

## Microwave absorption and molecular structure of some substituted acetic acids in dilute solutions of dioxane

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**Abstract.** The dielectric constants and losses of phenyl acetic acid, 2-4 dinitro phenyl acetic acid, 2-4 dinitro phenoxy acetic acid, chloro acetic acid and amino acetic acid have been measured in dilute solution of dioxane at three temperatures 30-40° and 50° C in the microwave region (3.13 cm). The static dielectric constant and the high frequency dielectric constant have been determined at 300 kHz and at optical frequency. The relaxation time and the dipole moment have been calculated using Higashi method. The distribution parameter and thermodynamical parameters have also been reported.

**Keywords.** Dielectric constants; molecular structure;  $\mu$ -microwave absorption.

### 1. Introduction

The study of dielectric properties of substances gives valuable information about their molecular structure (Smyth 1955). Determination of dipole moment can provide an insight into the properties like distinguishing functional groups, whereas relaxation time and distribution parameter throw light on the other molecular properties such as size, shape and rigidity, etc. In the present study, the Higashi method has been used to determine the relaxation time, dipole moment and distribution parameter (Higashi 1966). The equations given by Higashi derived by simplifying the semiempirical relation of Cole and Cole (1941) for dilute solutions can provide good results if the parameters are accurate.

Thermodynamic parameters have been computed using Eyring's (1941) rate process theory as discussed in Mehrotra (1969).

### 2. Experimental

The dielectric constant ( $\epsilon'$ ) and the loss factor ( $\epsilon''$ ) were measured using the standing wave technique of Roberts and Von Hippel (1946) and its subsequent simplification by Dakin and Works (1947). Microwaves have been generated by 723 A/B Klystron. The  $\epsilon'$  and  $\epsilon''$  measurements were to be within 1% and 5% accuracy

respectively. Refractive index has been determined by Abbey's refractometer. The static permittivity  $\epsilon_0$  at 300 kHz has been measured by a dipole meter based on the principle of heterodyne beat method.

All the compounds used are of pure quality obtained from the British Drug House. Analar dioxane also of the purest quality obtained from the British Drug House was distilled before use.

### 3. Results and Discussion

The values of static dielectric constant ( $\epsilon_0$ ), the dielectric constant ( $\epsilon'$ ), the loss factor ( $\epsilon''$ ) and the high frequency dielectric constant ( $\epsilon_\infty$ ) are given in table 1 along with the values of concentration  $W$ . Table 2 shows the values of slopes,  $a_0$ ,  $a'$ ,  $a''$  and  $a_\infty$ . The relaxation time ( $\tau$ ), the dipole moment ( $\mu$ ) and the distribution parameter ( $\alpha$ ) are given in table 3. The thermodynamical parameters have been reported in table 4.

#### 3.1. Relaxation time

The value of  $\tau$  for all the compounds investigated decreased with increase of temperature and agreed with the Debye equation (1929) for polar molecule. The relaxation time of 2-4 dinitrophenyl acetic acid was higher (also highest among all the compounds investigated) than that of phenyl acetic acid due to the large size and the greater steric hindrance experienced by the former molecule in free rotation. The relaxation time of 2-4 dinitro phenoxy acetic acid is however smaller than that of 2-4 dinitrophenyl acetic acid although the size of the former molecule is larger as compared to the latter. This may be due to the intramolecular rotation of phenoxy group in the former molecule, resulting in the decrease of the relaxation time. Chloroacetic acid exhibits a larger relaxation time compared to amino acetic acid and this is due to the bigger size of the former molecule as well as the intramolecular rotation of amino group in the latter molecule. The dipole orientation is therefore contributed by both the molecular as well as intramolecular rotations.

#### 3.2. Distribution parameter $\alpha$

The finite value of distribution parameter, calculated for the molecule, suggests two possible relaxation mechanisms of the Debye type, i.e., overall rotation and intramolecular rotation. The two relaxation times  $\tau_1$  and  $\tau_2$  could not be resolved because of single microwave frequency measurements.

#### 3.3. Dipole moment

The calculated value of dipole moment for 2-4 dinitrophenyl acetic acid is higher than that of phenyl acetic acid and agrees with the variation of their relaxation times. The dipole moments of all other compounds are also distributed according to their relaxation times.

Table 1. Dielectric constant  $\epsilon'$ , dielectric loss  $\epsilon''$ , static dielectric constant  $\epsilon_0$  and high frequency dielectric constant  $\epsilon_\infty$  with concentration  $W$  at temperatures 30°, 40° and 50°C.

Compound	30° C					40° C					50° C						
	$W \times 10^{-2}$	$\epsilon_0$	$\epsilon'$	$\epsilon''$	$\epsilon_\infty$	$\epsilon_0$	$\epsilon'$	$\epsilon''$	$\epsilon_\infty$	$\epsilon_0$	$\epsilon'$	$\epsilon''$	$\epsilon_\infty$	$\epsilon_0$	$\epsilon'$	$\epsilon''$	$\epsilon_\infty$
Phenyl acetic acid	2.11	2.325	2.350	0.010	2.237	2.184	2.308	0.006	2.135	2.107	2.299	0.002	2.016	2.141	2.349	0.009	2.050
	3.90	2.400	2.370	0.021	2.244	2.262	2.360	0.015	2.144	2.141	2.349	0.009	2.050	2.219	2.409	0.014	2.063
	5.71	2.452	2.439	0.028	2.255	2.314	2.420	0.024	2.158	2.219	2.409	0.014	2.063	2.310	2.460	0.020	2.067
	7.49	2.535	2.489	0.032	2.259	2.425	2.479	0.031	2.166	2.310	2.460	0.020	2.067	2.413	2.498	0.028	2.078
	9.00	2.581	2.530	0.040	2.262	2.497	2.516	0.037	2.179	2.413	2.498	0.028	2.078				
2,4 Dinitro phenyl acetic acid	1.01	2.310	2.291	0.007	2.240	2.157	2.279	0.005	2.155	2.020	2.270	0.002	2.058	2.189	2.319	0.013	2.061
	2.43	2.329	2.350	0.019	2.245	2.189	2.320	0.013	2.162	2.082	2.319	0.013	2.061	2.263	2.369	0.022	2.070
	3.35	2.390	2.386	0.022	2.248	2.263	2.369	0.022	2.169	2.155	2.358	0.022	2.070	2.340	2.399	0.036	2.079
	4.61	2.451	2.419	0.029	2.253	2.340	2.399	0.036	2.178	2.246	2.390	0.032	2.079	2.414	2.450	0.050	2.085
	7.86	2.574	2.551	0.060	2.262	2.414	2.450	0.050	2.185	2.430	2.452	0.046	2.089				
2,4 Dinitro phenoxy acetic acid	1.92	2.336	2.310	0.006	2.242	2.208	2.301	0.003	2.126	2.065	2.283	0.003	2.016	2.283	2.350	0.003	2.023
	3.94	2.410	2.371	0.015	2.246	2.283	2.352	0.012	2.130	2.131	2.350	0.003	2.023	2.198	2.411	0.014	2.029
	5.80	2.471	2.439	0.023	2.251	2.339	2.430	0.018	2.138	2.263	2.460	0.025	2.038	2.403	2.480	0.030	2.044
	7.61	2.522	2.489	0.036	2.257	2.403	2.480	0.030	2.144	2.263	2.460	0.025	2.038	2.467	2.521	0.039	2.052
	9.20	2.589	2.540	0.044	2.261	2.467	2.521	0.039	2.152	2.328	2.506	0.032	2.041				
Chloro acetic acid	1.56	2.318	2.316	0.010	2.234	2.167	2.295	0.006	2.123	2.124	2.281	0.003	2.012	2.213	2.316	0.011	2.021
	3.14	2.364	2.321	0.016	2.245	2.213	2.316	0.011	2.136	2.173	2.301	0.007	2.021	2.277	2.351	0.015	2.031
	4.53	2.412	2.380	0.018	2.250	2.277	2.351	0.015	2.140	2.236	2.332	0.002	2.031	2.329	2.400	0.023	2.038
	6.86	2.484	2.461	0.029	2.255	2.329	2.400	0.023	2.148	2.273	2.381	0.018	2.038	2.403	2.451	0.033	2.053
	7.83	2.520	2.479	0.046	2.261	2.403	2.451	0.033	2.153	2.358	2.413	0.028	2.040				
Amino acetic acid	1.90	2.371	2.341	0.014	2.236	2.223	2.331	0.010	2.134	2.046	2.321	0.006	2.015	2.296	2.406	0.016	2.050
	3.84	2.439	2.432	0.027	2.244	2.296	2.418	0.022	2.143	2.129	2.406	0.016	2.050	2.408	2.510	0.036	2.062
	5.53	2.538	2.521	0.042	2.251	2.408	2.510	0.036	2.156	2.197	2.498	0.031	2.062	2.497	2.587	0.055	2.067
	7.30	2.634	2.601	0.061	2.262	2.497	2.587	0.055	2.163	2.308	2.578	0.049	2.067	2.594	2.681	0.076	2.073
	9.33	2.743	2.702	0.082	2.269	2.594	2.681	0.076	2.179	2.334	2.673	0.069	2.073				

**Table 2.** Values of  $a_0$ ,  $a'$ ,  $a''$  and  $a_\infty$  at 30°, 40° and 50° C.

Compound	Temp ° K	$a_0$	$a'$	$a''$	$a_\infty$
Phenyl acetic acid	303	4.46	4.52	0.80	0.46
	313	4.31	4.49	0.72	0.36
	323	4.15	4.48	0.65	0.27
2-4 dinitro phenyl acetic acid	303	4.01	3.65	0.63	0.37
	313	3.85	3.62	0.58	0.28
	323	3.74	3.61	0.53	0.17
2-4 dinitro phenoxy acetic acid	303	3.50	3.00	0.46	0.41
	313	3.32	2.95	0.41	0.32
	323	3.22	2.93	0.37	0.22
Chloro acetic acid	303	3.25	3.08	0.44	0.28
	313	3.10	3.06	0.41	0.19
	323	3.04	3.04	0.37	0.09
Amino acetic acid	303	3.12	2.86	0.36	0.32
	313	2.99	2.83	0.30	0.27
	323	2.84	2.81	0.22	0.19

**Table 3.** Values of relaxation time  $\tau$ , dipole moment  $\mu$  and distribution parameter  $a$ .

Compound	Temp ° K	$\tau \times 10^{12}$ sec.	$\mu \times 10^{18}$ Debye	$a$
Phenyl acetic acid	303	16.39	2.26	0.24
	313	14.10	2.31	0.20
	323	12.58	2.34	0.18
2-4 dinitro phenyl acetic acid	303	20.31	2.63	0.33
	313	19.15	2.75	0.27
	323	17.08	2.79	0.25
2-4 dinitro phenoxy acetic acid	303	17.03	2.31	0.38
	313	15.30	2.33	0.36
	323	13.82	2.37	0.29
Chloro acetic acid	303	15.93	2.14	0.18
	313	14.06	2.20	0.14
	323	13.04	2.21	0.12
Amino acetic acid	303	14.38	20.07	0.26
	313	13.80	2.10	0.25
	323	12.70	2.19	0.20

Table 4. Relaxation time and molar activation energy parameters.

Compound	Temp ° K	$\tau \times 10^{12}$ sec.	$\Delta F_\tau \times$ $10^{-3}$ J/mol	$\Delta F_\eta \times$ $10^{-3}$ J/mol	$\Delta H_\tau \times$ $10^{-3}$ J/mol	$\Delta S_\tau$ J/mol	$\Delta S_\eta$ J/mol
Phenyl acetic acid	303	16.39	11.34	11.79		-20.51	-7.37
	313	14.10	11.46	11.84	5.12	-20.38	-7.61
	323	12.58	11.50	11.92		-20.37	-7.78
2-4 dinitro phenyl acetic acid	303	20.31	11.68	11.79		-17.53	-7.37
	313	19.15	11.79	11.84	6.36	-17.20	-7.61
	323	17.08	11.92	11.92		-17.07	-7.78
2-4 dinitro phenoxy acetic acid	303	17.03	11.52	11.79		-14.20	-7.37
	313	15.30	11.60	11.84	7.22	-14.00	-7.61
	323	13.82	11.74	11.92		-14.30	-7.78
Chloro acetic acid	303	15.93	11.20	11.79		-11.54	-7.37
	313	14.06	11.25	11.84	7.67	-11.38	-7.61
	323	13.04	11.32	11.92		-11.32	-7.78
Amino acetic acid	303	14.38	10.88	11.79		-5.32	-7.37
	313	13.80	10.94	11.84	9.25	-5.40	-7.61
	323	12.10	10.10	11.92		-5.71	-7.78

$$\Delta H_\eta = 9.54 \times 10^3 \text{ J/mol.}$$

### 3.4. Thermodynamic parameters

The most probable enthalpies of activation are less than the corresponding free energies so that the entropies of activation are negative. According to Branin and Smyth (1952) a negative entropy of activation 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. This may indicate the existence of cooperative orientations of the molecules resulting from the steric forces. Similar results have been obtained by Man Singh (1964).

The free energies of activation for the process of viscous flow are greater than those for dipole orientations because the process of a viscous flow involves both rotation and translation while the process of dipole orientation involves only rotation of molecules. Similar results have been observed by Fong and Smyth (1963). Further, the ratio of  $\Delta F_\eta$  and  $\Delta F_\tau$  approaches unity for some of the compounds investigated, which suggests that the moving units participating in the two processes are identical and that the activation takes place in the same degree of freedom because the same bonds have to be broken before either motion is possible.

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