6.56
323	13.38	4.59	6.83	325	13.0	6.23	6.42
331	12.90	3.40		338	13.5	4.58	5.19
				345	13.0	3.41	

$\Delta H_\tau = 1.68$ K Cal/Mole
$\Delta H_\eta = 1.81$ K Cal/Mole
$\gamma = 0.91$

$\Delta H_\tau = 2.61$ K Cal/Mole
$\Delta H_\eta = 2.53$ K.Cal/Mole
$\gamma = 0.79$

TABLE IIIb

$f = 38.8$ K Mc/s $f = 38.8$ K Mc/s

2.62×10^{-4} Mole/cc in CCl_4				2.61×10^{-4} Mole/cc in paraffin			
T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta^\gamma} \times 10^7$	T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta^\gamma} \times 10^7$
277	6.89	19.20	10.96	300	5.42	22.79	
287	7.54	16.73	11.08	310	6.06	19.46	10.49
297	8.19	14.44	10.87	320	6.71	16.78	10.68
307	8.62	13.24	11.13	330	7.36	14.56	10.73
317	9.05	11.97	11.28	340	8.01	12.69	10.69
327	9.50	10.83	11.28	350	8.66	11.06	10.59
337	9.91	9.71	11.22				

$\Delta H_\tau = 1.52$ K Cal/Mole
$\Delta H_\eta = 2.44$ K Cal/Mole
$\gamma = 0.62$

$\Delta H_\tau = 2.35$ K Cal/Mole
$\Delta H_\eta = 6.33$ K Cal/Mole
$\gamma = 0.37$

TABLE IVa

o-Dichlorobenzene

$f = 37.9$ K Mc/s

$f = 38.8$ K.Mc/s

2.63×10^{-4} Mole/cc in benzene				2.65×10^{-4} Mole/cc in CCl_4			
T°K	$\tan\delta\times10^3$	$\tau\times10^{12}$ sec	$\frac{\tau T}{\eta^\gamma}\times10^7$	T°K	$\tan\delta\times10^3$	$\tau\times10^{12}$ sec	$\frac{\tau T}{\eta^\gamma}\times10^7$
275	19.0	16.09	9.44	276	18.3	15.91	10.30
285	21.0	13.62	9.31	290	21.0	13.17	10.31
295	23.2	11.74	9.32	299	22.0	11.74	10.21
305	25.0	10.09	9.08	308	22.6	10.74	10.26
315	26.0	9.11	9.34	319	23.5	9.71	10.38
325	26.9	8.17	9.42	330	24.3	8.75	10.37
335	27.6	7.37	9.45	343	25.2	7.75	10.45
345	28.3	6.46	9.30				
$\Delta H_\tau = 1.81$ K.Cal/Mole $\Delta H_\eta = 2.53$ K.Cal/Mole $\gamma = 0.72$				$\Delta H_\tau = 1.38$ K Cal/Mole $\Delta H_\eta = 2.44$ K Cal/Mole $\gamma = 0.57$			

TABLE IVb

3.8 K.Mc/s

2.64×10^{-4} mole/cc in Paraffin				
T°K	$\tan\delta\times10^3$	$\tau\times10^{12}$ sec	$\frac{\tau T}{\eta^\gamma}\times10^7$	η in millipoise
300	16.5	17.91	—	—
310	17.3	16.33	19.71	112.0
320	18.0	14.89	19.94	78.0
330	19.1	13.59	19.97	57.0
340	19.9	12.41	19.88	43.0
349	20.6	11.53	19.87	34.0

$\Delta H_\tau = 1.25$ K Cal/Mole
$\Delta H_\eta = 6.33$ K Cal/Mole
$\gamma = 0.20$

TABLE V

α-Chloronaphthalene

$f = 38.8$ K.Mc/s $f = 38.8$ K.Mc/s

2.93×10^{-4} mole/cc in benzene				2.93×10^{-4} mole/cc in paraffin			
T°K	$\tan\tau \times 10^3$	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta^\gamma} \times 10^7$	T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta^\gamma} \times 10^7$
277	6.45	23.98	21.75	303	4.63	30.73	16.40
287	6.89	21.49	22.18	313	5.23	26.19	16.96
297	7.34	19.30	22.42	323	5.83	22.56	17.02
306	7.78	17.55	22.28	333	6.23	20.31	17.41
316	8.20	15.89	22.23	343	6.64	18.25	17.79
326	8.67	14.43	22.28	353	7.00	16.69	18.06
336	9.10	13.11	22.02				
346	9.56	11.91	21.90				
	$\Delta H_\tau = 1.32$ K.Cal/Mole $\Delta H_\eta = 2.53$ K.Cal/Mole $\gamma = 0.52$				$\Delta H_\tau = 2.17$ K.Cal/Mole $\Delta H_\eta = 6.33$ K.Cal/Mole $\gamma = 0.34$		

TABLE VI

Solution in Carbontetrachloride

$f = 38.8$ K.Mc/s $f = 38.8$ K.Mc/s

2.93×10^{-4} mole/cc of α-chloro-naphthalene				3.18×10^{-4} mole/cc of fluorobenzene			
T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta^\gamma} \times 10^7$	T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta^\gamma} \times 10^7$
278	5.60	27.70	17.54	275	12.1	11.87	15.57
286	6.00	24.77	17.54	286	12.5	10.74	15.47
295	6.56	22.34	17.73	299	12.9	9.61	15.39
304	6.89	20.16	17.68	310	13.1	8.91	15.36
314	7.32	18.20	17.80	320	13.1	8.26	15.23
324	7.75	16.51	17.86	333	12.9	7.82	15.63
334	8.19	14.98	17.86	346	12.5	7.76	
344	8.62	13.38	17.62				
	$\Delta H_\tau = 1.43$ K.Cal/Mole $\Delta H_\eta = 2.44$ K.Cal/Mole $\gamma = 0.59$				$\Delta H_\tau = 0.70$ K.Cal/Mole $\Delta H_\eta = 2.44$ K.Cal/Mole $\gamma = 0.29$		

It is seen from Eqn. (2) that

$$\frac{\tau \cdot T}{\eta_{AB}} = \frac{6g^2\sigma_{AB}}{2k} \qquad \ldots \quad (4)$$

and since $g^2\sigma_{AB}$ is expected to remain constant, $\frac{\tau \cdot T}{\eta_{AB}}$ should not vary with temperatures. The values of $\tau \cdot T/\eta_{AB}$ at different temperatures for some of the solutions are given in Tables VII to IX.

It is easily seen from the tables that the values of $\frac{\tau \cdot T}{\eta_{AB}}$ do not remain constant with temperature but increases with increase of tmperature which is contrary to the expectation from Hill's equation.

b) *Comparison of Chau, Lefevre and Tardiff's expression for τ with the experimental values*

Chau *et al.* (1957) proposed the following empirical relation between the time of relaxation and the molecular and physical parameter of the polar solute molecules and the non-polar solvents respectively,

$$\tau = \frac{\pi}{2kT} \eta(ABC) \exp{(\Delta)}(\epsilon+2)^{-1} \qquad \ldots \quad (5)$$

where η is the macroscopic viscosity, Δ the depolarisation factor and ϵ the static dielectric constant of the solvent at the temperature T. A, B and C (with $A \geqslant B \geqslant C$) are the axial lengths characterising the solute polarisibility ellipsoid. It is seen from Eqn (5) that

$$\frac{\tau \cdot T}{\eta'} = \frac{\pi}{2k} ABC = \text{const.} \qquad \ldots \quad (6a)$$

where

$$\eta' = \eta \exp{(\Delta)}(\epsilon+2)^{-1} \qquad \ldots \quad (6b)$$

In order to test the constancy of the values of $\tau \cdot T/\eta'$ for different polar compounds in solutions in different non-polar solvents at various temperatures, the values of η' have been computed from the macroscopic viscosities (η), the static dielectric constants (ϵ) of the solvents at different temperatures and the experimental values of depolarisation factor (Δ) at different temperatures reported by Rao (1927, 28) and Krishnan and Rao (1929, 30)

The values of $\tau \cdot T/\eta'$ at different temperatures for the different solutions are shown in Table X-XII

It is easily seen from the tables that the values of $\tau \cdot T/\eta'$ instead of remaining constant, increase with the increase of temperatures. From the results presented in the above sections it is clear that neither the Hill's expression nor that of Chau *et al* for the time of relaxation is in agreement with the conclusion arrived at from the experimentally determined τ-values for the various compounds in solutions in the different solvents. In the next section it is proposed to investigate the relation between the τ-values and the macroscopic viscosities of the solutions.

(c) *Relation between the time of relaxation* (τ), *the internal viscosity* (η_{int}) *and the macroscopic viscosity* (η)

The Debye relation as modified by Perrin (1934) for ellipsoidal molecules with rigid dipoles lying along one of the principal axes of the ellipsoid is given by

$$\tau = \frac{4\pi abc \cdot f\,\eta_{int}}{kT} \qquad \ldots \quad (7a)$$

whence

$$\eta_{int} = \frac{\tau kT}{4\pi abcf} \qquad \ldots \quad (7b)$$

where a, b, c are the semi axes of the ellipsoidal molecules, f is a factor tabulated by Budo *et al* (1939), K is the Boltzman constant and η_{int} is the internal viscosity of the medium in which the ellipsoidal molecules are rotating under the influence of the applied microwave field. The value of a, b and c are determined from data on atomic radii (Fischer, 1949) and η_{int} is calculated from the experimental values of τ with the help of Eqn. (7b). The molecular parameters are given in Table XIII which also contains the values of 'f', the molecular volume ($\frac{4}{3}\pi abc$) and the kinetic theory volume wherever available included for the sake of comparison.

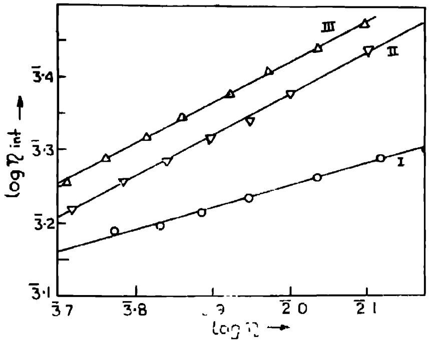

Fig 2a. Graphs showing variation of log η_{int} against log η
Curve I Fluorobenzene in solution in carbon tetrachloride
Curve II Orthodichlorobenzene in solution in carbon tetrachloride
Curve III α-Chloronaphthalone in solution in carbon tetrachloride

TABLE VII

Chlorobenzene

Solution in benzene				Solution in CCl$_4$			
T°K	η_{AB} millipoise	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta_{AB}} \times 10^7$	T°K	η_{AB} millipoise	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta_{AB}} \times 10^7$
277	9.04	14.13	4.33	278	11.28	14.27	3.52
289	7.63	12.35	4.68	290	9.13	13.02	4.13
299	6.71	11.10	4.94	298	8.00	12.07	4.50
311	5.82	10.10	5.40	305	7.20	11.48	4.86
325	5.01	9.06	5.88	315	6.22	10.54	5.34
336	4.47	8.41	6.32	325	5.43	9.66	5.78
348	3.98	7.73	6.75	335	4.79	8.82	6.17
				345	4.24	8.21	6.67

TABLE VIII

Bromobenzene

Solution in benzene				Solution in CCl$_4$			
T°K	η_{AB} millipoise	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta_{AB}} \times 10^7$	T°K	η_{AB} millipoise	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta_{AB}} \times 10^7$
275	11.83	15.81	3.67	276	14.98	19.75	3.64
289	9.66	12.89	3.86	286	12.59	16.99	3.87
299	8.41	11.25	4.00	296	10.64	14.74	4.10
309	7.45	10.03	4.16	304	9.40	13.25	4.29
319	6.61	8.90	4.28	314	8.13	12.13	4.69
330	5.84	8.02	4.53	324	7.03	11.08	5.11
348	4.81	6.83	4.86	334	6.19	10.11	5.45
				343	5.52	9.24	5.74

TABLE IX

α-Chloronaphthalene

Solution in benzene				Solution in CCl_4			
T°K	η_{AB} millipoise	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta_{AB}} \times 10^7$	T°K	η_{AB} millipoise	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta_{AB}} \times 10^7$
277	14.80	23.98	4.49	278	22.05	27.70	3.49
287	12.28	21.49	5.02	286	18.75	24.77	3.78
297	10.38	19.30	5.52	295	15.78	22.34	4.18
306	8.92	17.55	6.02	304	13.50	20.16	4.54
316	7.72	15.89	6.49	314	11.42	18.20	5.00
326	6.65	14.43	7.08	324	9.78	16.51	5.47
336	5.72	13.11	7.69	334	8.16	14.98	5.91
346	5.07	11.91	8.13	344	7.46	13.38	6.17

TABLE X

Solution in Carbontetrachloride

Chlorobenzene				Bromobenzene			
T°K	η' millipoise	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta'} \times 10^7$	T°K	η' millipoise	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta'} \times 10^7$
278	3.11	14.27	12.75	276	3.25	19.75	16.77
298	2.26	12.07	15.89	296	2.34	14.74	18.65
315	1.83	10.51	18.09	314	1.84	12.13	20.70
335	1.46	8.82	20.21	334	1.45	10.11	23.29
345	1.30	8.21	21.78	343	1.32	9.24	24.00
o-Dichlorobenzene				α-Chloronaphthalene			
T°K	η' millipoise	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta'} \times 10^7$	T°K	η' millipoise	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta'} \times 10^7$
276	3.25	15.91	13.51	278	3.11	27.70	24.74
299	2.25	11.74	15.61	295	2.38	22.34	27.69
319	1.73	9.71	17.91	314	1.84	18.20	31.06
330	1.52	8.75	19.00	331	1.45	14.98	34.49
343	1.32	7.74	20.14	344	1.31	13.38	35.14

TABLE XI

Solution in benzene

Chlorobenzene				o-Dichlorobenze			
T°K	η' millipoise	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta'} \times 10^7$	T°K	η' millipoise	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta'} \times 10^7$
277	3.06	14.13	12.79	275	3.20	16.09	13.82
299	2.14	11.10	15.47	295	2.27	11.74	15.26
325	1.56	9.06	18.89	315	1.77	9.11	16.21
336	1.39	8.41	20.38	335	1.42	7.37	17.40
348	1.22	7.73	22.04	345	1.26	6.46	17.67
m-Dichlorobenzene				α-Chloronaphthalene			
T°K	η' millipoise	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta'} \times 10^7$	T°K	η' millipoise	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta'} \times 10^7$
276	3.13	12.51	11.04	277	3.06	23.98	21.71
295	2.27	9.43	12.26	297	2.21	19.30	25.94
315	1.77	7.23	12.86	316	1.75	15.89	28.64
325	1.56	6.23	12.49	336	1.39	13.11	31.78
345	1.26	3.41	9.33	346	1.25	11.91	32.97

TABLE XII

Solution in hexane

Bromobenzene				*m*-Dichlorobenzene			
T°K	η' millipoise	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta'} \times 10^7$	T°K	η' millipoise	$\tau \times 10^{12}$ sec	$\frac{\tau T}{\eta'} \times 10^7$
278	1.07	8.50	22.09	279	1.06	8.73	22.98
288	0.97	7.60	22.70	289	0.96	7.73	23.38
297	0.88	7.96	23.50	299	0.86	6.73	23.40
307	0.80	6.25	24.11	309	0.78	5.94	23.55

TABLE XIII

Compound	Semi-axial length in Å			*f*	4/3 π Å³	Kinetic Theory volume Å³
	a	*b*	*c*			
C_6H_6	3.11	3.11	1.27	--	51.5	48.0
C_6H_5F	$3.\overrightarrow{28}$	3.11	1.27	1.43	54.3	54.0
C_6H_5Cl	$3.\overrightarrow{46}$	3.11	1.50	1.44	67.6	61.0
C_6H_5Br	$3.\overrightarrow{56}$	3.11	1.70	1.27	78.8	64.0
o-$C_6H_4Cl_2$	3.11	$3.\overrightarrow{01}$	1.50	1.26	58.8	—
m-$C_6H_4Cl_2$	3.31	$3.\overrightarrow{11}$	1.50	1.35	64.7	—
α-$C_{10}H_7Cl$	4.04	$3.\overrightarrow{46}$	1.50	1.35	87.8	—

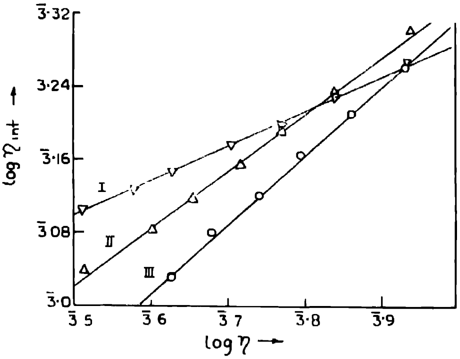

Fig 2b. Graphs showing variation of log η_{int} again log η
Curve I Chlorobenzene in solution in benzene
Curve II Bromobenzene in solution in benzene
Curve III Metadichlorobenzene in solution in b

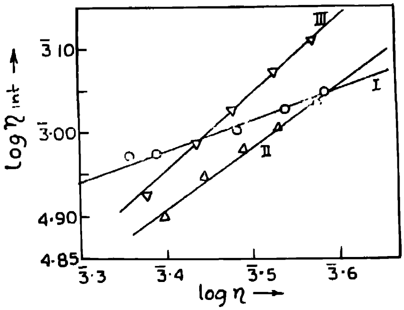

Fig. 2c Graphs showing variation of log η_{int} against η
Curve I Chlorobenzene in solution in hexane
Curve II Bromobenzone in solution in hexane
Curve III Metadichlorobenzene in solution in hexane

In order to find out the relation between the values of η_{int} so calculated and the microscopic viscosities of the solvents, the calculated values of log η_{int} have been plotted against the values of log $\bar{\eta}$. Some of these graphs are shown in Figures 2a, 2b, 2c and 2d . It is seen from these graphs that log η_{int} is connected with the log η values by the linear relation,

$$\log \eta_{int} = G + \gamma \log \eta \tag{8}$$

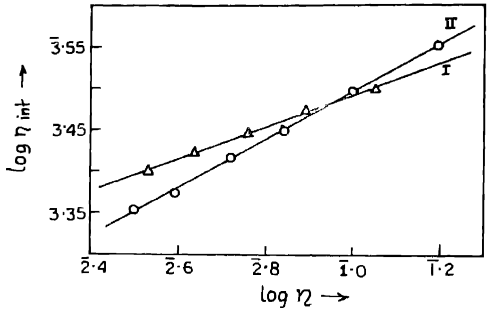

Fig. 2d. Graphs showing variation of log η_{int} against log η
Curve I Orthodichlorobenzene in solution in paraffin
Curve II α-Chloronaphthalene in solution in paraffin

where G is a constant and the slope of the straight line is equal to the ratio $\Delta H\tau/\Delta H\eta$ given at the feet of the Tables (I—IV). From Eqn (8) is obtained $\eta_{int} = \text{const}\ \eta^{\gamma}$ which in conjunction with Eqn. (7b) gives

$$\frac{\tau \cdot T}{\eta^{\gamma}} = \text{const.} \tag{9}$$

It is seen from the Tables I-VI, that the values of $\tau T/\eta^{\gamma}$ are almost constant for the different compounds in solutions in the various non-polar solvents. This is in conformity with the results obtained previously (Sinha *et al.*, 1965).

The discussions of the experimental results presented in the previous sections, therefore, lead to the conclusion that the internal viscosity (η_{int}) is a function of the macroscopic viscosity (η) and may be represnted by an equation of the form $\eta_{int} = \text{const.}\ \eta^{\gamma}$.

REFERENCES

Bhattacharyya, J., Sinha, B., Roy, S. B., Kastha, G. S., (1964), *Indian J. Phys.*, *38*, 413.
Budo, A., Fischer, E. and Miyamoto, S., (1939), *Physic Z.*, *49*, 337.
Chau, J. Y. H., Le Fevre, R. J. W. and Tardif, J., (1957), *J. Chem. Soc.*, 2293.
Fischer, E., (1939), *Phys. Z.*, *49*, 645
Fischer, E., (1949), *Z. Naturf.*, *4A*, 707.
Hase, H., (1953), *Z. Naturf.*, *8A*, 695
Hill, N. E., (1954), *Proc. Phys. Soc.*, *B 67*, 149.
Krishnan, K. S. and Rao, S. R., (1929-30), *Indian J. Phys.*, *4*, 39
Perrin, F., (1934), *J. de Phys.*, (7) *5*, 497.
Rao, S. R., (1927-28), *Indian J. Phys.*, *2*, 179
Sinha, B., Roy, S. B. and Kastha, G. S., (1965), *Indian J. Phys.*, *30*, 328
Wirtz, K. and Spernol, A., (1953), *Z. Naturf.*, *8A*, 522
Wirtz, K. and Gierer, A., (1953), *Z. Naturf.*, *8A*, 532.