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Dielectric Relaxation of Some Aliphatic Ketones in Dilute Solution

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Synopsis. Measurements of the relative permittivity at frequency of 10 GHz, and of the refractive index, have been made at 25 °C for (a) 2-haxanone, (b) 3-hexanone, (c) 3-Methyl-2-pentanone, (d) 3,3-dimethyl-2-butanone,(e) 2-heptanone, (f) heptanal, and (g) cyclohexanone, in dilute solutions of cyclohexane, decalin, and 1,4-dioxane, Dielectric relaxation times have been evaluated. It has been concluded that in the ketones and heptanal under study, dipole reorientation occurs mainly by an intramolecular relaxation process.

Crossley[1–3] has studied some ketones at a single concentration at different frequencies and has shown that dipole reorientation occurs primarily by the intramolecular rotation of the terminal acetyl group. The present work examines the dielectric absorption of five ketones together with heptanal and cyclohexanone in three nonpolar solvents, namely, cyclohexane, decalin, and 1,4-dioxane. Viscoelastic behaviour of these polar molecules is discussed in terms of intramolecular as well as overall molecular rotations. The possibility of solute-solvent interactions between the dioxane and these molecules is also discussed.

The polar materials as well as solvents used were of purest available grade and were distilled, whereever felt necessary, before use. The measured values of the refractive indices of polar materials and solvents were in agreement with the literature values where available.

Measurements of the relative permittivity ε' and dielectric loss factor ε'' at a frequency of 10 GHz were made by the 3-db technique using a Sanders VSWR Amplifier MKIII. Six samples at different concentrations in the range 0—0.03 weight fraction were studied for each material. The refractive index was measured using an Abbe refractometer.

Results

The values of a', a'', and a_D which are, respectively the slopes[4] of the plots of ε', ε'', and n_D^2 *versus* weight fraction of the solute, are given in Table 1. These slopes a', a'', and a_D were determined within 2, 4, and 5% respectively, by least square fitting using an appropriate program on a PDP8 digital computer. Values of a_∞, the slope of the plot of the relative permittivity at infinite frequencies, ε_∞, *versus* weight fraction of the solute, were calculated using the relation $a_\infty = 1.1\ a_\mathrm{D}$. Dielectric relaxation time τ, has been evaluated using the relation[5,6)]

$$\tau = \frac{a''}{\omega(a' - a_\infty)}.$$

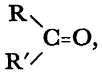
Discussion

Values of τ are given in Table 2 and the same are compared with the literature values where availble.

TABLE 1. VALUES OF a', a'', a_D, AND a_∞ FOR MOLECULES AT 25 °C

Chemical	a'	a''	a_D	a_∞
	Solvent cyclohexane			
2-Hexanone	5.732	1.54	−0.146	−0.131
3-Hexanone	5.809	1.44	−0.160	−0.144
3-Methyl-2-pentanone	5.916	1.91	−0.162	−0.071
3,3-Dimethyl-2-butanone	6.138	1.11	−0.137	−0.123
2-Heptanone	5.268	1.44	−0.152	−0.137
Heptanal	3.951	0.96	−0.094	−0.085
Cyclohexanone	8.008	2.18	+0.109	+0.121
	Solvent decalin			
2-Hexanone	6.833	2.21	−0.281	−0.253
3-Hexanone	6.769	2.13	−0.289	−0.260
3-Methyl-2-pentanone	6.287	2.68	−0.275	−0.247
3,3-Dimethyl-2-butanone	6.836	1.74	−0.298	−0.268
2-Heptanone	5.658	2.22	−0.269	−0.242
Heptanal	4.119	1.30	−0.208	−0.187
Cyclohexanone	8.389	3.28	−0.134	−0.121
	Solvent 1,4-dioxane			
2-Hexanone	7.969	3.65	−0.091	−0.082
3-Hexanone	7.912	3.55	−0.079	−0.071
3-Methyl-2-pentanone	7.749	3.94	−0.136	−0.122
3,3-Dimethyl-2-butanone	8.189	3.02	−0.084	−0.076
2-Heptanone	6.634	3.34	−0.073	−0.066
Heptanal	4.814	2.11	−0.057	−0.051
Cyclohexanone	9.507	5.13	+0.102	+0.112

The measured values of τ for 2-hexanone in cyclohexane and decalin and for cyclohexanone in cyclohexane are found to compare well with the literature values. Values of τ are of the same order of magnitude as the relaxation time for acetyl group rotation in aromatic molecules[8–10] (≈7 p s) and for acetone[11,12] (3.2 p s) in dilute solution and are smaller than those acticipated for overall molecular rotation. This gives an indication that dipole reorientation in ketones occurs mainly by intramolecular rotation of the terminal acetyl group. The relaxation time for 2-hexanone is almost equal to that for 3-hexanone. This indicates that the location of the carbonyl group on the hydrocarbon chain has relatively little affect on the relaxation time for hexanones. Crossley,[1] too, has made the same conclusion from the studies on nonanones and decanones. The structure of ketones can be expressed as



$$\mathrm{R}(\mathrm{R'})\mathrm{C{=}O},$$

Table 2. Values of τ, τ_{Lit}, $\tau_{\mathrm{Dec}}/\tau_{\mathrm{c}}$, and $\tau_{\mathrm{Diox}}/\tau_{\mathrm{c}}$

Chemical	τ / ps	τ_{Lit} / ps	$\tau_{\mathrm{Dec}}/\tau_{\mathrm{c}}$	$\tau_{\mathrm{Diox}}/\tau_{\mathrm{c}}$
	Solvent cyclohexane			
2-Hexanone	4.1	4.0[1]	1.20	1.73
3-Hexanone	3.9	—	1.24	1.83
3-Methyl-2-pentanone	5.1	—	1.29	1.57
3,3-Dimethyl-2-butanone	2.8	3.2[3] (benzene)	1.38	2.06
2-Heptanone	4.2	—	1.40	1.85
Heptanal	3.8	—	1.28	1.82
Cyclohexanone	4.4	4.4[7]	1.37	1.97
	Solvent decalin			
2-Hexanone	4.9	5.2[2]		
3-Hexanone	4.8	—		
3-Methyl-2-pentanone	6.5	—		
3,3-Dimethyl-2-butanone	3.9	—		
2-Heptanone	6.0	—		
Heptanal	4.8	—		
Cyclohexanone	6.0	—		
	Solvent 1,4-dioxane			
2-Hexanone	7.2	—		
3-Hexanone	7.1	—		
3-Methyl-2-pentanone	7.9	—		
3,3-Dimethyl-2-butanone	5.8	—		
2-Heptanone	7.8	—		
Heptanal	6.9	—		
Cyclohexanone	8.7	—		

and the molecule may relax either by overall molecular reorientation or by twisting around the R–C and R′–C bonds. Second type of intramolecular relaxation process appears to make a large contribution to the absorption in the ketones under study. The dielectric relaxation behaviour of diphenyl ether and related compounds is also explained by the same type of relaxation process.

The relaxation time for 3,3-dimethyl-2-butanone in cyclohexane at 25 °C is 2.8 p s., which is comparable to that for acetone in benzene at 25 °C (=3.2 p s). In this molecule the *t*-butyl group R is compact in size and, therefore, dipole reorientation occurs by twisting around the R′–C bond only.

Values of τ for 2-heptanone is only slightly longer than that for 2-hexanone and the difference increases again with the increase in the viscosity of the solvent. Also, the ratio of the relaxation times in decalin to that in cyclohexane ($\tau_{\mathrm{Dec}}/\tau_{\mathrm{c}}$) for all the compounds in the present study is $\approx$1.3 (Table 2) which is rather smaller than the ratio of the viscosities of the solvents ($\eta_{\mathrm{Dec}}/\eta_{\mathrm{c}}$) which is $\approx$2.5. This indicates that the contribution of the overall molecular rotation to the relaxation process is quite small. The relative contribution to the value of τ by the intramolecular rotation and overall molecular rotation and with the increased viscosity of the solvent has been discussed in detail by Crossley.[3]

The relaxation time of heptanal has been found to be almost equal to that of 2-heptanone. Also, the value of $\tau_{\mathrm{Dec}}/\tau_{\mathrm{c}}$ for heptanal is comparable to those for 2-hexanone and 3-hexanone. This shows that dipole reorientation in alkanals also takes place largely by intramolecular relaxation process. The value of τ for cyclohexanone is seen to be comparable to that for 2-hexanone and 2-heptanone in all the three solvents and the values of $\tau_{\mathrm{Dec}}/\tau_{\mathrm{c}}$ and $\tau_{\mathrm{Diox}}/\tau_{\mathrm{c}}$, too, are almost the same. Cyclohexanone is known to be a rigid spherical molecule. Probably the dipole reorientation of the spherical cyclohexanone molecule involves roughly the same displacement of the surrounding molecules as in the case of the segment rotations of 2-hexanone or 3-methyl-2-pentanone. This is also confirmed from dielectric relaxation studies of ketones in a polystyrene matrix,[14] where dielectric dispersion for cyclohexanone has been found to occur in the same temperature region as for the low temperature dispersion (which has been attributed to the acetyl group rotation) for 2-hexanone and 2-heptanone.

The value of $\tau_{\mathrm{Diox}}/\tau_{\mathrm{c}}$ for all the molecules under study (except for 3-methyl-2-pentanone) is$\sim$1.9 (Table 2) and is much larger than $\eta_{\mathrm{Diox}}/\eta_{\mathrm{c}}$ (=1.33). Values of τ for these molecules in 1,4-dioxane are longer when compared with those in decalin though the viscosity of the latter is almost double than the former. It is known that the ketone molecule is a resonance hybrid in which the carbon atom of the carbonyl group assumes a positive character. This positive carbonyl carbon is liable to interact strongly with the lone-pair electrons of the oxygen atom in 1,4-dioxane resulting in large values of τ. Similar results have been reported for trihaloganated esters[15] and nitroalkanes.[6]

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