ON THE RELATION BETWEEN THE ENERGY OF ACTIVATION FOR DIELECTRIC RELAXATION AND THE INTERACTION ENERGY OF POLAR ORGANIC MOLECULES IN DILUTE SOLUTIONS IN NON-POLAR SOLVENTS

(Miss) B. SINHA, S. B. Roy and G. S. KASTHA
Optics Department,
Indian Association for the Cultivation of Science,
Calcutta-32.

(*Received August* 8, 1966)

ABSTRACT. The results of measurement in the 7 mm. microwave region on the temperature dependence of the time of relaxation (τ) of a number of polar organic molecules of different shape, size and dipole moment dispersed in very dilute solutions in non-polar solvents have been reported. It has been shown that the dependence of τ at any temperature (T) on the viscosity (η) of the solution may be represented by $\tau.T=\text{const.}\ \eta^{\gamma}$ where γ is the ratio of the experimentally determined heats of activation for dielectric relaxation and viscous flow. The relation between the activation energy for dipole rotation for a large number of polar organic molecules in dilute solution in CCl_4 and the total energy due to dipole-dipole, dipole-induced dipole and London dispersion forces between the solute and solvent molecules has been discussed. It is found that the agreement between the experimental and the calculated energy values is fairly satisfactory for many of the compounds and the probable causes for somewhat large discrepancies in a few cases have been suggested.

INTRODUCTION

Recently (Sinha *et al.*, 1965, 1966) it has been shown that the time of relaxation (τ) of organic polar molecules in very dilute solutions in non-polar solvents at any temperature (T) is not dependent linearly on the viscosity (η) of the solutions, but may be expressed as $\tau.T = \text{const.}\ \eta^{\gamma}$ where γ is the ratio of the experimentally determined values of the heat of activation for dielectric relaxation and viscous flow. However, no attempt was made to correlate the values of the heat of activation for dipole orientation with the energies of various intermolecular interactions between the solvent and solute molecules. Bhanumati (1963) had shown that in the case of some pure polar organic liquids the experimental values of the activation energy for dipole-orientation agree fairly well with the total interaction energies calculated from the dipole-dipole and dipole-induced dipole forces. In the case of dilute solutions of polar molecules in nonpolar solvents it will be interesting to find out the contributions made by different intermolecular interactions to the total activation energy required for the process of the orientation of the dipoles. For this purpose, use has been made of the results of measurements of the temperature dependence of the time of relaxation of a number of polar organic compounds, having molecules of different shape, size and dipole moment, in solutions in different non-polar solvents and those reported in the papers mentioned above.

EXPERIMENTAL

The chemicals nitromethane, nitroethane, chloroform, acetone, ethyl acetate α-bromonaphthalene and methyl, ethyl and benzyl esters of benzoic acid used in, this investigation were of chemically pure quality and the samples were subjected to fractional distillation and distillation under reduced pressure before use. Carefully dehydrated carbon tetrachloride, benzene and n-hexane used as solvents, showed slight losses in a path-length of 24 cm in the frequency region of 7.7 mm and these were properly taken into account for determining the overall losses due to the solutions. The experimental arrangements and the method of calculation of loss tangent (tan δ) were the same as described in a previous paper (Bhattacharyya *et al.*, 1964). The values of the viscosity of the solvents were taken from the data published in the standard literatures.

RESULTS AND DISCUSSION

The time of relaxation (τ) for the molecules of the various polar compounds in very dilute solution in the different 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 C is the concentration in moles/cc, ϵ' is the dielectric constant of the solution at the angular frequency of measurement (ω), μ is the dipole moment of the polar molecule and the other symbols have their usual meanings. The values of ϵ' were taken to be the same as the static dielectric constant of the pure solvents and the dipole moments of the molecules of ethyl and benzyl benzoates, and α-bromonaphthalene were taken from the published data and those of the remaining compounds were determined experimentally (see Section a). The values of T, tan δ, τ and $\frac{\tau T}{\eta\gamma}$ are given in Tables I–IX

TABLE I

Nitromethane

1.84×10^{-4} moles/cc in CCl_4				1.84×10^{-4} moles/cc in C_6H_6				1.86×10^{-4} moles/cc in C_6H_{14}			
T°K	tanδ	$\tau\times10^{12}$ Sec	$\frac{\tau.T}{\eta^{\gamma}}\times10^{7}$	T°K	tanδ	$\tau\times10^{12}$ Sec	$\frac{\tau.T}{\eta^{\gamma}}\times10^{7}$	T°K	tan δ	$\tau\times10^{12}$ Sec	$\frac{\tau.T}{\eta^{\gamma}}\times10^{7}$
275	.0392	2.42	4.78	275	.0440	4.75	5.83	276	.0280	1.45	2.93
284	.0370	2.30	4.79	285	.0430	4.35	5.88	282	.0268	1.41	2.96
296	.0345	2.18	4.85	293	.0420	3.99	5.83	289	.0254	1.36	2.96
305	.0327	2.09	4.86	303	.0400	3.62	5.76	296	.0240	1.31	2.97
315	.0305	1.97	4.82	313	.0383	3.40	5.88	305	.0224	1.24	2.98
325	.0286	1.87	4.78	323	.0367	3.20	5.96	315	.0208	1.18	2.99
335	.0268	1.77	4.73	333	.0345	2.87	5.74	325	.0191	1.12	2.97
345	.0250	1.67	4.67	343	.0330	2.71	5.82	335	.0178	1.06	2.97

CCl_4	C_6H_6	C_6H_{14}
$\Delta H_{\tau}=0.31$ K.Cal/mole	$\Delta H_{\tau}=0.95$ K.Cal/mole	$\Delta H_{\tau}=0.43$ K.Cal/mole
$\Delta H_{\eta}=2.44$ K.Cal/mole	$\Delta H_{\eta}=2.53$ K.Cal/mole	$\Delta H_{\eta}=1.84$ K.Ca./mole
$\gamma=0.13$	$\gamma=0.37$	$\gamma=0.23$

TABLE II

Nitroethane

1.4×10⁻⁴ moles/cc in CCl_4				1.4×10⁻⁴ moles/cc in C_6H_6				1.4×10⁻⁴ moles/cc in C_6H_{14}			
T°K	tanδ	$\tau\times10^{12}$ Sec	$\frac{\tau T}{\eta^{\gamma}}\times10^7$	T°K	tanδ	$\tau\times10^{12}$ Sec	$\frac{\tau T}{\eta^{\gamma}}\times10^7$	T°K	tanδ	$\tau\times10^{12}$ Sec	$\frac{\tau . T}{\eta^{\gamma}}\times10^7$
274	.0324	7.04	2.47	275	.0321	6.89	5.84	274	.0344	2.89	4.17
279	.0330	6.50	2.48	283	.0327	6.17	5.77	282	.0327	2.73	4.22
828	.0336	5.68	2.54	290	.0333	5.41	5.53	290	.0311	2.59	4.28
296	.0339	4.83	2.44	295	.0330	5.25	5.69	297	.0293	2.47	4.32
306	.0333	4.10	2.37	305	.0324	4.90	5.89	307	.0277	2.28	4.31
316	.0321	3.65	2.42	315	.0318	4.40	5.89	317	.0256	2.10	4.31
326	.0305	3.27	2.44	325	.0309	4.27	6.29	327	.0235	1.92	4.22
336	.0289	3.00	2.53	335	.0296	3.52	5.69	333	.0224	1.83	4.21
				345	.0284	3.28	5.81				

CCl_4	C_6H_6	C_6H_{14}
$\Delta H_\tau=1.94$ K.Cal/mole	$\Delta H_\tau=1.38$ K.Cal/mole	$\Delta H_\tau=0.87$ K.Cal/mole
$\Delta H_\eta=2.44$ K.Cal/mole	$\Delta H_\eta=2.53$ K.Cal/mole	$H_\eta=1.84$ K.Cal/mole
$\gamma=0.79$	$\gamma=0.55$	$\gamma=0.47$

TABLE III

Acetone

1.35×10^{-4} moles/cc in CCl_4				1.35×10^{-4} moles/cc in C_6H_6				2.71×10^{-4} moles/cc in C_6H_{14}			
T°K	$\tan\delta$	$\tau\times10^{12}$ Sec	$\frac{\tau . T}{\eta^{\gamma}}\times10^{7}$	T°K	$\tan\delta$	$\tau\times10^{12}$ Sec	$\frac{\tau . T}{\eta^{\gamma}}\times10^{7}$	T°K	$\tan\delta$	$\tau\times10^{12}$ Sec	$\frac{\tau . T}{\eta^{\gamma}}\times10^{7}$
274	.0258	4.44	3.52	274	.0241	2.75	5.51	274	.0396	1.90	2.63
282	.0252	4.10	3.58	282	.0229	2.61	5.49	281	.0372	1.79	2.62
289	.0243	3.56	3.37	289	.0220	2.51	5.50	288	.0348	1.69	2.65
297	.0233	3.24	3.34	296	.0211	2.41	5.50	295	.0324	1.58	2.63
307	.0222	3.06	3.47	306	.0199	2.30	5.52	305	.0297	1.47	2.66
317	.0211	2.88	3.59	316	.0188	2.19	5.54	315	.0270	1.36	2.68
325	.0200	2.68	3.58	326	.0180	2.07	5.49	325	.0243	1.24	2.62
$\Delta H_{\tau}=1.17$ K.Cal/mole $\Delta H_{\eta}=2.44$ K.Cal/mole $\gamma=0.48$				$\Delta H_{\tau}=0.36$ K.Cal/mole $\Delta H_{\eta}=2.53$ K.Cal/mole $\gamma=0.14$				$\Delta H_{\tau}=0.92$ K.Cal/mole $\Delta H_{\eta}=1.84$ K.Cal mole $\gamma=0.50$			

TABLE IV

Chloroform

3.73×10^{-4} mole/cc in CCl_4				3.72×10^{-4} moles/cc in C_6H_6				3.73×10^{-4} moles/cc in C_6H_{14}			
T°K	tanδ	$\tau\times10^{12}$ Sec	$\frac{\tau.T}{\eta^{\gamma}}\times10^7$	T°K	tanδ	$\tau\times10^{12}$ Sec	$\frac{\tau.T}{\eta^{\gamma}}\times10^7$	T°K	tanδ	$\tau\times10^{12}$ Sec	$\frac{\tau.T}{\eta^{\gamma}}\times10^7$
274	.0101	8.52		278	.0103	8.07	1.60	275	.0125	3.19	3.81
285	.0106	7.41	1.14	288	.0109	6.77	1.72	283	.0118	2.89	3.72
295	.0110	6.38	1.12	298	.0113	5.55	1.76	289	.0113	2.74	3.76
305	.0114	5.00	1.07	306	.0115	4.10	1.52	295	.0108	2.61	3.81
317	.0112	4.10	1.08	315	.0111	3.59	1.59	305	.0099	2.32	3.73
325	.0108	3.46	1.10	325	.0105	3.12	1.66	315	.0092	2.15	3.80
333	.0103	3.20	1.14					325	.0085	1.99	3.82

$\Delta H_{\tau}=3.07$ K.Cal/mole	$\Delta H_{\tau}=3.17$ K.Cal/mole	$\Delta H_{\tau}=1.13$ K.Cal/mole
$\Delta H_{\eta}=2.44$ K.Cal/mole	$\Delta H_{\eta}=2.53$ K.Cal/mole	$\Delta H_{\eta}=1.84$ K.Cal/mole
$\gamma=1.26$	$\gamma=1.25$	$\gamma=0.62$

TABLE V

Ethyl acetate

3.06×10^{-4} moles/cc in CCl_4				2.05×10^{-4} moles/cc C_6H_6				2.05×10^{-4} moles/cc in C_6H_{14}			
T°K	tan δ	$\tau \times 10^{12}$ Sec	$\frac{\tau.T}{\eta^\gamma} \times 10^7$	T°K	tan δ	$\tau \times 10^{12}$ Sec	$\frac{\pi.T}{\eta^\gamma} \times 10^7$	T°K	tan δ	$\tau \times 10^{12}$ Sec	$\frac{\tau.T}{\eta^\gamma} \times 10^7$
274	.0196	6.55	2.23	274	.0130	6.38	4.04	274	.0159	2.09	3.76
283	.0200	5.74	2.28	281	.0135	5.39	3.75	281	.0150	1.98	3.72
291	.0203	4.73	2.16	289	.0133	5.14	4.06	288	.0143	1.91	3.78
298	.0200	4.49	2.28	305	.0128	4.59	4.43	295	.0136	1.83	3.79
308	.0193	3.65	2.09	315	.0124	3.69	4.03	306	.0125	1.70	3.78
318	.0186	3.51	2.30	325	.0118	3.24	3.96	316	.0115	1.60	3.78
328	.0175	3.09	2.30	335	.0111	2.95	4.02	326	.0110	1.49	3.73
338	.0168	2.98	2.48	345	.0105	2.71	4.10	336	.0097	1.38	3.66
	$\Delta H\tau = 1.97$ K.Cal/mole				$\Delta H\tau = 1.71$ K.Cal/mole				$\Delta H\tau = 0.57$ K.Cal/mole		
	$\Delta H\eta = 2.44$ K.Cal/mole				$\Delta H\eta = 2.53$ K.Cal/mole				$\Delta H\eta = 1.84$ K.Cal/mole		
	$\gamma = 0.81$				$\gamma = 0.68$				$\gamma = 0.31$		

TABLE VI

Methyl benzozte

2.29×10^{-4} moles/cc in CCl_4				3.05×10^{-4} moles/cc in C_6H_6				2.29×10^{-4} moles/cc in C_6H_{14}			
T°K	tan δ	$\tau\times10^{12}$ Sec	$\frac{\tau.T}{\eta^\gamma}\times10^7$	T°K	tan δ	$\tau\times10^{12}$ Sec	$\frac{T.\tau}{\eta^\gamma}\times10^7$	TsK	tan δ	$\tau\times10^{12}$ Sec	$\frac{T.\tau}{\eta^\gamma}\times10^7$
275	.0086	23.24	12.09	276	.0173	1240	6.26	276	.0162	9.51	7.23
285	.0096	19.29	11.61	285	.0188	10.77	6.30	286	.0172	8.28	7.31
294	.0104	17.06	11.56	294	.0203	9.26	6.28	295	.0177	7.39	7.32
304	.0110	15.38	11.91	304	.0218	7.82	6.14	304	.0 83	6.44	7.15
317	.0116	13.77	12.27	316	.0222	6.87	6.31	313	.0186	5.78	7.18
330	.0126	11.85	12.10	328	.0229	5.86	6.27	329	.0186	4.66	7.10
343	.0132	10.60	12.40	338	.0237	4.85	—	336	.0181	3.54	—
	$\Delta H_\tau=1.58$ K.Cal/mole				$\Delta H_\tau=2.01$ K.Cal/mole				$\Delta H_\tau=1.76$ K.Cal/mole		
	$\Delta H_\eta=2.44$ K.Cal/mole				$\Delta H_\eta=2.53$ K.Cal/mole				$\Delta H_\eta=1.84$ K.Cal/mole		
	$\gamma=0.65$				$\gamma=0.79$				$\gamma=0.96$		

TABLE VII

Ethyl benzoate

2.07×10^{-4} moles/cc in CCl_4				2.07×10^{-4} moles/cc in C_6H_6				2.07×10^{-4} moles/cc in C_6H_{14}			
T°K	tan δ	$\tau\times10^{12}$ Sec	$\frac{\tau.T}{\eta^{\gamma}}\times10^7$	T°K	tan δ	$\tau\times10^{12}$ Sec	$\frac{\tau.T}{\eta^{\gamma}}\times10^7$	T°K	tan δ	$\tau\times10^{12}$ Sec	$\frac{\tau.T}{\eta^{\gamma}}\times10^7$
275	.0069	25.05	15.01	276	.0081	21.09	—	276	.0135	11.67	10.48
285	.0077	21.69	14.93	285	.0090	18119	16.82	287	.0143	10.21	10.40
295	.0081	19.29	15.44	294	.0096	16.30	16.90	295	.0150	9.22	10.52
304	.0088	17.39	15.03	303	.0103	14.62	16.77	304	.0156	8.22	10.40
317	.0095	15.11	15.05	313	.0109	13.08	16.60	318	.0163	7.05	10.54
331	.0103	13.12	14.98	323	.0113	11.99	16.90	335	.0169	5.63	—
345	.0110	11.42	15.00	333	.0120	10.73	16.58				
				343	.0124	9.81	16.60				
ΔH_τ =1.45 K.Cal/mole				ΔH_τ =1.43 K.Cal/mole				ΔH_τ =1.54 K.Cal/mole			
ΔH_η =2.44 K.Cal/mole				ΔH_η =2.53 K.Cal/mole				ΔH_η =1.84 K.Cal/mole			
γ =0.59				γ =0.56				γ =0.84			

TABLE VIII

Benzyl benzoate

2.08×10^{-4} moles/cc in CCl_4				1.56×10^{-4} moles/cc in C_6H_6				1.56×10^{-4} moles/cc in C_6H_{14}			
T°K	tan δ	$\tau\times10^{13}$ Sec	$\frac{\tau.T}{\eta^{\gamma}}\times10^7$	T°K	tan δ	$\tau\times10^{12}$ Sec	$\frac{\tau.T}{\eta^{\gamma}}\times10^7$	T°K	tan δ	$\tau\times10^{12}$ Sec	$\frac{\tau.T}{\eta^{\gamma}}\times10^7$
278	.0053	38.04	15.53	274	.0050	29.93	18.47	278	.0087	16.42	13.47
288	.0059	32.79	15.81	283	.0053	25.88	18.24	288	.0092	14.90	13.98
298	.0065	28.56	16.04	292	.0061	22.56	18.17	298	.0096	13.50	14.45
308	.0072	25.10	16.01	300	.0067	19.97	17.96	308	.0100	12.27	14.85
317	.0076	22.89	16.46	311	.0072	17.47	18.01	318	.0107	10.87	14.87
326	.0080	20.82	16.64	323	.0078	15.9	18.27	328	.0114	9.56	14.56
335	.0084	19.32	17.14	333	.0082	14.15	18.53	335	.0118	8.744	14.41
343	.0088	17.88	—	346	.0089	12.10	18.21				
$\Delta H\tau$ = 1.85 K.Cal/mole $\Delta H\eta$ = 2.44 K.Cal/mole γ = 0.76				$\Delta H\tau$ = 1.73 K.Cal/mole $\Delta H\eta$ = 2.53 K.Cal/mole γ = 0.69				$\Delta H\tau$ = 1.69 K.Cal/mole $\Delta H\eta$ = 1.84 K.Cal/mole γ = 0.92			

TABLE IX

α-bromonaphthalene

2.82×10^{-4} moles/cc in CCl_4				2.82×10^{-4} moles/cc in C_6H_{14}			
T°K	tan δ	$\tau\times10^{12}$ Sec	$\frac{\tau.T}{\eta^\gamma}\times10^7$	T°K	tan δ	$\tau\times10^{12}$ Sec	$\frac{\tau.T}{\eta^\gamma}\times10^7$
276	.0044	34.38	22.5	276	.0090	15.94	22.09
286	.0048	30.32	22.7	286	.0094	14.49	22.02
296	.0052	26.80	22.7	296	.0099	13.19	21.84
306	.0056	23.99	22.6	306	.0100	12.01	21.65
319	.0060	21.29	22.9	316	.0105	11222	21.95
333	.0064	18.96	23.3	326	.0107	10.48	22.05
343	.0066	17.72	23.9				

ΔH_τ = 1.37 K.Ca./mole
ΔH_η = 2.44 K.Cal/mole
γ = 0.56

ΔH_τ = 0.94 K.Cal/mole
ΔH_η = 1.84 K.Cal/mole
γ = 0.51

TABLE X

Compound	Dipole moment in Debye Unit (μ_D) in soln. in			Other microwave measurement (μD) in C_6H_6 solution	
	CCl_4	C_6H_6	C_6H_{14}		
Nitromethane		2.85		2.87^b	2.81^c
Nitroethane	3.00	2.97			
Chloroform	1.08	1.08		1.13^a	1.23^b (in heptane)
Acetone	2.54			2.58^b	2.6^c
Ethylacetate	1.55	1.54			
Methyl benzoate			1.82	1.32^c	

(*a*) Jackson and Powles (1946)
(*b*) Whiffen and Thompson (1946)
(*c*) Cripwell and Sutherland (1946)

TABLE XI

(α_s) Polarisability of CCl_4 molecule 105.0×10^{-25} cc.

(I_s) Ionisation potential of ,, 11·47 ev

$$f = \frac{I_p}{I_p+I_s}$$

Compound μ_D	Polarisability αp $\times10^{25}$cc	Ionisation potential Ip ev	Activation energy ΔH_T K. Cal/mole	$\frac{\Delta H}{f\alpha_p}\times10^{-25}$	E_L* K.Cal/mole calculated for	
					$r=5.25$Å	$r=5.43$Å
Nitro methane 2.85	49.0	11.00	0.31	.013	.48 (.61)	.39 (.50)
Nitro ethane 3.00	69.0	10.00	1.94	.064	.60 (.74)	.49 (.60)
Acetone 2.54	63.3	10.10	1.17	.038	.58 (.68)	.47 (.55)
Chloroform 1.08	82.3	11.50	3.07	.070	.82 (.84)	.67 (.68)
Ethylacetate 1.55	88.0	9.50	1.97	.049	.79 (.83)	.64 (.67)
Fluoro benzene 1.45	102.0	9.0.2	0.70	.015	.90 (.93)	.74 (.77)
Chloro benzene 1.56	122.5	8.80	0.90	.019	1.06 (1.10)	.86 (.89)
Bromo benzene 1.50	136.0	8.98	1.46	.025	1.16 (1.19)	.95 (.98)
nitro benzene 3.97	129.2	9.00	1.65	.029	1.15 (1.39)	.94 (1.13)
o-dichloro benzene 2.20	141.7	9.06	1.38	.022	1.24 (1.31)	1.02 (1.08)
m-dichloro benzene 1.48	142.3	9.00	1.52	.024	1.27 (1.30)	1.04 (1.07)
o-nitro toluene 3.66	149.0	8.0–9.0	1.55	.023–.026	1.19–1.33 (1.39–1.53)	.97–1.09 (1.13–1.25)
m-nitro toluene 4.14	149.0	8.0–9.0	0.78	.012–.013	1.17–1.33 (1.43–1.59)	.96–1.09 (1.15–1.29)
p-nitro toluene 4.42	134.0	8.0–9.0	0.85	.014–.016	1.07–1.20 (1.36–1.49)	.87–.98 (1.10–1.21)
Methyl benzoate 1.82	151.0	8.0–9.0	1.58	.023–.026	1.20–1.35 (1.25–1.40)	.98–1.10 (1.02–1.14)
Ethyl benzoate 1 88	171.0	8.0–9.0	1.45	.019–.021	1.36–1.53 (1 41–1 58)	1.11–1.25 (1 15–1 29)

TABLE XI (*cont.*)

Compound μ_D	Polarisability αp $\times 10$ cc	Ionisation potential Ip ev	Activation energy ΔH_T K.Cal/mole	$\frac{\Delta H_T}{f\alpha_p} \times 10^{-25}$	E_L K.Cal/mole calculated for	
					$r = 5.25$Å	$r = 5.43$Å
Benzyl benzoate	252.0	8.0–9.0	1.85	.016–.018	2.21	1.80
2 00					(2.27)	(1.85)
α-chloro naphthalene	193.0	8.2	1.43	.018	1·61	1.32
1 50					(1.64)	(1.35)
α-bromo naphthalene	197.0	8.2	1.37	.017	1.64	1.35
1 50					(1.67)	(1.38)

*The quantities in the parentheses give the values of $E_L + E_D$ when the interaction energy due to dipole-induced dipole forces is considered. For $\mu < 2D$ the contribution due to E_D is less than 5% of E_L. Only for $\mu > 2$ is the contribution appreciable.

The molar heats of activation (ΔH_T) for dielectric relaxation and (ΔH_η) for viscous flow were determined from the plots of log (τT) and log η against $1/T$ as usual. These values and also their ratio (γ) are given at the foot of the respective Tables.

(a) *Determination of the dipole moment* (μ)

It is seen from equation (1) that the graphs of $T \tan \delta/c$ against $\omega\tau$ and consequently T would show a maximum at a certain temperature T_{max} for which the condition $\omega\tau = 1$ is satisfied. Some of these curves are shown in figures 1(a)-(c) The μ-values have been calculated from the maximum value of $T \tan \delta/c$ obtained from the graph at the temperature T_{max} and are given in Table X. The μ-values reported by other workers from measurements in the microwave region are included in the table for comparison. The agreement between these values is seen to be satisfactory.

(b) *Dependence of time of relaxation on viscosity and molecular size* :

The results presented in Tables I—IX show that for a given polar molecule the τ-value at a temperature T increases with the increase in the viscosity of the solvent, while in the case of any of the solvents the τ-values of the different polar molecules arrange themselves roughly accordingly to the size of the molecules. This shows τ may be expressed as $\tau = f(\eta)(f(v)$. In order to determine the functional dependence of τ on η at any temperature T, the values of log $(\tau.T)$ have been plotted against log η—values. The linear plots give

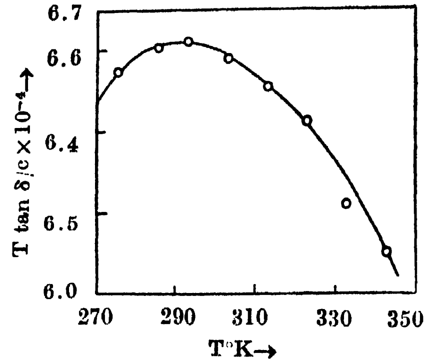

Fig. 1a. Plot of $\frac{T.\,tan\delta}{-}$ vs T

Nitromethane in solution in benzene.

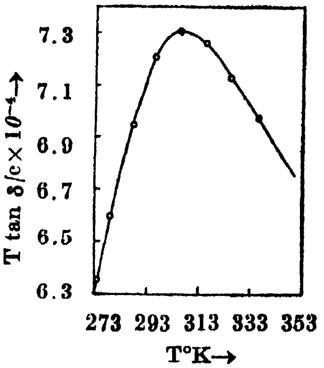

Fig. 1b. Plot of $\frac{T\,.\,tan\delta}{c}$ vs T.

Nitroethane in a solution in carbon tetrachloride.

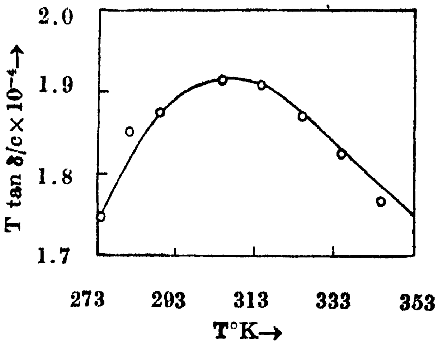

Fig. 1c. Plot of $\frac{T\,tan\,\delta}{c}$ vs T

Ethylacetate in solution in benzene.

the required relation τT = const. η^{γ} as obtained in an earlier paper (Sinha *et al.*, 1966). The constancy in the values $\tau \cdot T/\eta^{\gamma}$ are seen from the data in Tables I-IX.

(c) *Activation energy and intermolecular forces* :

In the case of solutions of polar organic compounds in non-polar solvents the three main types of intermolecular forces (Ketelaar, 1953) are :

(i) dipole-dipole interaction, the energy of interaction

$$E_K = -\frac{2}{3}\,\frac{}{R^6 k} \qquad \ldots \quad (2a)$$

(ii) dipole-induced dipole interaction, the energy of interaction

$$E_D = -2\frac{\alpha_s\mu^2_p}{R^6} \qquad \ldots \quad (2b)$$

and

(iii) London dispersion forces, the energy being

$$E_L = -\frac{3}{2}\,\frac{\alpha_s \cdot \alpha_p}{r^6}\cdot\frac{I_s . I_p}{I_s + I_p} \qquad \ldots \quad (2c)$$

where μ is the dipole moment, α the polarisability, I the ionisation potential, R is the separation between dipoles and r the average distance between the solvent and solute molecules, the suffixes s and p denoting quantities of the solvent and solute molecule respectively.

If we neglect the possibility of other interactions e.g. hydrogen bond formation etc., then the sum of the above energies should be equal to the activation energy required for dipole orientation. However, we may note that for very dilute solutions since R is large E_k will be negligible while if μ is not very large and α not too small the contribution due to E_D will also be small (about 2-5% of E_L if $\mu < 2$). Thus the interaction energy due to London forces E_L would chiefly determine the activation energy. For this purpose the necessary values of α_P have been taken from the values published in the literature wherever available and in other cases these values have been calculated from the refractive index and molar volume data. The ionisation potential values have been taken from the published papers (Kandel, 1955; Watanabe, 1957; Vileşov and Terenin, 1957; Streiswieser, 1960). In case where the values for the substituted compounds are not available, the required ionisation potential have been estimated from that of the parent compound. The values of ΔH_τ for the different compounds in solution in carbon tetrachloride obtained in the present and previous investigations (Sinha *et al.*, 1965, 1966) have been used because the polarisability of the molecule of CCl_4 is the same in all directions. With these value E_L may be written as

$$E_L = -gf\alpha_P \qquad \ldots \quad (3)$$

where
$$g = \frac{3}{2}\,\frac{I_S . \alpha_S}{r^6}$$

is constant for the particular solvent if r is taken to be almost constant. $f = I_P/I_P + I_S$ varies between 0.4 and 0.5 for most of the molecules. If I_P, I_S are expressed in K.Cal/mole, r in cm and α_P, α_S in cc. then E_L would be expressed in K.Cal/mole. From equation (3) it is evident that for a given solvent if E_L is put equal to ΔH_T then $\Delta H_T/f\alpha_P$ should be constant. These are shown in Table XI. The ratio $\Delta H_\tau/f\alpha_P$ are seen to be approximately constant for the different molecules.

On the other hand with the value of r estimated from the total number of molecules per cc. of the carbon tetrachloride solution the values of E_L have been obtained from equation (3) for two values of r. These are shown in the same table. The agreement between the experimental ΔH_T values and the calculated values of E_L is fairly satisfactory. This table also contains the values of the total interaction energy E_L+E_D when the energy due to dipole-induced dipole forces is not neglected. Even then in some cases, however, there are somewhat large discrepancies between the two energy values. This might be due to the following reasons :

(1) In calculating the values of E_L the average values of the polarisability (α_P) has been used which in these cases may not be quite justified, and

(2) The value of r the average distance of separation has been taken to be approximately the same in all cases, but actually the value may be somewhat different in different cases.

(3) The calculated value of E_L shows the largest disagreement in the case of chloroform for which the experimental values of activation energy in solutions in CCl_4 and C_6H_6 are also larger than those for viscous flow. In the case of solution in C_6H_{14} however, the activation energy is smaller (see Table IV). These facts indicate that probably the proton donor chloroform molecules form weak intermolecular bounds with the solvent molecules of CCl_4 and C_6H_6. The formation of such bonds, the possibility of which has been excluded from consideration, may account for the large deviation between the experimental and the calculated values in the case of chloroform.

REFERENCES

Bhanumati, A. (Mrs.), 1963, *Ind. J. Pure. Appl. Phys.*, **1**, 79.

Bhattacharyya, J., Sinha, B. (Miss), Roy, S. B., and Kastha, G. S., 1964, *Indian J. Phys.*, **38**, 413.

Cripwell, F. J., and Sutherland, G. B. B. M., 1946, *Trans. Farad. Soc.*, **42A**, 149.

Jackson, W., and Powles, J. G., 1946, *Trans. Farad. Soc.*, **42A**, 101.

Kandel, R. J., 1955, *J. Chem. Phys.*, **23**, 84.

Ketelaar, J. A. A., 1953, *Chemical Constitution*, Elsevier Publishing Company.

Sinha, B. (Miss), Roy, S. B., and Kastha, G. S., 1965, *Indian J. Phys.*, **39**, 328.

——————————————, 1966, *Indian J. Phys.*, **40**, 101.

Streiswieser, A. (Jr.), 1960, *J. Am. Chem. Soc.*, **88**, 4123.

Vilesov, F. I. and Terenin, A. N., 1957, *Dok. Akad. Nauk. U.S.S.R.*, **115**, 744.

Watanabe, K., 1957, *J. Chem. Phys.*, **26**, 541.

Whiffen, D. H. and Thompson, H. W., 1946, *Trans. Farad. Soc.*, **42A**, 114, 122.