

Dielectric investigation of relaxation in some heterocyclic compounds

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Abstract. The dielectric relaxation mechanism in five heterocyclic compounds in dilute solutions using microwave technique is reported. Measurements have been made at different temperatures in order to calculate dipole moments and free energies of activation for the process of dipole orientation and viscous flow. It has been observed that the relaxation time is very closely related with the molecular parameters, such as size, shape and nature of the solute molecule.

Keywords. Relaxation time; dipole moment; heterocyclic compounds.

1. Introduction

Relaxation time and dipole moment which are among the important properties of a polar molecule throw considerable light on their structures. Relaxation time and dipole moment have been determined from the concentration variation method of Gopala Krishna (1957) using the following equations:

$$\tau = \frac{\lambda}{2\pi C} \left(\frac{dY}{dX} \right) \quad (1)$$
$$\mu = \left[\frac{9kTM}{4\pi Nd} \left(1 + \left(\frac{dY}{dX} \right)^2 \frac{dX}{dW} \right) \right]^{1/2}$$

where λ is the free space wavelength, k the Boltzmann's constant, M the molecular weight of the solute, D the density of the solvent, T the absolute temperature, W the weight fraction of the solute and the factors X and Y are given by:

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

where ϵ' = dielectric constant and ϵ'' = loss factor.

The thermodynamical parameters have been calculated using the equations of Glasstone *et al* (1941) as discussed in an earlier paper of Mehrotra *et al* (1969).

2. Experimental

The dielectric constant ϵ' and the loss factor ϵ'' of solution required for the calculation of the relaxation time and dipole moment have been determined by using the standing wave technique of Roberts and Von Hippel (1946) as discussed in an earlier paper (Mehrotra and Saxena 1967). The accuracy of the measurements for dielectric constant and loss was found to be within $\pm 2\%$ and $\pm 5\%$ respectively. The viscosity of benzene was measured while for the compounds it was taken from literature.

3. Materials

All the compounds investigated were of pure quality (L R grade) and obtained from Messrs British Drug House. The purest quality of benzene was obtained from British Drug House and the compounds distilled before use.

4. Results

Table 1 gives the values of the weight fraction W , ϵ' and ϵ'' at different temperatures. The observed values of the relaxation time at different temperatures along with the values of dipole moments and thermodynamical parameters are given in table 2.

The relaxation times of the compounds investigated are found to decrease with rise in temperature and this is in conformity with the Debye (1929) equation for polar molecules. It is observed from the table that both quinoline and isoquinoline exhibit long relaxation times as could be expected in view of the larger and virtually equal sizes. The higher relaxation time of isoquinoline as compared to quinoline cannot be explained with the help of Debye's equation as the two solutes are similar in size and approximately equal in viscosity. In quinoline the axis of the molecular dipole is nearly parallel to the short axis of the molecule in the plane of the rings, while in isoquinoline it makes an angle slightly less than 30° with the long axis in the plane of the rings. This effectively increases the radius of the orienting unit taking part in dipole orientation, resulting in the increased relaxation time.

Thiophene and furane have low viscosities and short relaxation times, those for thiophene being slightly greater than the corresponding value for furane at the same temperature. The structures of two molecules are almost identical. Both are aromatic five membered rings, the only difference being that thiophene has a sulphur atom in the ring whereas furane has an oxygen atom. Furane has a slightly larger dipole moment between the two, but the considerably larger polarizability of sulphur atom as compared to oxygen may account for the higher relaxation time of the thiophene.

This variation of the relaxation time can also be explained in terms of nuclear magnetic resonance investigations of these compounds. The chemical shift of the aromatic protons adjacent to a heteroatom should be strongly dependent on the location and orientation of nearby aromatic molecules. It has been observed by Corey and his coworkers (1958) that the chemical shift for thiophene is greater than that for furane. This indicates that the heteroatom in thiophene interacts more

Table 1. Experimental data for the determination of relaxation time

Compound	Weight fraction W	20°C		30°C		40°C	
		ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
Quinoline	0.0054	2.28	0.06	2.31	0.08	2.33	0.07
	0.0080	2.31	0.01	2.34	0.11	2.36	0.10
	0.0097	2.36	0.17	2.36	0.14	2.40	0.13
	0.0111	2.37	0.19	2.39	0.18	2.42	0.17
	0.0122	2.38	0.23	2.40	0.18	2.45	0.20
Isoquinoline	0.0102	2.23	0.05	2.26	0.04	2.28	0.05
	0.0115	2.24	0.06	2.27	0.05	2.30	0.07
	0.0124	2.30	0.12	2.33	0.12	2.35	0.11
	0.0164	2.32	0.15	2.37	0.18	2.36	0.11
	0.0174	2.39	0.20	2.40	0.20	2.43	0.19
Furane	0.0104	2.27	0.06	2.29	0.06	2.35	0.10
	0.0136	2.28	0.06	2.30	0.06	2.36	0.12
	0.0156	2.29	0.07	2.32	0.07	2.31	0.14
	0.0182	2.31	0.08	2.33	0.08	2.42	0.17
	0.0232	2.33	0.09	2.35	0.09	2.48	0.23
Thiophene	0.0033	2.24	0.05	2.25	0.05	2.28	0.06
	0.0062	2.25	0.06	2.26	0.06	2.30	0.07
	0.0087	2.27	0.09	2.29	0.09	2.31	0.08
	0.0105	2.28	0.09	2.31	0.11	2.32	0.09
	0.0141	2.32	0.10	2.33	0.12	2.33	0.11
Pyrrole	0.0012	2.27	0.04	2.29	0.03	2.30	0.03
	0.0032	2.32	0.06	2.30	0.04	2.31	0.04
	0.0080	2.35	0.07	2.36	0.06	2.36	0.07
	0.0094	2.38	0.09	2.40	0.07	2.41	0.08
	0.0100	2.40	0.11	2.42	0.09	2.42	0.10

Table 2. Relaxation time, dipole moment and thermodynamical parameters

Compound	T°K	10^{12} sec	μ_{obs} $\times 10^{18}$ Debye	μ_{lit} $\times 10^{18}$ Debye	$\Delta F\tau$ kcal/ mol	$\Delta F\eta$ kcal/ mol	$\Delta H\tau$ kcal/ mol	$\Delta H\eta$ kcal/ mol	$\Delta S\tau$ cal/ mol°K	$\Delta S\eta$ cal/ mol°K
Quinoline	293	17.22	2.21	2.18 ^a	2.76	2.90	1.48	2.27	-4.30	-2.14
	303	13.30	—	—	2.77	2.91	1.48	2.27	-4.26	-2.12
	313	11.12	—	—	2.79	2.93	1.48	2.27	-4.18	-2.10
Isoquinoline	293	21.22	2.59	2.52 ^a	2.96	2.90	2.04	2.27	-3.14	-2.14
	303	19.94	—	—	2.98	2.91	2.04	2.27	-3.10	-2.12
	313	17.54	—	—	3.01	2.93	2.04	2.27	-3.09	-2.10
Furane	293	8.12	0.61	0.63 ^b	2.30	2.90	2.25	2.27	-0.17	-2.14
	303	7.54	—	—	2.32	2.91	2.25	2.27	-0.23	-2.12
	313	6.32	—	—	2.33	2.93	2.25	2.27	-0.25	-2.10
Thiophene	293	10.12	0.59	0.54 ^c	2.60	2.90	1.82	2.27	-2.66	-2.14
	303	9.14	—	—	2.63	2.91	1.82	2.27	-2.67	-2.12
	313	8.32	—	—	2.64	2.93	1.82	2.27	-2.62	-2.10
Pyrrole	293	5.98	2.03	1.83 ^d	2.20	2.90	1.76	2.27	-1.50	-2.14
	303	4.24	—	—	2.24	2.91	1.76	2.27	-1.58	-2.12
	313	3.72	—	—	2.27	2.93	1.76	2.27	-1.62	-2.10

^a, Le Fevre and Smith (1932); ^b, Hunter and Partington (1931); ^c, Higashi (1932);
^d, Corley and Partington (1932)

strongly with solvent and other solute molecules than in furane. A similar correlation of the dielectric relaxation with the chemical shift has also been made by Fong and Smyth (1966). The relaxation time of pyrrole is found to be smaller than those of thiophene and furane as is to be expected from the smaller size of the former molecule (Mehrotra *et al* 1967).

The variation of the relaxation times with the size of the molecules, therefore, leads us to conclude that the dipole orientation may be due to the rotation of the entire molecule.

The observed values of dipole moment of the compounds investigated are found to be in good agreement with literature values.

The free energies of activation for dipole orientation and viscous flow are found to increase with rise in temperature while relaxation time decreases. The rise in temperature causing an increase in the thermal agitation is believed to be the reason for the increase in activation energies. Similar results have also been reported by Shukla *et al* (1968) for some substituted benzaldehydes. The negative values of the entropy of activation found for most of the compounds investigated indicate that there are fewer configurations possible in the activated state and for these configurations the activated state is more ordered than the normal state.

The values of free energy of activation for dipole orientation are found to be smaller than those for viscous flow, because the process of dipole orientation involves only rotation while the process of viscous flow involves both rotation and translation. Similar results have earlier been observed by Mehrotra *et al* (1966) in the case of substituted benzoic acids.

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