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# Dielectric relaxation studies. II. Phenolic Mannich bases in dilute solution

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The dielectric relaxation processes in phenolic Mannich bases have been investigated by measuring the dielectric permittivity and loss in dilute solutions of benzene at three different microwave frequencies at 30°, 45°, and 60°C. Results are analyzed in terms of Cole-Cole arc plots and two distinct relaxation times. The results establish the intramolecular hydrogen bonding of the -OH group. The overall molecular relaxation appears to be the predominant mechanism in these substituted phenols. Activation parameters have been calculated assuming dielectric relaxation to be an Eyring-type rate process.

## INTRODUCTION

Extensive dielectric relaxation studies on substituted phenols<sup>1,2</sup> in dilute solutions have established the existence of two relaxation processes arising from the rotation of the hydroxyl group and the orientation of the molecule as a whole. Antony<sup>3</sup> and Fong *et al.*'s analyses of dielectric data of numerous hydroxy compounds in terms of molecular and intramolecular relaxation times have brought to light the significant contribution of -OH group rotation to the observed dielectric losses of these compounds. A dielectric absorption attributed to the phenolic group has also been observed in the solid state by Meakins.<sup>5</sup> The present study examines the dielectric relaxation of six phenolic Mannich bases (Fig. 1) in solutions of benzene in the microwave region at three different temperatures. These molecules are particularly interesting for relaxation studies due to the presence of a bulky group *ortho* to phenolic -OH which is capable of forming intramolecular hydrogen bonding and thus sterically affecting the free rotation of the hydroxyl group. The dielectric data of these compounds are analyzed in terms of the Cole-Cole arc plots and superposition of two Debye-type absorptions.

## EXPERIMENTAL

The dielectric permittivity and loss of dilute solution at 8.45, 12.2, and 30.5 GHz were determined by the measurement of wavelength in the dielectric and the standing wave ratio using a short circuited plunger by the method suggested by Heston *et al.*<sup>6</sup> The apparatus used for the measurement was described previously by Khanna and Sobhanadri.<sup>7</sup> The estimated accuracy of measurement was  $\pm 1\%$  for  $\epsilon'$  and  $\pm 5\%$  for  $\epsilon''$ . A Marconi bridge (Type 1312A) was used for determining static dielectric constant at 1 kHz. Refractive index was measured with Abbe's refractometer. The temperature in each experiment was kept constant within  $\pm 1^\circ\text{C}$  by circulating water from a thermostat (a Coloro K1395).

## CHEMICALS

The phenolic Mannich bases used in the present study were prepared in this laboratory following a method given by Grillot *et al.*<sup>8</sup> The purity of these compounds

was tested using thin layer chromatography (TLC) and the compounds were further characterized by NMR and IR spectroscopy. Dried and twice distilled Analar benzene (BDH, India) was used as the solvent.

## ANALYSIS OF DATA

$\epsilon_0$ ,  $\epsilon'$ , and  $\epsilon''$  have been measured for solutions of varying concentrations within a range which did not, in general, exceed 0.05 weight fraction. Since  $\epsilon_0$ ,  $\epsilon'$ , and  $\epsilon''$  for dilute solutions have been shown to be linear functions of concentration,<sup>6</sup> plots have been made with these quantities against weight fractions and the respective slopes  $a_0$ ,  $a'$ , and  $a''$  have been used in the analysis. The calculated values of  $a_0$ ,  $a'$ , and  $a''$  obtained for these compounds at three temperatures are listed in Table I along with the maximum concentration (in weight fraction) used for each substance. Fairly smooth Cole-Cole plots could be drawn through the experimental points (typical Cole-Cole plots for a Mannich base at three temperatures are shown in Fig. 2). The distribution parameter " $\alpha$ " and the most probable relaxation time " $\tau_0$ " determined from such depressed arc plots are listed in Table II.

## RESULTS AND DISCUSSION

Cole-Cole plots with finite values of distribution parameter  $\alpha$  suggest the presence of another relaxation process, in addition to the overall molecular rotation. In the present group of liquids, the values of  $\alpha$  are found to be lower than their respective pure liquid values.<sup>9</sup> Such a tendency towards symmetric distribution in dilute solutions has been observed by many experimenters.<sup>10</sup> The decrease of  $\alpha$  with increase in temperature indicates the increase in uniformity of the potential barriers hindering the dipolar orientation throughout the liquid. Cole-Cole plots further reveal that the loss maxima of these compounds fall in the UHF region as observed by Aihara and Davies<sup>1</sup> in similar compounds.

2,6-Di-*t*-butylphenol, a molecule with unhindered phenolic group, has been reported to have a relaxation time of 8.6 psec in *p*-xylene solution by Magee and Walker.<sup>11</sup> One can see from Table II that all these Mannich bases, which are smaller than the 2,6-di-*t*-butylphenol molecule, have longer relaxation times. Earlier studies of Purcell<sup>12</sup> and Grubb *et al.*<sup>13</sup> on flexible molecules have revealed that the presence of a freely

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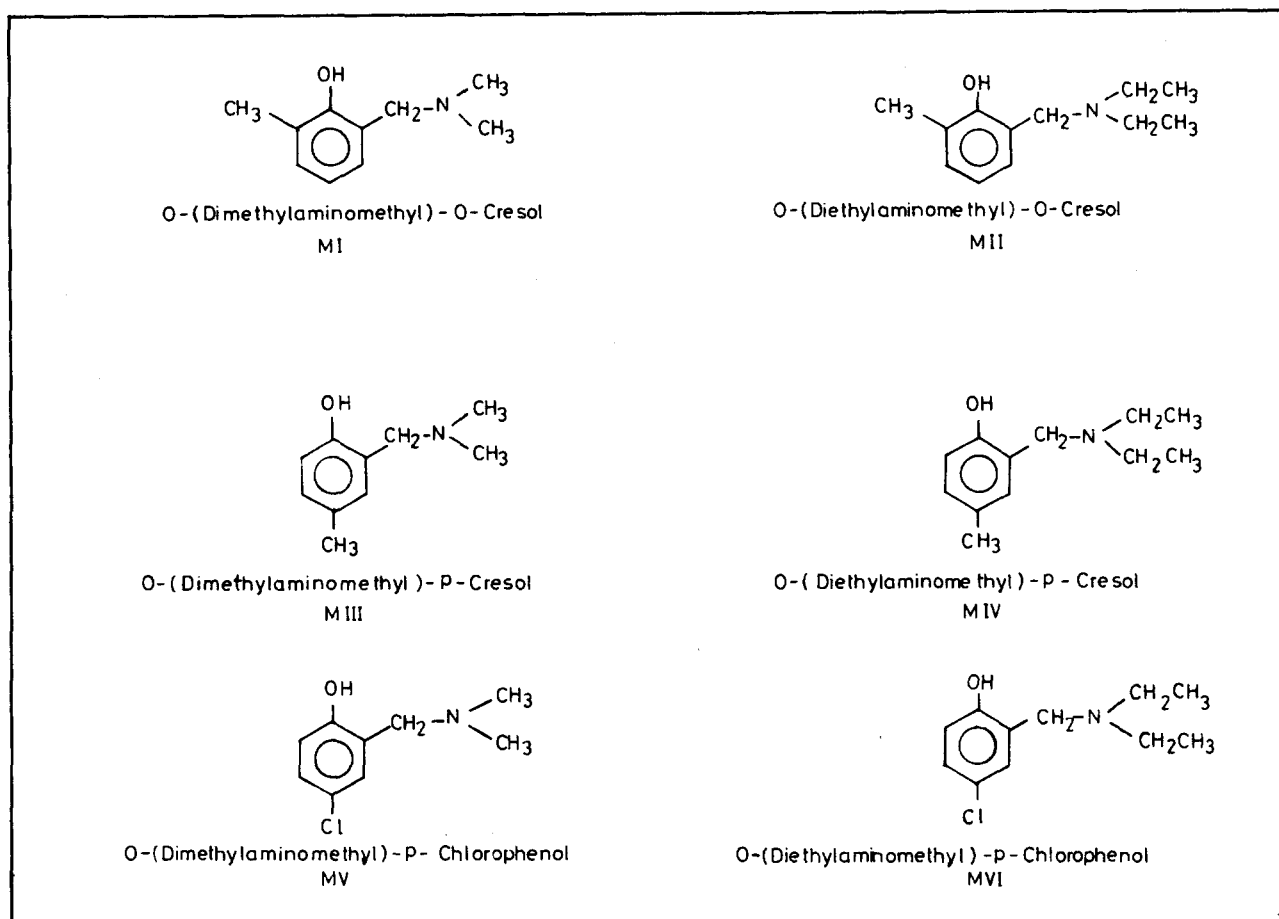


FIG. 1. Molecular formula of the compounds.

rotating "polar group" (whose moment component does not lie along the axis of group rotation) leads to lowering of relaxation times. Although the internal hydroxyl group rotation can be expected to occur in the present group of liquids, fairly large relaxation times observed for these compounds indicate the absence of "free-OH." Restricted rotation of -OH makes the molecule less flexible and the mean relaxation time  $\tau_0$  increases to the order expected of a rigid molecule. The hindrance to free rotation of -OH in these molecules can be expected to arise from the intramolecular hydrogen bonding, owing to the mutual interaction between hydrogen of the -OH group and the lone pair of electrons from nitrogen in the side chain (Fig. 3). Such intramolecular hydrogen bonding and its hindrance to the free rotation of the hydroxyl group have been reported by Antony *et al.*<sup>3</sup> in some *ortho*-substituted phenols.

To confirm the presence of intramolecular hydrogen bonding and to understand the relative strength of the bond, IR spectroscopic measurements were made in dilute solutions of carbon tetrachloride in the region of -OH stretching fundamentals. The spectra were recorded on Perkin-Elmer-257 grating spectrophotometer at slow speed using 2 mm NaCl matched cells. The concentration of the solutions used are of the order of 0.02 mole. All these compounds exhibit a broad band around  $3350\text{ cm}^{-1}$  indicating the complete absence of free -OH, whose band normally occurs around  $3600\text{ cm}^{-1}$

in phenolic compounds.<sup>14</sup> Intramolecularly bonded -OH is shifted towards the C-H stretching regions. Intermolecular hydrogen bonding is almost ruled out since no peak characteristic of such a band was found in the range of dilutions used. A typical IR spectrum of a phenolic Mannich base is shown in Fig. 4.

The intramolecular hydrogen bonding, established from IR studies, seems to prevent largely, if not wholly, the intramolecular free rotation of the -OH group. Thus,

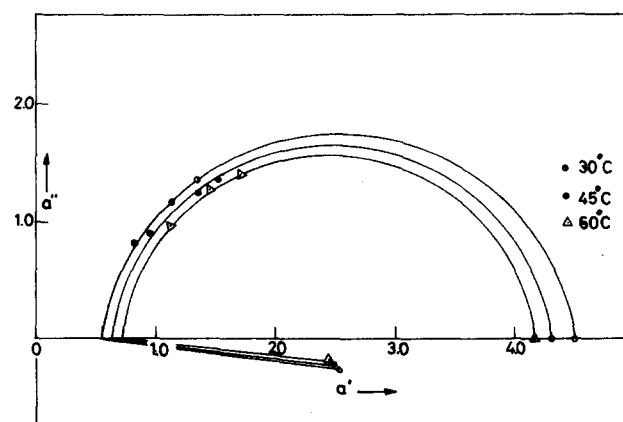
FIG. 2. Cole-Cole plots of *o*-(diethylaminomethyl)-*o*-cresol (MI).

TABLE I. Slopes for the dependence of  $\epsilon'$  and  $\epsilon''$  on weight fraction in benzene solution.

Frequency (GHz)	30 °C		45 °C		60 °C	
	$a'$	$a''$	$a'$	$a''$	$a'$	$a''$
<i>o</i> -(Dimethylaminomethyl)- <i>o</i> -cresol (MI-0.054)						
8.45	1.26	1.65	1.43	1.68	1.68	1.71
12.20	0.98	1.42	1.13	1.48	1.35	1.55
30.50	0.54	0.95	0.68	1.03	0.83	1.13
Static	4.90	...	4.68	...	4.50	...
<i>o</i> -(Diethylaminomethyl)- <i>o</i> -cresol (MII-0.052)						
8.45	1.34	1.34	1.52	1.35	1.72	1.39
12.20	1.15	1.12	1.35	1.25	1.45	1.28
30.50	0.81	0.83	0.95	0.93	1.10	0.98
Static	4.54	...	4.31	...	4.15	...
<i>o</i> -(Dimethylaminomethyl)- <i>p</i> -cresol (MIII-0.057)						
8.45	1.65	1.81	1.96	1.84	2.25	1.78
12.20	1.32	1.62	1.57	1.64	1.76	1.64
30.50	0.67	1.08	0.94	1.20	1.11	1.25
Static	4.57	...	4.45	...	4.30	...
<i>o</i> -(Diethylaminomethyl)- <i>p</i> -cresol (MIV-0.056)						
8.45	1.50	1.88	1.75	1.91	2.03	1.93
12.40	1.18	1.70	1.38	1.73	1.60	1.76
30.50	0.59	1.14	0.73	1.18	0.89	1.23
Static	4.86	...	4.69	...	4.54	...
<i>o</i> -(Dimethylaminomethyl)- <i>p</i> -chlorophenol (MV-0.056)						
8.45	2.00	2.09	2.31	2.16	2.59	2.18
12.20	1.71	1.84	1.96	1.90	2.21	1.94
30.50	1.06	1.30	1.30	1.42	1.53	1.48
Static	6.32	...	6.11	...	5.92	...
<i>o</i> -(Diethylaminomethyl)- <i>p</i> -chlorophenol (MVI-0.052)						
8.45	1.75	2.18	2.12	2.25	2.30	2.36
12.20	1.35	1.88	1.62	2.01	1.91	2.10
30.50	0.85	1.36	7.11	1.44	1.30	1.65
Static	6.60	...	6.37	...	6.15	...

the molecule is apparently stabilized and gives rise to a relaxation time as if overall rotation alone exists for the molecule. From Table II, one can also observe that the mean relaxation times of MI and MII (methyl group in position 6) are larger than similar compounds MIII and MIV with the methyl group in position 4. In the case of di-*ortho*-substituted compounds (MI and MII), the substituent  $\text{CH}_3$  in position 6 causes further hindrance to the rotation of  $-\text{OH}$  group and leads to added stability of the molecule. Such steric hindrance by the adjacent methyl groups to the rotation of the polar group has been reported by Purcell *et al.*<sup>15</sup> in the case of bis(chloromethyl)durene. It is further observed that the relaxation

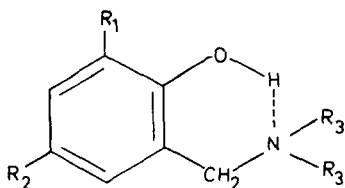


FIG. 3.  $R_1 = \text{CH}_3$ ,  $R_2 = \text{H}$ ,  $R_3 = (\text{CH}_3)_2$  or  $(\text{C}_2\text{H}_5)_2$ ;  $R_1 = \text{H}$ ,  $R_2 = \text{Cl}$  or  $\text{CH}_3$ ,  $R_3 = (\text{CH}_3)_2$  or  $(\text{C}_2\text{H}_5)_2$ .

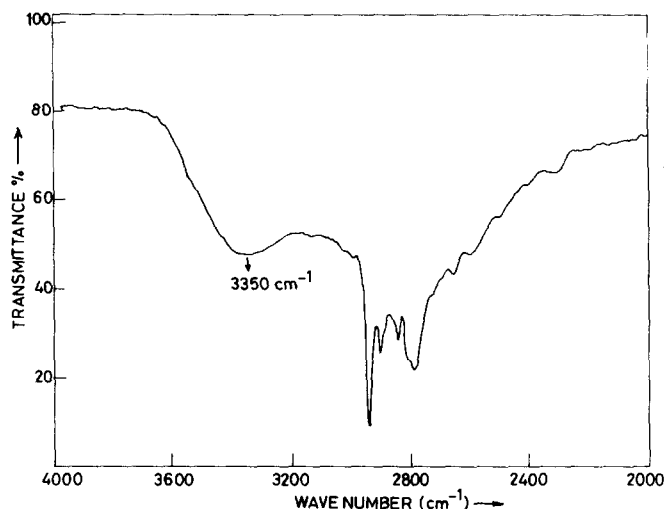


FIG. 4. Infrared spectrum of a phenolic Mannich base in the  $-\text{OH}$  stretching region.

time is greater for molecules with the "chloro" group at the *para* position (MV and MVI) than for similar molecules with the "methyl" group (MIII and MIV). The increase in relaxation time is probably a result of an increase in molecular size and due to weak bonding with the solvent (benzene effect) as has been explored by Higasi.<sup>16</sup>

## DOUBLE RELAXATION ANALYSIS

An attempt was carried out to determine the relaxation times corresponding to the  $-\text{OH}$  group rotation ( $\tau_2$ ), the overall molecular rotation ( $\tau_1$ ), and their respective weight factors ( $C_1$  and  $C_2$ ) based on Budo's<sup>17</sup> equations:

$$\frac{a' - a_\infty}{a_0 - a_\infty} = A = \frac{C_1}{1 + \omega^2 \tau_1^2} + \frac{C_2}{1 + \omega^2 \tau_2^2}, \quad (1)$$

TABLE II. Dielectric parameters of phenolic Mannich bases.

Mannich base	Temperature (°C)	Distribution parameter $\alpha$	Mean relaxation time $\tau_0$ ( $\times 10^{12}/\text{sec}$ )
MI	30	0.09	24.8
	45	0.08	20.8
	60	0.06	17.1
MII	30	0.09	26.9
	45	0.07	22.0
	60	0.06	17.5
MIII	30	0.10	18.2
	45	0.09	16.3
	60	0.08	14.4
MIV	30	0.08	21.3
	45	0.07	18.2
	60	0.06	16.3
MV	30	0.11	23.7
	45	0.09	20.2
	60	0.08	16.8
MVI	30	0.09	25.4
	45	0.08	21.0
	60	0.07	16.6

$$\frac{a''}{a_0 - a_\infty} = B = \frac{C_1 \omega \tau_1}{1 + \omega^2 \tau_1^2} + \frac{C_2 \omega \tau_2}{1 + \omega^2 \tau_2^2}$$

( $\omega =$  angular frequency) (2)

and

$$C_1 + C_2 = 1 \quad (3)$$

The simplified relation is

$$\frac{1 - A}{B\omega} = (\tau_1 + \tau_2) - \frac{A\omega}{B} \tau_1 \tau_2 \quad (4)$$

The values of  $\tau_1$ ,  $\tau_2$ , and  $C_1$  are evaluated by a computer least-square minimization procedure. To avoid the uncertainty in the high frequency intercept  $a_\infty$ , it is varied in steps of 0.02 around the value obtained from Cole-Cole plots. For each minimization  $a_\infty$  is held constant and  $\tau_1$ ,  $\tau_2$ , and  $C_1$  are determined. With these values,  $a'$  and  $a''$  are calculated from Eqs. (1) and (2). Calculated values of  $a'$  and  $a''$  are compared with the experimental values and the set of  $\tau_1$ ,  $\tau_2$ , and  $C_1$  which gives the minimum mean square deviation is taken. All the calculations were carried out at an IBM 370/155 computer. Results of the above analysis are presented in Table III.

The values of  $\tau_1$  are of expected order and exhibit variation with temperature as might be expected for overall rotation.  $\tau_2$ , pertaining to hydroxy group relaxation, shows relatively very little dependence on temperature as might be expected for an intramolecular process. Within the uncertainty inherent in the method of analysis used,  $\tau_2$  is independent of the substituted groups  $\text{CH}_3$  or  $\text{Cl}$  in position 6. The  $-\text{OH}$  group relaxation time in the present group of liquids (10 psec) compares very well with the relaxation time for intramolecularly bonded hydroxyl groups obtained by Antony and Smyth<sup>18</sup> for 2,6-dibromophenol ( $\tau_2 = 12.7$  psec) in ben-

TABLE III. Molecular and intramolecular relaxation times of phenolic Mannich bases.

Mannich base	Temperature (°C)	$a_\infty$	$\tau_1$ ( $\times 10^{12}$ /sec)	$\tau_2$ ( $\times 10^{12}$ /sec)	$C_1$
MI	30	0.21	47.6	11.0	0.78
	45	0.30	40.6	11.0	0.75
	60	0.38	34.7	10.9	0.70
MII	30	0.50	53.6	10.6	0.77
	45	0.58	44.8	10.9	0.69
	60	0.68	35.8	10.2	0.68
MIII	30	0.25	33.7	9.8	0.74
	45	0.40	27.5	9.0	0.73
	60	0.50	23.6	8.5	0.71
MIV	30	0.15	36.9	10.4	0.75
	45	0.20	31.4	10.1	0.74
	60	0.37	26.6	10.7	0.69
MV	30	0.55	45.6	10.2	0.74
	45	0.70	37.9	9.9	0.71
	60	0.87	31.0	9.4	0.70
MVI	30	0.33	47.7	10.4	0.78
	45	0.50	38.7	9.2	0.78
	60	0.57	33.2	9.7	0.71

TABLE IV. Activation parameters and dipole moments of phenolic Mannich bases.<sup>a</sup>

Mannich base	$\Delta H^*$	$\Delta G^*$	$\Delta S^*$	Dipole moment $\mu$	
				Higasi	Guggenheim
MI	1.85	3.10	-3.94	2.58	2.60
MII	2.08	3.14	-3.32	2.68	2.70
MIII	1.03	2.96	-6.06	2.57	2.58
MIV	1.43	3.04	-5.05	2.70	2.68
MV	1.67	3.08	-4.43	3.14	3.34
MVI	1.95	3.11	-3.64	3.53	3.55

<sup>a</sup> $\Delta H^*$  and  $\Delta G^*$  in kcal/mole,  $\Delta S^*$  in cal/mole °K,  $\mu$  in D.

zene and that estimated by Aihara and Davies<sup>1</sup> for 2,4,6-trichlorophenol (8.4 psec). In all these Mannich bases, the weight factor related to the molecular relaxation time is larger (around 0.75) than that for group rotation. Magee and Walker<sup>11,19</sup> from the consideration of group moments and bond moments have shown that for hydroxylic compounds the value of  $C_2 (= 1 - C_1)$  should be about 0.8 to 0.9 in the absence of any perturbing field. The lower values of  $C_2$  obtained for these Mannich bases indicate the presence of a perturbing field —presumably the intramolecular bonding.

Treating dielectric relaxation as a rate process, the free energy  $\Delta G^*$ , enthalpy  $\Delta H^*$ , and entropy  $\Delta S^*$  are evaluated by the usual method<sup>20</sup> using Eyring's equation<sup>21</sup>

$$\tau_0 = \frac{h}{kT} \exp(\Delta G^*/RT), \quad \Delta G^* = \Delta H^* - T\Delta S^* .$$

Within the experimental error,  $\Delta G^*$  and  $\Delta S^*$  are found to be independent of temperature. The values of  $\Delta H^*$  and the average values of  $\Delta G^*$  and  $\Delta S^*$  are presented in Table IV. It is observed that the values of  $\Delta H^*$  are lower than  $\Delta G^*$ , resulting in a negative value of molar entropy of activation. This means that the activated state is more ordered than the ground state. Such observation of negative entropy has been explained on the basis of cooperational orientation of molecules by Branin and Smyth.<sup>22</sup>

The dipole moment of these molecules calculated from  $a_0$  and  $a_\infty$  values using Higasi's<sup>23</sup> equation and the values evaluated from Guggenheim's<sup>24</sup> method at radiofrequency are also presented in Table IV. From a comparison of reported values<sup>25</sup> of dipole moment of *o*-cresol ( $\mu = 1.27$  D), *p*-cresol ( $\mu = 1.58$  D), and *p*-chlorophenol ( $\mu = 2.27$  D) with the dipole moments of respective Mannich bases, one can see that the presence of side chain  $-\text{CH}_2\text{N}(\text{CH}_3)_2$  or  $-\text{CH}_2\text{N}(\text{CH}_3\text{CH}_2)_2$  in the *ortho* position has a considerable influence on the molecular dipole moment. It is also observed that the replacement of  $\text{CH}_3$  by  $\text{Cl}$  in the *para* position increases the dipole moment consistent with the fact that  $\text{Cl}$  is a highly polar group when compared to  $\text{CH}_3$ .

## CONCLUSION

From the analysis of results, one can conclude that the intramolecular hydrogen bonding between the *ortho*-substituted groups seems to influence the dielectric relaxation process of these phenolic compounds. The

molecules relax predominantly by overall molecular rotation.

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- <sup>1</sup>A. Aihara and M. Davies, *J. Colloid. Sci.* **11**, 671 (1956).
- <sup>2</sup>M. Davies and R. J. Meakins, *J. Chem. Phys.* **26**, 1584 (1957).
- <sup>3</sup>A. A. Antony, F. K. Fong, and C. P. Smyth, *J. Phys. Chem.* **68**, 2035 (1964).
- <sup>4</sup>F. K. Fong and C. P. Smyth, *J. Am. Chem. Soc.* **85**, 1565 (1963).
- <sup>5</sup>R. J. Meakins, *Trans. Faraday Soc.* **52**, 320 (1956).
- <sup>6</sup>W. M. Heston Jr., A. D. Franklin, E. J. Hennelly, and C. P. Smyth, *J. Am. Chem. Soc.* **72**, 3443 (1950).
- <sup>7</sup>R. K. Khanna and J. Sobhanadri, *J. Phys. D* **5**, 1453 (1972).
- <sup>8</sup>G. F. Grillot and W. T. Gormley Jr., *J. Am. Chem. Soc.* **67**, 1968 (1945).
- <sup>9</sup>M. Jeyaraj and J. Sobhanadri, *J. Chem. Soc. Faraday Trans. 2* (in press).
- <sup>10</sup>E. Hill, W. E. Vaughan, A. H. Price, and M. Davies, *Dielectric Properties and Molecular Structure* (Van Nostrand, New York, 1969).
- <sup>11</sup>M. D. Magee and S. Walker, *Can. J. Chem.* **49**, 1106 (1971).
- <sup>12</sup>W. P. Purcell and C. P. Smyth, *J. Am. Chem. Soc.* **82**, 1061 (1961).
- <sup>13</sup>E. L. Grubb and C. P. Smyth, *J. Am. Chem. Soc.* **83**, 4873 (1962).
- <sup>14</sup>Linus Pauling, *The Nature of Chemical Bond* (Cornell University, Ithaca, 1960), Chap. 12.7.
- <sup>15</sup>W. P. Purcell, K. Fish, and C. P. Smyth, *J. Am. Chem. Soc.* **82**, 6299 (1960).
- <sup>16</sup>K. Higasi, *Dielectric Relaxation and Molecular Structure* (Research Institute of Applied Electricity, Sapporo, 1961).
- <sup>17</sup>A. Budo, *Phys. Z.* **39**, 706 (1938).
- <sup>18</sup>A. A. Antony and C. P. Smyth, *J. Am. Chem. Soc.* **86**, 156 (1970).
- <sup>19</sup>M. D. Magee and S. Walker, *J. Phys. Chem.* **74**, 2378 (1970).
- <sup>20</sup>E. J. Hennelly, W. M. Heston Jr., and C. P. Smyth, *J. Am. Chem. Soc.* **70**, 4102 (1948).
- <sup>21</sup>H. Eyring, S. Glasstone, and K. J. Laidler, *The Theory of Rate Processes* (McGraw Hill, New York, 1941).
- <sup>22</sup>F. H. Branin and C. P. Smyth, *J. Chem. Phys.* **20**, 1121 (1952).
- <sup>23</sup>K. Higasi, *Bull. Chem. Soc. Jpn.* **39**, 2157 (1966).
- <sup>24</sup>E. A. Guggenheim, *Trans. Faraday Soc.* **45**, 714 (1949).
- <sup>25</sup>N. K. Mehrotra, J. P. Shukla, and M. C. Saxena, *Indian J. Pure. Appl. Phys.* **5**, 35 (1967).