BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 356—358 (1972) [Vol. 45, No. 2

Study of Dielectric Relaxation Mechanism and Mutual Viscosity in Some Aromatic Compounds

N. K. Mehrotra, T. C. Pant, and M. C. Saxena
Physics Department, Lucknow University, Lucknow, India

(Received October 23, 1970)

Relaxation time and mutual viscosity of seven substituted benzenes, *p*-toludine, *o*-nitroaniline, 2,4-dichloroanisole, 2,3-dichloroanisole, 2,5-dichloronitrobenzene, 3,4-dichloronitrobenzene, and 4-chloro-1,3-dinitrobenzene have been determined in the 3.13 cm (9585 MHz) microwave region, and at three different 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.

Investigation of dielectric relaxation in a number of organic compounds shows wide disagreement between the observed values of relaxation time and those calculated using the Debye equation.[1] This discrepancy can be explained if in the Debye equation we use a mutual viscosity parameter η_{12} representing the interaction between both solute and solvent molecules, instead of solvent viscosity η_1. The expression for the coefficient of mutual viscosity η_{12} as proved by Hill[2] is given by:

$$\eta_m\sigma_m = x_1^2\eta_1\sigma_1 + x_2^2\eta_2\sigma_2 + 2x_1x_2\eta_{12}\sigma_{12} \tag{1}$$

where η_m, η_1, and η_2 are the coefficients of viscosity of the solution, solvent and solute, respectively, and the quantities σ represent the average intermolecular distances.

On rearrangement Eq. (1) yields

$$\frac{(\eta_m\sigma_m - x_1^2\eta_1\sigma_1)}{x_2^2\sigma_2^2} = \eta_2 + 2(x_1/x_2)\cdot(\sigma_{12}/\sigma_2)\eta_{12} \tag{2}$$

This equation represents a straight line and its slope gives mutual viscosity η_{12}.

It is interesting to note that an expression involving mutual viscosity η_{12} was also proposed by Vaughan and his co-workers.[3] The results obtained using this expression are in good agreement with those obtained using Hill's equation. Their equation in the present notation is

$$\eta_m = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2\eta_{12} \tag{3}$$

which yields on rearrangement, the relation

$$\frac{(\eta_m - x_1^2\eta_1)}{x_2^2} = \eta_2 + 2x_1/x_2\cdot\eta_{12} \tag{4}$$

The slope of this straight line gives the mutual viscosity.

A good approximation of the relation between the viscosity and relaxation-time was suggested by Kalman and Smyth,[4] who found that the equation

$$\tau = \frac{c'}{T}\eta^{\alpha} \quad \text{where} \quad \alpha = \Delta H\tau/\Delta H\eta$$

gives very satisfactory results over a small temperature range. We have used this equation for a comparative study.

The free energies of activation for the process of dipole orientation and viscous flow have also been calculated using Eyring's equation.[5,6]

Experimental

Chemicals. 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.

The dielectric constant ε' and the loss factor ε'' were measured using the standing wave technique of Roberts and Von Hippel[7] and its subsequent simplification by Dakin and Works.[8] The estimated accuracies in the measurements of ε' and ε'' were $\pm 1\%$ and $\pm 5\%$, respectively. The relaxation time was then determined using the concentration variation method of Gopala Krishna.[9]

Viscosities were measured to an accuracy of $\pm 2\%$ with a Hoppler precision viscometer. This method requires the determination of time of fall of a glass or metal ball between two marks in a glass tube filled with a liquid with known density. Viscosity η_m of the liquid is calculated using the relation

$$\eta_m = F(S_K - S_F)K \tag{5}$$

where F is the time of fall of the ball in seconds, S_k is the specific gravity of the ball, S_F is the specific gravity of the liquid, and K is the ball constant (=0.009495).

Results and Discussion

Table 1 contains the values of relaxation time τ, mutual viscosity η_{12}, and ratios $T\tau/\eta$, $T\tau/\eta_{12}$ and $T\tau/\eta\alpha$. The values of the relaxation times and molar activation energy parameters at different temperatures are given in Table 2.

The relaxation time of *p*-toluidine is found to be smaller than that of *o*-nitroaniline. This can be explained on the basis that the intramolecular rotation of the $-NH_2$ group is comparatively less hindered by the $-CH_3$ group at the para position than by the $-NO_2$ group at the ortho position in the latter molecule. Further, the variation of relaxation time is in accordance with the

---

[1] P. Debye, "Polar Molecules," Reinhold Publishing Corp., New York, (1929), Chap. 5.

[2] N. E. Hill, *Proc. Phys. Soc.*, **67**, 149 (1954).

[3] W. E. Vaughan, W. P. Purcell, and C. P. Smyth, *J. Amer. Chem. Soc.*, **83**, 571 (1961).

[4] O. F. Kalman and C. P. Smyth, *ibid.*, **82**, 783 (1960).

[5] S. Glasstone, K. J. Laider, and H. Eyring, "The Theory of Rate Process," McGraw-Hill Co., Inc., New York (1941), p. 548.

[6] N. K. Mehrotra, T. C. Pant, and M. C. Saxena, *Trans. Faraday Soc.*, **65**, 2078 (1969).

[7] S. Roberts and A. Von Hippel, *J. Appl. Phys.*, **17**, 610 (1946).

[8] T. W. Dakin and C. N. Works, *ibid.*, **18**, 610 (1947).

[9] K. V. Gopala Krishna, *Trans. Faraday Soc.*, **53**, 767 (1957).

Table 1. Values of the relaxation time (τ), average mutual viscosity η_{12} and the ratio ($T\tau/\eta_1$), ($T\tau/\eta_{12}$), ($T\tau/\eta_1^\alpha$) for the compounds investigated

Compound	Temp. °K	$\tau\times10^{12}$ sec	η_1 cp	η_{12} cp Eq. (2)	η_{12} cp Eq. (4)	η_1^α $\times10^3$	$T\tau/\eta_1$ $\times10^8$	$T\tau/\eta_{12}$ $\times10^8$	$T\tau/\eta_1^\alpha$ $\times10^8$
p-Toluidine	293	7.3	0.65	0.67	0.64	4.42	32.74	31.82	0.48
	303	6.2	0.56	0.61	0.60	3.79	33.59	31.57	0.49
	313	5.4	0.50	0.53	0.52	3.29	34.43	31.74	0.51
o-Nitroaniline	293	7.2	0.65	0.68	0.68	22.77	34.95	32.63	9.29
	303	6.4	0.56	0.64	0.62	20.46	35.88	31.54	9.83
	313	5.7	0.50	0.59	0.55	18.54	35.85	30.07	9.54
2,4-Dichloroanisole	293	10.7	0.65	0.87	0.87	9.02	48.50	36.27	0.34
	303	9.1	0.56	0.75	0.73	7.90	49.33	37.20	0.35
	313	8.0	0.50	0.64	0.67	6.99	50.71	36.40	0.36
2,3-Dichloronitrobenzene	293	11.7	0.65	0.91	0.94	8.12	53.07	37.68	0.42
	303	10.0	0.56	0.79	0.79	7.08	53.78	38.39	0.43
	313	8.7	0.50	0.74	0.73	6.26	55.21	36.86	0.44
2,5-Dichloronitrobenzene	293	13.8	0.65	0.92	0.93	8.97	62.37	43.75	0.45
	303	11.6	0.56	0.89	0.88	7.84	62.81	39.23	0.45
	313	10.4	0.50	0.82	0.80	6.95	67.95	39.05	0.47
3,4-Dichloronitrobenzene	293	17.5	0.65	1.20	1.21	76.14	79.45	42.69	6.74
	303	15.8	0.56	1.19	1.21	70.78	85.17	39.99	6.75
	313	14.5	0.50	1.17	1.18	66.19	92.02	38.58	6.85
4-Chloro-1,3-dinitrobenzene	293	24.1	0.65	1.25	1.25	2.93	108.92	56.52	0.024
	303	19.9	0.56	1.21	1.21	2.48	107.55	49.96	0.024
	313	16.9	0.50	1.19	1.21	2.13	107.38	45.76	0.025

Table 2. Relaxation time and molar activation energy parameters of polar compounds in dilute solution of benzene (at 9585 MHz)

Compound	Temp. °K	$\tau\times10^{12}$ sec	ΔF_τ $\times10^{-3}$ J/mol	ΔF_η $\times10^{-3}$ J/mol	$\Delta F_{\eta_{12}}$ $\times10^{-3}$ J/mol	ΔH_τ $\times10^{-3}$ J/mol	ΔH_η $\times10^{-3}$ J/mol	$\Delta H_{\eta_{12}}$ $\times10^{-3}$ J/mol	ΔS_τ J/mol	ΔS_η J/mol	$\Delta S_{\eta_{12}}$ J/mol
p-Toluidine	293	7.3	9.34	12.18	12.36	10.26	9.54	8.72	+3.14	−8.99	−12.46
	303	6.2	9.35	12.23	12.56	10.26	9.54	8.72	+3.00	−8.90	−12.69
	313	5.4	9.40	12.30	12.62	10.26	9.54	8.72	+2.64	−8.82	−12.47
o-Nitroaniline	293	7.2	9.39	12.18	12.39	7.16	9.54	5.42	−7.43	−8.29	−22.73
	303	6.4	9.44	12.23	12.67	7.16	9.54	5.42	−7.51	−8.90	−23.91
	313	5.7	9.49	12.30	12.86	7.16	9.54	5.42	−7.43	−8.82	−23.87
2,4-Dichloroanisole	293	10.7	10.28	12.18	13.00	8.91	9.54	8.91	−4.77	−8.99	−13.97
	303	9.1	10.34	12.23	13.07	8.91	9.54	8.91	−4.71	−8.90	−13.75
	313	8.0	10.40	12.30	13.24	8.91	9.54	8.91	−4.78	−8.82	−13.95
2,3-Dichloroanisole	293	11.7	10.53	12.18	13.13	9.11	9.54	8.13	−4.97	−8.99	−17.05
	303	10.0	10.55	12.23	13.19	9.11	9.54	8.13	−4.80	−8.90	−16.71
	313	8.7	10.63	12.30	13.47	9.11	9.54	8.13	−4.86	−8.82	−17.12
2,5-Dichloronitrobenzene	293	13.8	10.92	12.18	13.16	8.92	9.54	4.45	−6.84	−8.99	−29.73
	303	11.6	10.94	12.23	13.53	8.92	9.54	4.45	−6.70	−8.90	−29.97
	313	10.4	11.11	12.20	13.74	8.92	9.54	4.45	−7.05	−8.82	−29.67
3,4-Dichloronitrobenzene	293	17.4	11.52	12.18	13.81	4.86	9.54	1.01	−22.74	−8.99	−43.80
	303	15.8	11.72	12.23	14.27	4.88	9.54	1.01	−22.66	−8.90	−43.76
	313	14.4	12.02	12.30	14.69	4.88	9.54	1.01	−23.22	−8.82	−43.69
4-Chloro-1,3-dinitrobenzene	293	24.1	12.30	12.18	13.91	11.04	9.54	1.65	−4.29	−8.99	−41.86
	303	19.9	12.31	12.23	14.30	11.04	9.54	1.65	−4.21	−8.90	−41.68
	313	16.9	12.38	12.30	14.73	11.04	9.54	1.65	−4.27	−8.82	−41.78

variation of their molecular volumes. 2,3-Dichloroanisole exhibits a larger relaxation time than 2,4-dichloroanisole, although the size of the two molecules is the same. This can be explained by considering the fact that both molecules contain $-OCH_3$ group at the ortho position, which is capable of intramolecular rotation round its bond with the benzene ring. The rotation of $-OCH_3$ group experiences greater steric hindrances due to the neighbouring chloro groups in 2,3-dichloroanisole than in 2,4-dichloroanisole, resulting in a greater relaxation time in the former molecule.

It is observed from the table that the relaxation time of 2,5-dichloronitrobenzene is smaller than that of 3,4-dichloronitrobenzene, which can be concluded from the consideration that the volume swept out for dipole orientation by the former molecule is also smaller. The largest relaxation time of 4-chloro-1,3-dinitrobenzene among all other compounds investigated can be attributed to its biggest size and the strong polarity of the $-NO_2$ groups.

It is apparent from Table 1 that the ratio increases with the rise of temperature for nearly all the compounds investigated. This is not in conformity with the Debye theory which requires the ratio to be constant for small change of temperature. The anomaly is explained if η_{12} the mutual viscosity of the solute and solvent is used instead of solvent viscosity η_1. The variation in the values of ratios $T\tau/\eta_{12}$ and $T\tau/\eta\alpha$ at different temperatures is negligibly small and this leads us to conclude that either η_{12} or $\eta_1{}^{\alpha}$ gives a more convincing account of the resistance confronted by the individual solute molecules during the process of rotation.

The values of the average mutual viscosity η_{12} as determind from Eq. (4) of Vaughan and co-workers are almost equal to those obtained using Hill's equation (2). This is because the form of the two equations is very nearly the same. We have determined the values of η_{12} for chlorobenzene using Eqs. (2) and (4). For chlorobenzene in benzene, Eq. (2) gives 0.74, while Eq. (4) gives 0.73. This indicates a fairly good agreement in the values of η_{12} obtained using the two equations.

The free energies of activation for dipole orientation and viscous flow are found to increase with the rise of temperature while the relaxation time decreases. An explanation is furnished from the consideration that with the rise of temperature, thermal agitation increases, resulting in the increase of the activation energies. Similar results have also been concluded by Shukla and Coworkers[10)] for some substituted benzaldehydes. The negative value of the entropy of activation found for most of the compounds investigated indicates that there are fewer configurations possible in the activated state and for these configurations the activated state is more ordered than the normal state. A comparison of the activation energies for the viscous flow using solvent viscosity η_1 and mutual viscosity η_{12} show that $\Delta F_{\eta_{12}}$ is a better representation of the potential barriers offering inner friction to the rotating molecules.

The higher values of ΔF_η as compared to ΔF_τ indicate 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 observed earlier in the case of substituted pyridines.[11)]

---

10) J. P. Shukla, S. I. Ahmad, D. D. Shukla, and M. C. Saxena, *J. Phys. Chem.*, **72**, 1013 (1968).

11) N. K. Mehrotra and M. C. Saxena, This Bulletin, **40**, 19 (1947).