

DIELECTRIC RELAXATION STUDIES IN SOME HORTICULTURAL MOLECULES

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The dielectric relaxation studies on three horticultural molecules have been undertaken. The dielectric relaxation times at varying temperatures were evaluated. It was observed that both molecular and internal rotational processes contribute to the dielectric dispersion. The enthalpies, associated with rotational processes were also evaluated and the data obtained supported the occurrence of the molecular reorientation process in one system and the group reorientation processes in other two systems.

Introduction.

The relaxation times of some fatty acids were reported earlier by POTAPENKO and WHEELER [1]. Later studies by BROOKS and HOBBS [2] on *meta*- and *para*-chloro and bromo-benzoic acids and by WILSON and WENZEKE [3] on *p*-nitrobenzoic acids were confined to the measurements and interpretation of the dipole moments only. Some hydroxy benzoic acids were studied in this laboratory [4] for their rotational behaviour. Studies on relaxation behaviour related to the microscopic and other viscosities on some halogenated benzoic acids were reported by SHUKLA and SAXENA [5] from this laboratory. The previous studies [6] on some acetic acids were also made on the measurements of dielectric constant and the formation of dimers. No data is available on the dielectric properties of the molecules of horticultural nature. These molecules, having an interdisciplinary application, were considered worthwhile to study for their relaxation behaviour including the assessment of the energies associated with different rotational modes. These could lead to some additional informations regarding their electrical properties and possibilities of extending further, their applicability to the rapid growth of plants. The dielectric investigations on three horticultural molecules; namely indol-3yl-acetic acid, indol-3yl-propionic acid, and gibberellic acid in dilute solution of dioxane were undertaken. The dielectric relaxation times and thermodynamic parameters for these systems were evaluated and compared.

Method and Experimental Procedures

The dielectric relaxation times have been determined using the fixed frequency method of GOPALA KRISHNA [7] for dilute solutions as discussed earlier, the technique adopted being that of ROBERTS and VON HIPPEL [8]. The microwaves were generated by a C. V. 129 Klystron and the dielectric constants (ϵ') and the losses (ϵ'') were determined using the simplified method of DAKIN and WORKS [9]. The measurements of ϵ' were accurate to $\pm 2\%$ and those for ϵ'' to $\pm 5\%$. The following relations were used for determining the dielectric relaxation times.

$$\tau = \frac{\lambda}{2\pi C} \frac{dy}{dx}$$

$$X = \frac{\epsilon'^2 + \epsilon''^2 + \epsilon' - 2}{(\epsilon' + 2)^2 + \epsilon''^2}$$

$$Y = \frac{3\epsilon''}{(\epsilon' + 2)^2 + \epsilon''^2}$$

where λ is the free space wavelength, ϵ' the dielectric constant and ϵ'' is the loss factor.

The thermodynamic parameters for the dielectric relaxation process were determined using Eyring's equation. The ΔH_e values are obtained by estimating the slope of the straight line drawn between $\log \tau T$ and $\frac{1}{T}$. The other values are obtained using the following equations of Eyring [10] as described earlier.

$$\tau = \frac{h}{kT} e^{\Delta F_e/RT}$$

$$\Delta F_e = \Delta H_e - T\Delta S_e$$

$$\eta = \frac{hN}{V} e^{\Delta F_\eta/RT}$$

$$\Delta F_\eta = \Delta H_\eta - T\Delta S_\eta$$

Since in the present investigation we are interested in relaxation times only, it was not necessary to determine the exact weight fractions of the compounds. The solutions were maintained sufficiently dilute such that $\text{tg } \delta$ was always less than 0.1.

Chemicals. The chemicals used were of purest available quality. Indol-3yl-acetic acid and indol-3yl-propionic acid of horticultural quality were obtained from B.D.H. England. Gibberellic acid of the same quality was obtained from Phylaxia, Budapest, Hungary. The melting points of all three solids were tested before use. Dioxane, of pure quality, obtained from B.D.H. was distilled twice before use.

Discussions

(A) *Indol-3-yl-acetic acid*

The dielectric relaxation time τ has been found to be 14.2—21.1 p.s. in the temperature range of 283—313 K. The enthalpy of activation ΔH_g has been observed to be $7.8 \text{ kJ} \cdot \text{mole}^{-1}$. Considering the molecular dimensions, the dielectric relaxation time seems to be appreciably longer, which could be expected from the reorientation of the entire molecule. In order to ascertain the rotational behaviour of this system, the dielectric data for a rigid molecule of equivalent size was taken into account. Quinoline, which would be only slightly smaller than indol-3-yl-acetic acid was considered for the purpose and data reported by MADAN ET AL. [11] was incorporated for comparison.

Dielectric relaxation time τ at 303 K for quinoline in dilute solution of benzene $\cong 7.9$ p.s. is shorter than for indol-3-yl-acetic acid $\cong 16.5$ p.s. This is due to the reasons that the latter is slightly of larger size and also due to the higher viscosity of the medium (dioxane) in which the measurements have been made. The enthalpy of activation of indol-3-yl-acetic acid $\cong 7.8 \text{ kJ} \cdot \text{mole}^{-1}$ is slightly higher than for quinoline ($\Delta H_g \cong 6.3 \text{ kJ} \cdot \text{mole}^{-1}$) which is a rigid system. The two values are however comparable, taking into account of slightly large size of indol-3-yl-acetic acid due to the attached group $-\text{COOH}$ at position 3 of the system. This shows that the observed process corresponds to the rotation of the entire molecule as a whole unit, although the resolution of the two processes is not possible in the present investigation.

Table I

Dielectric parameters of the molecules

Molecule	283 K		293 K		303 K		313 K	
	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
Indol-3-yl-Acetic Acid	2.187	.027	2.203	.019	2.203	.021	2.221	.019
	2.190	.031	2.202	.027	2.218	.027	2.224	.027
	2.197	.036	2.192	.029	2.219	.030	2.229	.031
	2.211	.045	2.206	.034	2.221	.036	2.238	.037
	2.219	.045	2.208	.037	2.225	.038	2.251	.037
Indol-3-yl-Propionic Acid	2.172	.025	2.185	.027	2.196	.020	2.211	.022
	2.184	.031	2.187	.031	2.193	.022	2.220	.027
	2.193	.032	2.212	.034	2.201	.030	2.226	.031
	2.197	.037	2.219	.038	2.215	.032	2.241	.033
	2.203	.041	2.226	.038	2.218	.035	2.249	.037
Gibberellic Acid	2.168	.020	2.179	.024	2.213	.031	2.238	.031
	2.170	.021	2.184	.025	2.225	.025	2.247	.025
	2.171	.026	2.182	.028	2.227	.026	2.252	.030
	2.175	.027	2.196	.029	2.229	.030	2.254	.030
	2.180	.029	2.203	.030	2.234	.030	2.256	.034

(B) *Indol-3-yl-propionic acid*

For this system, the dielectric relaxation time was found to vary from 6.6–8.3 p.s. in the temperature range of 283–313 K. A comparison of τ (7.3 p.s.) for this molecule with τ (16.5 p.s.) for indol-3-yl-acetic acid at 303 K shows that the latter value is much longer than for the present case. This shows that the two processes are entirely different. Has this been also a molecular process the relaxation time τ_B would have been greater than τ_A . It can be seen from the molecular structure that the only other process which could give rise to dielectric absorption would be due to the internal rotation of $-\text{CH}_2\text{COOH}$ group attached to the ring. It would thus be justified to assign this absorption to the rotation of $-\text{CH}_2\text{COOH}$ group which yields a relaxation time of 7.3 p.s. at 303 K.

The enthalpy of activation associated to the above process has been found to be $3.2 \text{ kJ} \cdot \text{mole}^{-1}$ only, which is much smaller than the enthalpy ($\cong 7.8 \text{ kJ} \cdot \text{mole}^{-1}$) for the molecular rotation of indol-3-yl-acetic acid system. This seems true as the internal rotation of such a small unit would be expected to yield an enthalpy of activation of this range.

The free energy of activation for the molecule ΔF_e increases as usual with increase in temperature. This is possible because at higher temperature the molecular collision rate increases with the result that the energy required to bring the molecules into the activated state will increase.

The entropy of the system has been found to be negative. This shows an ordered behaviour for the molecular system. A comparison shows that ΔS_e for the present molecule is smaller than for the previous system, which is true in view of shorter rotational unit involved in the system.

Table II
Dielectric Relaxation Times and Energy Parameters of the Molecules

Molecule	Temperature K	$\tau \times 10^{12}$ S	ΔF_e $\text{kJ} \cdot \text{mole}^{-1}$	ΔH_e $\text{kJ} \cdot \text{mole}^{-1}$	ΔS_e $\text{J} \cdot \text{mole}^{-1} \text{ deg}^{-1}$
Indol-3-yl-Acetic Acid	283	21.1	11.4	7.8	-12.5
	293	19.8	11.7		-13.2
	303	16.5	11.7		-12.9
	313	14.2	11.8		-12.7
Indol-3-yl-Propionic Acid	283	8.3	9.2	3.2	-20.9
	293	7.6	9.4		-20.9
	303	7.3	9.7		-21.2
	313	6.6	9.8		-20.9
Gibberellic Acid	283	14.5	10.5	3.7	-23.8
	293	13.1	10.7		-23.8
	303	12.4	11.0		-24.0

(C) *Gibberellic Acid*

Among all the three horticultural molecules, gibberellic acid has complicated molecular structure, with two $-\text{OH}$ groups and one $-\text{COOH}$ group attached at various positions. Looking at the size of the three molecules, this has the largest molecular dimensions. The dielectric relaxation time τ for this molecule has been

found to lie in the range 12.4 to 14.5 p.s. in the observed temperature range of 283–303 K. The value at 303 K has been found to be 12.4 p.s. A comparison of τ ($\cong 12.4$ p.s.) for the present molecule with the other two systems shows that it is close to τ ($\cong 16.5$ p.s.) at 303 K for indol-3yl-acetic acid, which is probably attributed to the molecular rotation. Gibberellic acid having much bigger molecular size would be expected to give rise to a longer relaxation time parameter, where as $\tau_{303} \cong 12.4$ p.s. is shorter than $\tau_{303} \cong 16.5$ p.s. observed for indol-3yl-acetic acid. The observed relaxation time, therefore, can not be assigned to the molecular reorientation of the system. It would thus be attributed to either internal rotation of —OH group or to that of —COOH group. Since —OH group is comparatively small than —COOH group, the τ observed here should be shorter than τ observed for indol-3yl-propionic acid, which has been assigned to give rise to a relaxation processes due to the rotation of —COOH group, but this value of τ_{303} ($\cong 12.4$ p.s.) is longer than τ_{303} ($\cong 7.3$ p.s.) for indol-3yl-propionic acid. The internal rotation of —OH group is therefore ruled out. The only absorption process left in the system would be due to rotation of —COOH group. The observed relaxation time would therefore be caused by the internal rotation of —COOH group. Since the value obtained for gibberellic acid τ ($\cong 12.4$ p.s.) is longer than τ ($\cong 7.3$ p.s.) for indol-3yl-propionic acid, it appears that probably in the present case, there exists restricted rotation to the —COOH group due to intramolecular hydrogen bonding between the hydrogen of —COOH and oxygen present at adjacent position in the ring, where as in the case of indol-3yl-propionic acid the rotation of —COOH group is completely free.

Table III

Relaxation Time, Viscosity and Energy Parameters for the Viscosity Process

Molecule	T K	$\tau \times 10^{12}$ S	$\eta \times 10^3$ Poise	ΔF_{η} kJ·mole ⁻¹	ΔH_{η} kJ·mole ⁻¹	ΔS_{η} J·Mole ⁻¹ deg ⁻¹
Indol-3yl- Acetic Acid	283	21.1	15.95	13.7	13.0	-26.6
	293	19.8	13.65	13.8		-27.8
	303	16.5	11.40	13.8		-28.8
	313	14.2	9.15	13.9		-29.4
Indol-3yl- Propionic Acid	283	8.3	15.95	13.7	13.0	-26.6
	293	7.6	13.65	13.8		-27.8
	303	7.3	11.40	13.8		-28.8
	313	6.6	9.15	13.9		-29.4
Gibberellic Acid	283	14.5	15.95	13.7	13.0	-26.6
	293	13.1	13.65	13.8		-27.8
	303	12.4	11.40	13.8		-28.8

The enthalpy of activation ΔH_e for gibberellic acid has been observed to be 3.7 kJ·mole⁻¹. A comparison of ΔH_e for the three molecules shows that ΔH_e for this molecule is about half of ΔH_e ($\cong 7.8$ kJ·mole⁻¹) for indol-3yl-propionic acid and slightly greater than ΔH_e ($\cong 3.2$ kJ·mole⁻¹) for indol-3yl-acetic acid. This exhibits an equivalent relaxation behaviour of the gibberellic acid and indol-3yl-propionic acid. It would therefore be appropriate to assign this process also to the rotation of —COOH group attached to the ring. Since the observed ΔH_e value is

slightly greater than for indol-3yl-propionic acid it appears that the rotation in the former case is not completely free. This is consistent with the results obtained for the relaxation time values also for above molecule.

The free energies of activation have been found to increase with rising temperature in an usual manner. The entropies for the above process have been found to be negative showing that the relaxation is a cooperative process, which is true for small rotational groups.

Conclusion

The present studies on the three horticultural molecules exhibit both the molecular and group relaxation processes. The Gopala Krishna method followed in the investigation gives in general an average assessment of the different absorption processes. However, as has been seen from both the dielectric relaxation times and enthalpies of activation for the three systems, at least in two cases of indol-3yl-propionic acid and gibberellic acid, predominant process contributing to the absorption appears to be from the internal motion of —COOH group attached to the ring. In case of indol-3yl-acetic acid, it is overall rotation of the entire molecule as a unit, which is responsible for the relaxation mechanism. It would be desirable to extend such studies and also studies related to the r.f. and microwave treatments to these horticultural materials which are widely used in the process of plant growth.

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ИЗУЧЕНИЕ ДИЭЛЕКТРИЧЕСКИХ СВОЙСТВ НЕКОТОРЫХ АГРО-ХИМИЧЕСКИХ ВЕЩЕСТВ

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Проведено изучение диэлектрических свойств трех агрохимических веществ. Найденны времена диэлектрической релаксации при разных температурах. Показано, что как молекулярные, так и внутримолекулярные вращения влияют на диэлектрическую дисперсию.