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Dielectric Relaxation and Molecular Structure. IV. Dielectric Relaxation and Hydrogen Bonding in Chloroanilines

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Measurements of relative permittivity were carried out at 30.0 °C in *p*-dioxane at 1 MHz and at 9.48 GHz for *ortho* (A), *meta* (B), and *para* (C) chloroanilines. The results are interpreted in terms of hydrogen bonding between amino hydrogens and the oxygen atoms of the dioxane molecule, the dipole moments and dielectric relaxation time values being given. The relative behaviour of chloroanilines has been discussed. It seems that a finite probability of H-Cl bond formation exists between one of the amino hydrogens and the neighbouring chlorine atom in *o*-chloroaniline.

Curran and Estok[1] assume that hydrogen bonding between amino hydrogens and dioxane oxygens is a normal phenomenon. Few and Smith[2] incline to the view that hydrogen bonding occurs when the actual structure is that of resonance between several possible structures and that it also receives considerable contribution from highly polar structures. Chitoku and Higasi[3] showed, from dipole moment and dielectric relaxation study, that an increase in the dielectric relaxation time of certain anilines in dioxane is a measure of the strength of hydrogen bonds and have verified the viewpoint of Few and Smith[2] by concluding that the strength of hydrogen bonds depends upon the increment in mesomeric moment of amino group. Smith and Walshaw[4] had demonstrated that the mesomeric interaction and presumably the *p*-character of the lone pair orbital of nitrogen atom increases upon *n*-methylation of the amino group and with the introduction of the electro-negative substituent in the phenyl ring. Cumper and Singleton[5] have carried out measurements on dipole moments of a large number of systems including chloroanilines. Their results support the observations of Smith and Walshaw.[4] They interpret the '$\Delta\mu$' increment (*i.e.*, $\mu_D - \mu_B$) as the increase in mesomeric moment since their results for '$\Delta\mu$' and mesomeric interaction correspond with each other in most of the systems they studied. The behaviour of different isomers can be estimated by this method. We have made measurements[6] on *o*-, *m*-, and *p*-, chloroanilines for calculating both the dipole moments and dielectric relaxation times in benzene and dioxane with the hope that additional relaxation data for these molecules might give more information on their relative behaviour.

Experimental and Results

Benzene and *p*-dioxane were purified by standard methods. Purification of solutes, instruments, methods of measurement and of analysis were given previously.[7]

TABLE 1. VALUES OF a_0 (slope of ε *vs.* concn curve), a' (Slope of ε' *vs.* concn curve), a'' (slope of ε'' *vs.* concn curve), AND a_D (slope of $n_D{}^2$ *vs.* concn curve)

Solvent	a_0	a'	a''	a_D
		o-Chloroaniline		
Benzene	3.14	2.80±0.02	0.88±0.02	0.106
p-Dioxane	4.32	2.37±0.02	1.20±0.02	0.410
		m-Chloroaniline		
Benzene	6.25	4.44±0.03	2.33±0.04	0.220
p-Dioxane	9.00	2.90±0.02	2.69±0.04	0.450
		p-Chloroaniline		
Benzene	7.96	4.90±0.03	2.49±0.04	0.256
p-Dioxane	11.50	3.47±0.02	3.10±0.06	0.470

TABLE 2. VALUES OF THE DIPOLE MOMENT AND DIELECTRIC RELAXATION TIME

	Dipole moment in benzene μ_B (Debyes)		Dipole moment in dioxane μ_D (Debyes)		Dielectric relaxation time 10^{-12} s			
					τ_B		τ_D	
	Present	Literature	Present	Literature	$\tau(1)_B$	$\tau(2)_B$	$\tau(1)_D$	$\tau(2)_D$
o-Chloroaniline (A)	1.88	1.77 to 1.84[a]	2.00	1.97[d]	5.5	6.5	10.3	27.4
m-Chloroaniline (B)	2.67	2.66 to 2.70[a]	2.98	3.06[d]	9.3	13.0	18.5	38.2
p-Chloroaniline (C)	3.02	2.90 to 3.00[a]	3.40	3.39[b] 3.37[c]	9.0	20.6	17.7	43.6

a) A. L. McClellan, "Tables of Experimental Dipole Moments", Freeman and Co., San Francisco, (1963).
b) A. V. Few and J. W. Smith, *J. Chem. Soc.*, **1949**, 2781. c) Ref. 1.

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[1] C. Curran and G. K. Estok, *J. Amer. Chem. Soc.*, **72**, 4575 (1950).

[2] A. V. Few and J. W. Smith, *J. Chem. Soc.*, **1949**, 753, 2663.

[3] K. Chitoku and K. Higasi, This Bulletin, **39**, 2160 (1966).

[4] J. W. Smith, *J. Chem. Soc.*, **1952**, 3532; **1953**, 109; J. W. Smith and S. M. Walshaw, *ibid.*, **1957**, 3217; **1959**, 3748.

[5] C. W. N. Cumper and A. Singleton, *J. Chem. Soc.*, *B*, **1968**, 645.

[6] These measurements formed a part of the Ph. D. thesis of one of the authors (J. K. Vij), Panjab University, Chandigarh, India, February 1969.

[7] K. K. Srivastava and J. K. Vij, This Bulletin, **43**, 2307 (1970).

TABLE 3. VALUES OF THE SOLVENT INCREMENT AND THE RATIO OF DIELECTRIC RELAXATION TIMES

Substance	$(\mu_D-\mu_B)$ (Debye) *i.e.* Present	$(\mu_D-\mu_B)$ (Debye) *i.e.* Literature	Ratios of dielectric relaxation time	
			$\tau(1)_D/\tau(1)_B$	$\tau(2)_D/\tau(2)_B$
o-Chloronailine (A)	0.12 ± 0.01	0.20[d]	1.9	4.2
m-Chloroaniline (B)	0.31 ± 0.01	0.39	2.0	2.9
p-Chloroaniline (C)	0.38 ± 0.01	0.37[e] 0.39[d]	2.0	2.1
Aniline (D)	—	0.25[f]	—	2.9[f]

d) Ref. 5. e) Ref. 10, Chap. X, p. 329. f) Ref. 3.

Both parts, real and imaginary, of relative permittivity were found, from observation, to be linear functions of solute concentration in the range studied.

The results have been discussed in terms of $\tau(1)$ and $\tau(2)$, which are the dielectric relaxation time values defined by the following two independent equations derived from the Debye equation for dilute solutions:

$$\tau(1) = \frac{1}{\omega}\frac{a''}{a'-a_D} \tag{1}$$

$$\tau(2) = \frac{1}{\omega}\frac{a_0-a'}{a''} \tag{2}$$

This method of analyzing the single frequency data has recently been proposed by Higasi *et al.*[8] and has been discussed in more detail.[9] The values of the "so-called slopes" for *o*-, *m*-, and *p*-, chloroanilines in *p*-dioxane are given in Table 1 along with those in benzene.[7] Possible errors in the value of the slopes are also indicated. Values for dipole moments and dielectric relaxation times are given in Table 2, and dipole moment increments (*i.e.*, $\Delta\mu=\mu_D-\mu_B$) and ratios of both $\tau(1)_D/\tau(1)_B$ and $\tau(2)_D/\tau(2)_B$ in Table 3.

Discussion

The values of moments show a close agreement with those in literature indicating the reliability of technique and purity of the chemicals.

A small increment in $\Delta\mu$ and consequently a small increase in mesomeric moment of amino group has been interpreted[5] as either of two possibilities:

(i) H–Cl bond between one of two amino hydrogens and the neighbouring chlorine atom, leaving the second hydrogen atom free for hydrogen bonding.

(ii) An electrostatic repulsion between the electronegative chlorine atom and the oxygen atoms of a dioxane molecule.

$\tau(1)$ at the experimental frequency is a combination of τ_1, and τ_2 whereas $\tau(2)$ corresponds very nearly to τ_1.[9] The relaxation data show that the ratio $\tau(1)_D/\tau(1)_B$ remains almost constant. This suggests that intramolecular relaxation time does not depend much on the solvent, whereas molecular relaxation time is affected possibly because of complex formation[3] of the molecule in *p*-dioxane. Intramolecular relaxation time seems to be independent as the result of its inversion mechanism postulated by Smyth.[10]

The ratio $\tau(2)_D/\tau(2)_B$ follows a decreasing trend in contrast to that observed from dipole moment studies and the ratio for *o*-chloroaniline, in particular, is large. This may imply that the system formed for this molecule in *p*-dioxane is relatively one with more complexities. It appears to favour (i), since (ii) would not lead to the large increase in the molecular relaxation time for *o*-chloroaniline in *p*-dioxane. Our observations support the postulates already made from the examination of the dissociation constants[11] and N–H stretching frequencies[12] in *o*-chloroanilines.

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[8] K. Higasi, Y. Koga, and M. Nakamura, This Bulletin **44**, 988 (1971).

[9] J. K. Vij, Iqbal Krishan, and K. K. Srivastava, *ibid.*, **46**, 17 (1973).

[10] C. P. Smyth, "Molecular Relaxation Processes," Chemical Society Publication No. 20, Academic Press, London (1966), p. 8.

[11] D. H. McDaniel and H. C. Brown, *J. Amer. Chem. Soc.*, **77**, 3756 (1955).

[12] P. J. Krueger, *Can. J. Chem.*, **40**, 2300 (1962).