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Dielectric studies in dilute solutions

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Abstract. Dielectric studies in dilute solutions of cyclohexane and benzene have been carried out in the temperature range 294–318°K. The observed data have been utilized to evaluate the relaxation times and thermodynamic parameters of these molecules. The high values of α for 2-acetyl pyridine indicate the occurrence of more than one relaxation time. In the remaining systems, the observed low α values indicate their rigid behaviour. The variation in the dielectric relaxation time is mostly correlated with the change in the heterocyclic configuration of the system.

Keywords. Heterocyclic compounds; relaxation time; distribution parameter; thermodynamic parameters.

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1. Introduction

Dielectric investigation is useful to understand the flexibility or rigidity of a molecule as to study the carcinogenic activity of the molecule. Dielectric absorption studies also provide useful information on the rotational energies of molecular systems in a given media. It was therefore considered interesting to investigate systematically the change in relaxation behaviour of heterocyclic molecules with the structural configuration changing from five-membered to seven-membered ring and how the substitution to a heterocyclic ring and phenyl ring affects the behaviour of the molecule. In the present investigation dielectric parameters were measured for five heterocyclic compounds: pyrrolidine (5-membered ring); piperidine (6-membered ring); hexamethyleneimine (7-membered ring); 2-methyl piperidine ($-CH_3$ group attached to piperidine) and 2-acetyl pyridine (acetyl group attached to pyridine). The relaxation behaviour was studied in dilute solutions of non-polar solvent.

2. Results and discussion

The values of relaxation time along with those of distribution parameter α are presented in table 1. Table 2 includes the measured dielectric parameters in the temperature range 294–318°K.

2.1 *Pyrrolidine*

The α value for pyrrolidine ranges between 0·01 and 0·03 in the temperature range 294–318°K. The most probable relaxation time varies from 7·5 to 5 psec in the same temperature range. This agrees with other reported values (Holland and Smyth 1955) of

Table 1. Relaxation time (τ in psec) and distribution parameter (α).

Compound	Temp (°K)	$\tau_{(1)}$	$\tau_{(2)}$	$\tau_{(0)}$	α	$\tau_{(OH)}$	$\tau_{(GK)}$
Pyrrolidine	294	7·5	7·9	7·7	0·01	7·5	7·3
	302	6·7	7·0	6·9	0·01	6·7	6·6
	310	6·0	6·4	6·2	0·01	6·3	5·9
	318	5·1	6·0	5.6	0·03	5·0	5·0
Piperidine	294	8·9	9·6	9·2	0·02	8·9	8·8
	302	8·5	8·8	8·7	0·01	8·5	8·3
	310	7·8	8·1	8·0	0·01	7·8	7·7
	318	7·3	7·6	7·5	0·01	7·3	7·0
Hexamethy-leneimine	294	12·3	13·1	12·7	0·02	12·5	12·2
	302	11·1	12·6	11·6	0·02	11·3	11·1
	310	10·3	11·4	10·9	0·03	10·6	10·2
	318	9·7	10·4	10·1	0·02	9·8	9·7
2-methyl-piperidine	294	9·7	10·4	10·1	0·03	9·8	9·4
	302	8·9	9·9	9·4	0·03	9·0	9·0
	310	7·8	9·1	8·4	0·05	7·7	7·8
	318	7·0	8·5	7·7	0·05	7·0	7·5
2-acetyl-pyridine	294	8·2	29·4	15·5	0·38	14·5	14·1
	302	7·8	27·1	14·6	0·37	12·4	12·5
	310	7·4	25·2	13·7	0·36	10·7	10·7
	318	7·1	23·1	12·8	0·35	9·2	10·0

From Higasi (1966); Higasi *et al* (1977); Gopala Krishna (1957).

Table 2. Dielectric parameters.

System	Concen-tration	294 K				302 K			
		ε_0	ε'	ε''	ε_{00}	ε_0	ε'	ε''	ε_{00}
Pyrrolidine	0·006	2·402	2·170	0·107	2·0573	2·607	2·172	0·109	2·0579
	0·016	2·421	2·179	0·114	2·0578	2·625	2·180	0·115	2·0584
	0·026	2·440	2·192	0·119	2·0583	2·643	2·192	0·121	2·0590
	0·035	2·462	2·205	0·125	2·0588	2·657	2·206	0·126	2·0594
	0·045	2·477	2·215	0·130	2·0592	2·674	2·215	0·132	2·0597
Piperidine	0·005	2·482	2·188	0·087	2·0777	2·655	2·192	0·084	2·0781
	0·013	2·497	2·199	0·093	2·0781	2·669	2·202	0·089	2·0784
	0·025	2·518	2·217	0·101	2·0791	2·690	2·215	0·097	2·0790
	0·035	2·537	2·232	0·108	2·0797	2·707	2·227	0·104	2·0795
	0·046	2·560	2·246	0·116	2·0803	2·727	2·240	0·110	2·0801
Haxamethyl-eneimine	0·007	2·623	2·346	0·342	2·3014	2·715	2·360	0·347	2·3020
	0·018	2·643	2·359	0·351	2·3025	2·735	2·373	0·354	2·3033
	0·029	2·665	2·373	0·360	2·3036	2·756	2·387	0·362	2·3046
	0·039	2·687	2·385	0·369	2·3046	2·774	2·398	0·370	2·3058
	0·052	2·401	2·401	0·378	2·3058	2·800	2·415	0·376	2·3072
2-methyl-piperidine	0·005	2·464	2·183	0·101	2·0913	2·645	2·194	0·107	2·0917
	0·014	2·480	2·194	0·107	2·0923	2·656	2·203	0·112	2·0926
	0·023	2·492	2·206	0·114	2·0932	2·668	2·212	0·117	2·0934
	0·032	2·514	2·218	0·120	2·0944	2·677	2·220	0·122	2·0942
	0·043	2·540	2·233	0·129	2·0956	2·693	2·230	0·128	2·0952

Table 2. (*Contd.*)

System	Concentration	294 K ε_0	294 K ε'	294 K ε''	294 K ε_∞	302 K ε_0	302 K ε'	302 K ε''	302 K ε_∞
2-acetyl pyridine	0·009	2·448	2·178	0·229	2·0779	2·633	2·183	0·227	2·0883
	0·019	2·480	2·195	0·238	2·0797	2·664	2·200	0·235	2·0900
	0·029	2·508	2·211	0·245	2·0813	2·692	2·217	0·243	2·0917
	0·040	2·547	2·232	0·255	2·0832	2·727	2·239	0·251	2·0934
	0·051	2·563	2·250	0·262	2·0856	2·762	2·258	0·257	2·0952
		310 K				318 K			
Pyrrolidine	0·006	2·741	2·180	0·112	2·0583	2·845	2·195	0·118	2·0587
	0·016	2·760	2·192	0·116	2·0586	2·857	2·206	0·122	2·0589
	0·026	2·777	2·206	0·122	2·0590	2·872	2·215	0·124	2·0589
	0·035	2·790	2·220	0·126	2·0593	2·884	2·228	0·129	2·0593
	0·045	2·805	2·233	0·131	2·0595	2·896	2·237	0·131	2·0596
Piperidine	0·005	2·808	2·194	0·092	2·0784	2·880	2·195	0·094	2·0782
	0·013	2·819	2·207	0·098	2·0788	2·888	2·203	0·098	2·0786
	0·025	2·836	2·218	0·104	2·0794	2·902	2·215	0·104	2·0792
	0·035	2·848	2·227	0·110	2·0794	2·914	2·224	0·110	2·0797
	0·046	2·865	2·240	0·116	2·0804	2·926	2·235	0·115	2·0802
Hexamethyl-eneimine	0·007	2·828	2·358	0·351	2·3023	2·890	2·355	0·356	2·3028
	0·018	2·847	2·370	0·358	2·3033	2·910	2·372	0·364	2·3039
	0·029	2·867	2·380	0·365	2·3043	2·931	2·387	0·371	2·3050
	0·039	2·885	2·390	0·371	2·3052	2·948	2·402	0·378	2·3060
	0·052	2·908	2·402	0·378	2·3063	2·974	2·420	0·387	2·3073
2-methyl-piperidine	0·005	2·795	2·185	0·118	2·0921	2·865	2·195	0·112	2·0921
	0·014	2·805	2·193	0·121	2·0929	2·873	2·202	0·115	2·0930
	0·023	2·813	2·202	0·123	2·0937	2·882	2·208	0·118	2·0940
	0·032	2·822	2·208	0·126	2·0945	2·887	2·215	0·121	2·0949
	0·043	2·834	2·218	0·131	2·0955	2·897	2·223	0·126	2·0959
2-acetyl-pyridine	0·009	2·780	2·192	0·237	2·0887	2·855	2·198	0·233	2·0885
	0·019	2·812	2·207	0·243	2·0904	2·884	2·209	0·240	2·0901
	0·029	2·838	2·223	0·251	2·0921	2·910	2·230	0·246	2·0917
	0·040	2·872	2·244	0·260	2·0938	2·944	2·249	0·254	2·0934
	0·051	2·902	2·263	0·269	2·0955	2·962	2·268	0·261	2·0950

8 psec at 40°C in pure state. The observed low α value indicates the rigid behaviour of pyrrolidine molecule in dilute solution. On further resolving the relaxation time into $\tau_{(1)}$ and $\tau_{(2)}$ parameters, the relaxation times were $\tau_{(1)}$ (= 7·4–5·1) psec and $\tau_{(2)}$ (= 7·9–6·01) psec which are close to each other and which further support the rigid nature of the molecule.

The enthalpies of activation (ΔH) associated with the dipolar rotation process corresponding to $\tau_{(2)}$ and $\tau_{(OH)}$ are 4·6 and 4·8 kJ mol^{-1}. The free energies of activation vary as 9·6–9·9 kJ mol^{-1} and 9·5–9·7 kJ mol^{-1} respectively. This results in a low negative entropy of activation 16·6–14·3 J mol^{-1}.

2.2 *Piperidine*

Piperidine also yielded low α (0·01–0·02) values. The average relaxation times τ_{OH} and τ_{GK} were in the range 9·2–7·5 psec and 8·9–7·3 psec respectively. On further resolving the absorption $\tau_{(1)}$ and $\tau_{(2)}$ range from 8·8–7·3 psec and 9·6–7·6 psec which are quite close to one another. This again indicates a non-flexible behaviour of piperidine molecule.

Also, the lengthening of the relaxation time $\tau_{(2)}$ from pyrrolidine to piperidine from 7·9 to 9·6 psec, being in the order of increasing molecular dimension implies that the process occurring was due to the overall molecular relaxation.

The enthalpies of activation (ΔH) $\tau_{(2)}$ and (ΔH) $\tau_{(OH)}$ were 4·7 and 5·2 kJ mol^{-1} respectively while ΔF varied from 10·1–10·5 kJ mol^{-1} and 9·9–10·4 kJ mol^{-1} for similar relaxation data. The entropies of activation were thus negative 18·4–16 J mol^{-1}.

2.3 *Hexamethyleneimine*

Hexamethyleneimine is a seven-membered closed heterocyclic ring system. The α values ranging from 0·02 to 0·03 indicates the non-flexible nature of the compound. The relaxation time parameters $\tau_{(1)}$ (11·1 psec) and $\tau_{(2)}$ (12·1 psec) are very close to each other. Also, the average relaxation time values, τ_{OH} (12·5 psec) and τ_{GK} (12·2 psec) are similar and agree with both $\tau_{(1)}$ and $\tau_{(2)}$. This further suggests that the molecule exhibits a rigid nature and there is no flexibility in the system.

The enthalpy of activation corresponding to the average relaxation time parameters $\tau_{(2)}$ and $\tau_{(OH)}$ are 4·8 and 5·5 kJ mol^{-1}. The free energy values of rotation varies from 10·8–11·3 kJ mol^{-1} and 10·7–11·2 kJ mol^{-1}. The relaxation process exhibited a negative entropy value.

2.4 2-*methyl piperidine*

The compound gave rise to a higher α value in the range 0·03–0·05 compared to piperidine, which indicates that methyl group substitution at position two introduces greater interference with the neighbouring molecules. The rotational behaviour of the system remained rigid as is indicated from the observed relaxation time reported in table 1. The observed relaxation parameter of 7 psec agrees with the literature value (Mukhija *et al* 1972) of 6·4 psec at 30°C.

The thermodynamic parameters ΔH and ΔF corresponding to $\tau_{(2)}$ and $\tau_{(OH)}$ were 6·2 and 6·5 kJ mol^{-1}, 10·3–10·8 kJ mol^{-1} and 10·1–10·3 kJ mol^{-1} respectively. The entropy of activation ΔS in this case also was negative. This exhibited an ordered behaviour.

2.5 2-*acetyl pyridine*

2-acetyl pyridine yielded an α of 0·35–0·38 in the temperature range 294-318°K. The most probable relaxation time $\tau_{(OH)}$ of 14·1 psec at 294°K is close to τ_{GK} of 14·1 psec and $\tau_{(0)}$ of 15·5 psec respectively. On resolving the absorption process into two separate relaxations $\tau_{(1)}$ and $\tau_{(2)}$ using Higasi *et al* (1971) method, the value obtained for $\tau_{(1)}$ and $\tau_{(2)}$ were in the range (8·2–7·1 psec) and (29·4–27·0 psec) respectively in the temperature

range 294 ≃ 318°K. These parameters being sufficiently different from each other may be attributed to two separate relaxation mechanisms. One, $\tau_{(2)}$, occurring from the molecular process and the other $\tau_{(1)}$ due to the process associated with the group relaxation, in the present case possibly due to the rotation of '–$COCH_3$' group attached in the ring. This is supported from the observed high α values. Also the present data agree with the acetyl group rotation of acetyl naphthalene and related molecules earlier studied by Crossley *et al* (1968).

The enthalpy of activation ΔH corresponding to $\tau_{(1)}$ obtained was 2·8 kJ mol^{-1} while for molecular rotation process ΔH was 5·3 kJ mol^{-1}. ΔF associated with group process was in the range 9·7–10·3 kJ mol^{-1} whereas for the molecular rotational process this was higher being in the range 12·8–13·4 kJ mol^{-1}. The entropies for both the molecular and group processes were negative which exhibited an ordered behaviour of the system.

3. Conclusion

Excepting 2-acetyl pyridine the study indicated the rigid nature of all the molecules. The relaxation times and thermodynamical parameters increase with the molecular dimensions as expected. The 2-acetyl pyridine molecule indicates the rotation of the acetyl group. The study will be extended to discuss the influence of viscosity of the media on the observed relaxation times of the systems and the results will be reported separately.

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