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Study of dielectric relaxation mechanism and mutual viscosity in some substituted anilines

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The present communication reports the relaxation times and mutual viscosity of dimethyl aniline; N-ethyl aniline; N-N-dimethyl aniline; *O*-ethyl aniline; benzyl aniline and N-ethyl-*O*-toluidine in dilute solutions of benzene at 3·13 cm wavelength (9585 MHZ) in microwave region, and at three temperatures 20°, 30° and 40°C. Correlation of mutual viscosity with relaxation time leads to the conclusion that the mutual viscosity is a better representation of the resistance to the rotation of the individual solute molecule. The molar free energies, the entropies and the enthalpies of activation have also been evaluated and compared.

1. Introduction

The discripancy between the observed values and the calculated values (using Debye equation) of relaxation time can be explained by using instead of solvent viscosity η_1 a mutual viscosity parameter η_{12} as derived by Hill (1954) and discussed in an earlier paper (Mehrotra 1971) by one of the authors. The average intermolecular distances i.e., σ's have been determined using the expressions as given in the paper (Mehrotra *et al* 1969).

It is interesting to note that an expression involving mutual viscosity parameter η_{12} was also proposed by Vaughan *et al* (1961). The results obtained using this expression are in good agreement with those obtained using Hill's equation (1954), also discussed in the earlier paper (Mehrotra 1971).

Kalman & Smyth (1961) found that the equation

$$\tau = \frac{C}{T}\,\eta_1^{\alpha}$$

where $\alpha = \Delta H\tau/\Delta H\eta$ which could be derived by using rate equations, gives satisfactory results over a small temperature range. However, they did not examine it for large number of compounds.

In the present investigation we have employed the above relations and undertaken a comparative study using the macroscopic viscosity term η_1, the average mutual viscosity term η_{12} and Kalman's viscosity parameter η_1^{α}. The

results obtained indicate that Kalman's equation gives a closer relation between viscosity and relaxation time. However, the average mutual viscosity η_{12} gives a still better correlation between the phenomena of relaxatiion and viscosity.

The free energies of activation for the process of dipole orientation and viscous flow have also been calculated using Eyring's equations (1941).

2. Experimentals

The dielectric relaxation times have been determined using the fixed frequency method of Gopala Krishna (1957) for dilute solutions. The standing) wave technique of Roberts & Von Hipple (1946) has been used for the measurement of dielectric constant ϵ' and the loss factor ϵ'' required for the calculation of τ.

The viscosities were determined with the help of Hoppler's precision viscometer to an accuracy of $\pm 2\%$.

All the compounds used are of pure quality, obtained from Messrs. British Drug House, Purest quality analar benzene obtained from Messrs. B. D. H. was distilled before use.

3. Results and Discussions

(i) *Relaxation Time*

The dielectric constant ϵ' and loss ϵ'' for the compounds at various concentrations and temperatures are given in table 1. The values of the relaxation time τ, the mutual viscosity η_{12} and the ratios $T\tau/\eta_1$, $T\tau/\eta_{12}$ and $T\tau/\eta_1^a$ are reported in table 2. The values of relaxation times and molar activation energy parameters at different temperatures are given in table 3.

The relaxation time of θ-ethyl aniline is found to be greater than that of N-ethyl aniline, although the size of both the molecules are approximately the same. This may be explained due to greater steric hinderance experienced by the rotating $-NH_2$ group by the neighbouring ethyl group at the ortho-position in the former molecule.

The relaxation times of dimethyl aniline and N-N-dimethyl aniline are of similar magnitude and are consistent with the sizes of the molecules.

Further the relaxation time of N-ethyl-θ-toluidine is much larger than that of N-ethyl aniline which is not only due to the bigger size of the former molecule but also due to the greater hinderance produced by the methyl group attached at the ortho position to the rotation of $-NH_2$ group in the former molecule.

Benzyl aniline has largest value of the relaxation time as compared to all other compounds investigated which may be partly due to the biggest size of the molecule and partly due to maximum hinderance offered by phenyl group to intramolecular rotations of the amino group.

(ii) *Correlation of Dielectric Relaxation Times and Viscosity Parameters*

The interdependence of the dielectric relaxation time and the viscosity factors has been studied by applying various equations. The values of different viscosity parameters are listed in table 2 together with the values of relaxation time.

Table 1. Dielectric constants ϵ' and losses ϵ'' of compounds

Concentration W	20°C		30°C		40°C	
	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
			Dimethyl Aniline			
0·0187	2·2346	0·02186	2·2372	0·01987	2·2552	0·01833
0·0204	2·1309	0·02960	2·2082	0·02193	2·1075	0·02376
0·0267	2·2095	0·04686	2·2018	0·05050	2·1967	0·04987
0·0271	2·2096	0·04708	2·1849	0·03718	2·1847	0·03393
0·0325	2·2018	0·08552	2·1658	0·07819	2·1719	0·07261
			N-N-Dimethyl Aniline			
0·0170	2·1604	0·07153	2·2133	0·06600	2·1732	0·06204
0·0213	2·1719	0·07877	2·1373	0·07583	2·2017	0·06455
0·0246	1·9525	0·05076	2·2133	0·05876	2·1874	0·10209
0·0289	2·2056	0·07717	2·2082	0·06428	2·1952	0·04586
0·0315	2·1797	0·08838	2·1952	0·06759	2·1901	0·06549
			N-ethyl aniline			
0·0295	2·1513	0·03771	2·1526	0·03496	2·1732	0·03008
0·0340	2·1602	0·04561	2·1977	0·03973	2·2991	0·04172
0·0378	2·2003	0·04198	2·2030	0·03472	2·2043	0·01346
0·0412	2·2094	0·10796	2·2107	0·07125	2·2120	0·12830
0·0451	2·1913	0·11850	2·2251	0·05617	2·2450	0·06213
			O-ethyl aniline			
0·0164	2·1476	0·01847	2·1905	0·01575	2·1956	0·01603
0·0212	2·1892	0·01872	2·2022	0·01859	2·2048	0·07144
0·0276	2·1943	0·03675	2·2008	0·02478	2·2073	0·02446
0·0305	2·2112	0·03934	2·1737	0·01252	2·2048	0·02853
0·0349	2·2283	0·04294	2·1878	0·03450	2·1979	0·03387
			N-ethyl-*O*-toluidine			
0·0262	2·1539	0·0184	2·1552	0·0346	2·1578	0·0301
0·0314	2·1642	0·0430	2·1655	0·0352	2·1680	0·0320
0·0363	2·1732	0·0499	2·1655	0·0477	2·1437	0·0464
0·0395	2·1809	0·0500	2·1822	0·0492	2·1861	0·0474
0·0434	2·1745	0·0523	2·1771	0·0561	2·1809	0·0501
			Benzyl aniline			
0·0122	2·1118	0·0178	2·1284	0·0122	2·1383	0·0325
0·0231	2·1500	0·0179	2·1539	0·0328	2·1475	0·0307
0·0286	2·1502	0·0378	2·1245	0·0343	2·1561	0·0339
0·0326	2·1591	0·0383	2·1655	0·0349	2·1433	0·0369
0·0383	2·1784	0·0392	2·1719	0·0369	2·1603	0·0773

Table 2. Values of the relaxation time (τ), average mutual viscosity η_{12} and ratio ($T\tau/\eta_1$), ($T\tau/\eta_{12}$) for the compounds investigated.

Compounds	Temp. °K	$\tau \times 10^{12}$ Sec	$\eta_1 Cp$	$\eta_{12}Cp$*	$\eta_{12}Cp$**	$\eta_1^e \times 10^3$	$\frac{T\tau}{\eta_1} \times 10^8$	$\frac{T\tau}{\eta_{12}} \times 10^8$	$\frac{T\tau}{\eta_1^e} \times 10^8$
Dimethyl aniline	293	9·33	0·652	0·728	0·730	21·610	41·927	37·550	12·650
	303	8·64	0·564	0·706	0·716	19·350	46·417	37·081	13·529
	313	7·83	0·503	0·675	0·694	17·734	48·723	36·308	13·819
N-N-dimethyl aniline	293	8·79	0·652	0·704	0·712	16·676	39·501	36·583	15·444
	303	8·08	0·564	0·673	0·662	14·821	43·408	36·378	16·510
	313	7·81	0·503	0·629	0·639	13·503	48·599	38·863	18·103
N-ethyl aniline	293	6·97	0·652	0·675	0·684	21·190	31·322	29·726	9·630
	303	6·71	0·564	0·687	9·690	18·963	36·048	30·301	10·722
	313	6·50	0·503	0·658	0·656	17·372	40·447	30·919	11·711
θ-ethyl aniline	293	10·79	0·652	0·789	0·790	13·117	48·488	40·087	24·102
	303	9·86	0·564	0·739	0·739	11·542	52·971	40·430	25,888
	313	8·93	0·503	0·711	0·721	10·491	55·568	39·364	26·642
N-ethyl-θ-toluidine	293	15·34	0·652	0·679	0·680	20·768	68·935	66·194	21·642
	303	14·54	0·564	0·661	0·670	18·575	78·113	66·651	23·718
	313	13·05	0·503	0·637	0·640	17·008	81·205	65·349	24·016
Benzyl aniline	293	16·32	0·652	0·589	0·590	13·927	73·339	82·230	34·334
	303	14·69	0·564	0·544	0·543	12·314	78·919	83·353	36·147
	313	13·71	0·503	0·524	0·520	11·173	85·312	84·679	38·407

* Equation of Hill.

** Equation of Vaughan.

Table 3. Relaxation time and molar activation energy parameters of polar compounds in dilute solutions of benzene

Compounds	Temp. °K	$\tau \times 10^{12}$ Sec.	ΔF_τ $\times 10^{-3}$ J/mole	ΔF_{η_1} $\times 10^{-3}$ J/mole	$\Delta F_{\eta_{12}}$ $\times 10^{-3}$ J/mole	ΔH_τ $\times 10^{-3}$ J/mole	ΔH_{η_1} $\times 10^{-3}$ J/mole	$\Delta H_{\eta_{12}}$ $\times 10^{-3}$ J/mole	$\Delta S\tau$	$\Delta S\eta_1$
Dimethyl aniline	293	9·33	2·35	2·90	2·97	1·92	2·52	4·60	1·46	−1·29
	303	8·64	2·39	2·92	3·07	1·92	2·52	4·60	1·55	−1·32
	313	7·83	2·45	2·94	3·16	1·92	2·52	4·60	−1·69	−1·34
N-N-dimethyl aniline	293	8·79	2·28	2·90	2·95	2·05	2·52	7·22	−0·78	−1·29
	303	8·08	2·34	2·92	3·04	2·05	2·52	7·22	−0·96	−1·32
	313	7·81	2·37	2·94	3·11	2·05	2'52	7·22	−1·02	−1·34
N-ethyl aniline	293	6·97	2·18	2·90	2·92	1·93	2·52	1·61	−0·85	−1·29
	303	6·71	2·20	2·92	3·04	1·93	2·52	1·61	−0·89	−1·32
	313	6·50	2·25	2·94	3·14	1·93	2·52	1·61	−1·03	−1·34
θ-ethyl aniline	293	10·79	2·43	2·90	3·01	2·17	2·52	7·31	−0·89	−1·29
	303	9·86	2·46	2·92	3·09	2·17	2·52	7·31	−0·96	−1·32
	313	8·93	2·52	2·94	3·53	2·17	2·52	7·31	−1·12	−1·34
N-ethyl-*θ*-toluidine	293	15·34	2·63	2·90	2·93	2·94	2·52	5·10	2·35	−1·29
	303	14·54	2·70	2·92	3·03	2·94	2·52	5·10	2·50	−1·32
	313	13·05	2·75	2·94	3·12	2·94	2·52	5·10	2·58	−1·34
Benzyl aniline	293	16·32	2·67	2·90	2·84	2·14	2·52	7·36	1·81	−1·29
	303	14·69	2·71	2·92	2·91	2·14	2·52	7·36	1·88	−1·32
	313	13·71	2·78	2·94	2·99	2·14	2·52	7·36	2·04	−1·34

It is apparent from table 2 that the ratio $T\tau/\eta_1$ increases with the rise in temperatures for nearly all the compounds investigated which is not in conformity with the Debye theory which requires the ratio to be constant for the compounds of same size for small change in temperature. This anomaly can be explained if η_1^{α}, the Kalmann viscosity parameter is used in place of η_1, where the variation in the values of ratio $T\tau/\eta_1^{\alpha}$ becomes small as compared to the values of the ratio $T\tau/\eta_1$ at different temperatures. Further if η_{12} i.e., the mutual viscosity of the solute and the solvent is used instead of η_1 and η_1^{α} the variation in the values of the ratios $T\tau/\eta_{12}$ at different temperatures is negligibly small and this leads us to conclude that η_{12} gives a more convincing account of the resistance confronted by the individual solute molecules during the process of rotation. The values of the averaged mutual viscosity for different solutions as determined from equation of Vaughan *et al* (1961) are almost equal to those of the corresponding mutual viscosities determined from the equation of Hill (1954). This is probably due to the fact that form of equation of Vaughan *et al* is very nearly the same as that of equation of Hill which has also been pointed out by Vaughan *et al* (1961).

(iii) *Thermodynamic Parameters*

It is evident from table 3 that the free energy of activation for the viscous flow process is always greater than that for the dielectric relaxation process in all the cases investigated. This is in agreement with the fact that while the process of dipole orientation involves only the rotation of the molecules, the process of viscous flow involves both rotation and translation. Similar results were obtained earlier by one of the authors (Mehrotra 1967) in the case of substituted pyridines.

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REFERENCES

Debye P. 1929 *Polar Molecules*, Chemical Catalogue Company, New York, p. 90.

Fong F. K. & Smyth C. P. 1963 *J. Am. Chem. Soc.* **85**, 548.

Glasstone S., Laidler K. J. & Eyring H. 1941 *The Theory of Rate Processes*, Mc-Graw Hill Book Company, Inc., New York, N.Y. p. 548.

Gopala Krishna K. V. 1957 *Trans. Faraday Soc.* **53**, 767.

Higasi K. 1961 *Dielectric Relaxation and Molecular Structure*, Hokkaido University, Sapporo, Japan.

Hill N. E. 1954 *Proc. Phys. Soc.* **67**, 149.
Kalmann O. F. & Smyth C. P. 1961 *J. Am. Chem. Soc.* **83**, 571.
Mehrotra N. K. & Saxena M. C. 1967 *Bull. Chem. Soc. Japan* **40**, 19.
Mehrotra N. K., Pant T. C. & Saxena M. C. 1969 *Trans. Faraday Soc.* No. 560, Pt. 8, 65.
Mehrotra N. K. 1971 *Ind. J. Phys.* **45**, 83.
Roberts S. & Von Hippel A. 1946 *J. Appl. Phys.* **17**, 610.
Shukla J. P., Shukla D. D. & Saxena M. C. 1969 *J. Phys. Chem.* **73**, 2187.
Vaughan W. E., Purcell W. P. & Smyth C. P. 1961 *J. Am. Chem. Soc.* **83**, 571.