

Dielectric relaxation of some heterocyclic compounds in highly viscous media

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Abstract. Dielectric measurements on three heterocyclic compounds namely pyrrolidine, piperidine and 2-acetylpyridine in paraffin oil and paraffin oil + cyclohexane mixtures over the temperature range (294–318 K) at 9.8 GHz have been made. The data have been analysed using the method of Higasi *et al* and their dependence on macroscopic viscosity has been examined. The effect of solvent viscosity on the dipolar rotational process of the molecules in highly viscous media is also discussed.

Keywords. Viscous media; relaxation time; distribution parameter; energy parameters; paraffin oil.

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1. Introduction

Dielectric relaxation measurement has provided a useful method for exploring the structural behaviour of organic polar molecules in different environments. The studies of heterocyclic compounds are important due to their physiological and industrial applications. Considerable work has been reported on the dependence of dielectric relaxation mechanism on the viscosity of the medium for rigid and flexible molecules. However, in view of the limited investigations reported for relaxation in highly viscous media specially using Higasi (1966) and Higasi *et al* (1971) method, it was considered worthwhile to extend our earlier investigations (Rajni *et al* 1984), on some heterocyclic molecules *viz* pyrrolidine, piperidine and 2-acetyl pyridine from dilute solutions to the solutions of varying viscosity in highly viscous media. It was intended to examine the rigidity of the first two systems in the much higher viscosity region as also the changes occurring in the flexible behaviour of the third system 2-acetylpyridine. The thermodynamics of the relaxation process is also analysed with the changing viscosity of the medium using Glasstone (1941) theory of rate process.

2. Preparation of samples

The different solvent mixtures were prepared by increasing the amount of paraffin oil (p.o.) in cyclohexane in the following ratio:

- (i) 75% cyclohexane + 25% p.o. (ii) 50% cyclohexane + 50% p.o.
(iii) 25% cyclohexane + 75% p.o. and (iv) 100% p.o.

Table 1. Relaxation times (τ in psec) and distribution parameter (α) of all the three compounds.

Solvent mixture	Temp. (K)	$\tau_{(1)}$	$\tau_{(2)}$	$\tau_{(O)}$	$\tau_{(OH)}$	α	η_s (mp)
Pyrrolidine							
75% cyclohexane	294	7.5	9.8	8.6	8.0	0.07	14.9
+	302	6.9	9.4	8.1	6.8	0.08	13.3
25% p.o.	310	6.1	8.7	7.3	6.0	0.08	10.9
	318	5.2	7.9	6.4	5.0	0.09	8.6
50% cyclohexane	294	7.6	13.1	10.0	7.9	0.15	41.6
+	302	6.9	12.2	9.2	7.0	0.15	31.7
50% p.o.	310	6.3	11.5	8.5	6.2	0.16	22.9
	318	5.3	10.2	7.4	5.0	0.16	16.2
25% cyclohexane	294	7.7	19.8	12.3	9.4	0.28	146.3
+	302	7.1	18.2	11.4	8.1	0.27	102.8
75% p.o.	310	7.1	18.1	11.3	8.0	0.27	69.3
	318	5.5	16.1	9.6	5.3	0.31	48.7
100% p.o.	294	7.9	32.5	16.0	15.5	0.42	563.5
	302	7.2	28.8	14.4	11.7	0.41	491.7
	310	7.1	28.0	14.1	11.1	0.40	415.5
	318	5.5	26.8	12.2	6.9	0.44	270.9
Piperidine							
75% cyclohexane	294	9.0	10.8	9.9	9.2	0.05	14.9
+	302	8.6	9.8	9.2	8.6	0.04	13.3
25% p.o.	310	7.9	9.1	8.5	8.0	0.04	10.9
	318	7.4	8.3	7.8	7.4	0.03	8.6
50% cyclohexane	294	9.1	15.3	11.8	10.1	0.16	41.6
+	302	8.6	14.1	11.0	9.3	0.14	31.7
50% p.o.	310	8.0	12.9	10.2	8.4	0.14	22.9
	318	7.5	12.0	9.5	7.7	0.13	16.2
25% cyclohexane	294	9.2	22.3	14.3	12.7	0.27	146.3
+	302	8.9	20.1	13.3	11.3	0.25	102.8
75% p.o.	310	8.1	19.3	12.5	9.9	0.26	69.3
	318	7.7	18.8	12.0	9.1	0.26	48.7
100% p.o.	294	9.3	35.6	18.2	22.8	0.40	563.5
	302	9.0	32.2	17.1	18.4	0.38	491.7
	310	8.4	30.7	16.0	15.7	0.39	415.5
	318	7.9	28.4	15.0	13.2	0.38	270.9
2-Acetyl pyridine							
75% cyclohexane	294	9.0	31.3	16.8	17.6	0.37	14.9
+	302	8.5	29.2	15.7	15.0	0.37	13.3
25% p.o.	310	7.9	28.0	14.9	13.0	0.38	10.9
	318	7.5	36.8	14.1	11.4	0.38	8.6
50% cyclohexane	294	10.4	35.3	19.2	24.3	0.36	41.6
+	302	10.6	33.2	18.8	22.6	0.34	31.7
50% p.o.	310	8.4	30.2	16.0	15.6	0.38	22.9
	318	8.0	30.0	15.5	14.4	0.39	16.2
25% cyclohexane	294	12.2	45.1	23.4	40.2	0.37	146.3
+	302	10.8	42.3	21.4	33.2	0.39	102.8
75% p.o.	310	9.8	39.8	19.8	27.6	0.41	69.3
	318	8.9	37.8	18.3	22.8	0.42	48.7
100% p.o.	294	14.2	63.6	30.0	79.4	0.38	563.5
	302	13.5	60.3	28.5	71.5	0.39	491.7
	310	12.5	58.2	26.9	64.1	0.42	415.5
	318	11.1	56.2	24.5	57.6	0.44	270.9

3. Results

The relaxation time along with the distribution parameter (α) and the macroscopic viscosity (η_s) of the solvent mixtures are reported in table 1. The thermodynamical parameters associated with the relaxation process having the relaxation time $\tau_{(1)}$ as well as for the overall rotational mechanism having relaxation time $\tau_{(OH)}$ at temp. 294 K are given in table 2.

4. Discussion

Table 1 indicates that for all the molecules studied the values of relaxation time decrease with increase in temperature even in highly viscous media. Also, the relaxation time keeps increasing systematically with increasing viscosity of the solvent mixture but not in the same ratio as the increasing viscosity for all the three molecules.

In highly viscous solvents, with increasing viscosity of the medium, the distribution parameter at 294 K varies from 0.07–0.42 and 0.05–0.40 for pyrrolidine and piperidine molecules respectively. These high values indicate the flexibility of these rigid molecules in such media and the α value becomes maximum for 100% p.o. used as a solvent. These results agree with our previous study (Singh *et al* 1983).

As τ_O and τ_{OH} correspond to the overall relaxation mechanism, these are in close agreement for less viscous solutions. The gap between the values of these relaxation parameters increases with the viscosity of the solvent, and for pyrrolidine and piperidine molecules $\tau_O > \tau_{OH}$ while for acetyl pyridine $\tau_O < \tau_{OH}$. τ_O is the geometric mean of $\tau_{(1)}$ and $\tau_{(2)}$. $\tau_{(1)}$ values are not much affected by the change of the viscosity of the medium, hence it may be presumed that $\tau_{(0)}$ cannot be the parametric measurement of the overall relaxation mechanism of viscous systems.

On resolving, the relaxation times $\tau_{(1)}$ and $\tau_{(2)}$ of pyrrolidine at 294 K vary from 7.5 to 7.9 psec and 9.8 to 32.5 psec respectively for solvent mixture of 25% p.o. to 100% p.o. For the same viscosity range, the variation of $\tau_{(1)}$ and $\tau_{(2)}$ is in the range (9–9.3) psec and (10.8–35.6) psec for piperidine molecule. As $\tau_{(1)}$ is almost constant w.r.t. viscosity of the medium and no group rotation is possible in the rigid molecules $\tau_{(1)}$ may be associated with some kind of segmental flexibility of the molecular systems. On the other hand, the relaxation parameter $\tau_{(2)}$, which has been observed as related to the molecular motion of the system, undergoes considerable increase with the increasing viscosity of the medium. The flexible behaviour observed for both the rigid systems can be interpreted in the light of the model of Balogun and Cumper (1973). The solvent molecules in highly viscous media form a type of cage around the solute molecules. Hence, the solute molecule faces hindrance caused by the cage of solvent molecules for dipolar rotational process.

In highly viscous media the displacement of the solvent is not a major factor in the relaxation process and the solute molecules rotate in isolated cavities in the network of flexible paraffin chains. The microscopic viscosity affecting the rotational process will be a considerable fraction of the bulk viscosity in pure paraffin and also the specific volume (effective volume) will be greater for 100% p.o. solution. Hence, for rotation of the molecular unit as a whole the number of cages formed around the solute molecule increases with increasing viscosity and hence the $\tau_{(2)}$ value also.

In 2-acetyl pyridine molecule $\tau_{(1)}$, *i.e.*, the group dipolar motion is almost independent

Table 2. Energy parameter for dipolar rotational process.

System	Solvent mixture	$\Delta H_{r(1)}$ (kcal/mol)	$\Delta F_{r(1)}$ (kcal/mol)	$\Delta S_{r(1)}$ (cal/mol)	$\Delta H_{r(OH)}$ (kcal/mol)	$\Delta F_{r(OH)}$ (kcal/mol)	$\Delta S_{r(OH)}$ (cal/mol)
Pyrrolidine	75% Cyclohexane + 25% p.o.	2.2	2.3	-0.3	1.7	2.3	-2.0
	50% Cyclohexane + 50% p.o.	2.1	2.3	-0.7	1.8	2.3	-1.7
	25% Cyclohexane + 75% p.o.	2.3	2.3	+0.0	2.2	2.4	-0.7
	100% p.o.	2.2	2.3	-0.3	3.0	2.7	+1.0
Piperidine	75% Cyclohexane + 25% p.o.	0.8	2.4	-5.4	1.2	2.4	-4.1
	50% Cyclohexane + 50% p.o.	0.8	2.4	-5.4	1.6	2.4	-2.7
	25% Cyclohexane + 75% p.o.	0.9	2.4	-5.1	2.2	2.6	-1.3
	100% p.o.	1.0	2.4	-4.7	3.3	2.9	+1.4
2-Acetyl pyridine	75% Cyclohexane + 25% p.o.	0.8	2.4	-5.4	2.4	2.8	-1.4
	50% Cyclohexane + 50% p.o.	1.2	2.5	-4.4	3.4	2.9	+1.7
	25% Cyclohexane + 75% p.o.	1.5	2.5	-3.4	3.9	3.2	+2.4
	100% p.o.	1.8	2.6	-2.7	—	3.6	—

of viscosity of the medium as observed by Crossley *et al* (1979). An interesting factor is that the change in α -value indicating the flexibility of the molecular system is no more significant than the rigid molecules earlier discussed. This can be interpreted as both the molecule and the acetyl group accounting for the two almost independent rotational processes having to face hindrances of the same strength relative to their individual structural dimensions caused by the solvent cage formation around the group and the molecule as well. Thus no sharp change in the α value occurs whereas for rigid systems the cage formation by solvent system together with the consequent trapping of solute molecules in solvent holes caused more flexible behaviour.

The thermodynamical energy parameters evaluated here indicate nothing anomalous in highly viscous media. For all rigid and flexible systems the activation energy corresponding to each relaxation process increases with increasing viscosity of the medium and is almost independent of temperature—a trend different from dilute solution studies. This may be interpreted as follows: with increase in temperature the strength of hindrances caused around the solute molecules by solvent cage goes on weakening, thus compensating the required high energy caused by thermal agitation for dipoles to attain equilibrium with the applied field.

ΔF and ΔS for the rigid systems are very close to each other which is reasonable as the relaxation mechanism occurring in the two rigid systems is similar. The reported $\Delta H_{\tau_{(\text{OH})}}$ values may not be very reliable. However, a common feature to all solutes is that $\Delta H_{\tau_{(\text{OH})}}$ increases with increasing viscosity. The negative value of entropy of activation implies a more ordered behaviour in the activated state than in the normal state. With increasing viscosity ΔS tends to be positive indicating that these states get disordered as the viscosity of the medium is increased. This agrees with Gupta *et al* (1983).

A maximum entropy of activation resulted in the case of pure p.o. solvent. Obviously, larger the percentage of p.o., larger will be the number of paraffin chains, and the solvent system becomes more complicated resulting in the solute molecule having to exert larger asymmetric forces on the walls of the cage formed by the solvent system around it. With pure paraffin solvent, the solute cavity is highly tightened around by paraffin chains. Undoubtedly, now the solute molecule will have to exert maximum force for dipolar rotational diffusion process resulting in a maximum ΔH value.

5. Conclusion

The present study reveals that in a non-interacting environment, such as would be approximated by dilute solutions in a non-polar solvent, the dielectric relaxation of a polar solute occurs from the rotational diffusion which require a cooperative motion of the solvent molecules forming the cage around the solute molecule.

The relaxation time of a molecule is related to its molar volume, which accounts for the higher values for 2-acetylpyridine molecule and also for a more marked change in $\Delta H_{\tau_{(\text{OH})}}$ values in this case than the values of $\Delta H_{\tau_{(\text{OH})}}$ of the remaining two molecules.

The comparison of $\Delta F_{\tau_{(\text{OH})}}$ values reflects directly upon the comparative sizes of all the three molecules. The rotation of the more bulky system of 2-acetylpyridine molecule will disrupt the local alignment of the solvent system to a greater extent and hence tends to give more positive values of $\Delta S_{\tau_{(\text{OH})}}$ than the other two compact rigid molecules.

Hence, the dielectric rotational diffusion process in highly viscous media depends on

the intermolecular forces (which the solute molecule experience from the surrounding cluster of solvent molecules) and the shape of solute molecule together with the viscous drag of the solvent molecules and their shape. For a more clear representation and better interpretation of viscous drag in highly viscous media for dipolar rotational process, further studies in this direction are needed.

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