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Dielectric Study of Aliphatic Esters in Cyclohexane Solutions at the Frequency of 100 GHz

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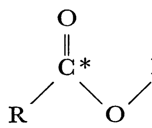
The dipole relaxation mechanism of carboxylic esters has been studied through the dielectric measurements of seventeen aliphatic esters in cyclohexane solution at 25 °C. The dielectric relaxation times obtained in this experiment are compared with those obtained for a number of rigid molecules under the same conditions. This result indicates that the dipole relaxation process of these esters RC*OOR′ is dominated by intramolecular rotation around the C–C bonds and/or the O–C bond rather than that around the C*–O bond.

This paper deals with the results of dielectric measurements of seventeen aliphatic esters in cyclohexane solution at 25 °C at the frequency of 100 GHz. The dielectric data obtained in this experiment and those by Crossley and Koizumi[1] obtained for the same esters under the same conditions using lower microwave frequencies were examined to explore the mechanism of the dielectric absorption of aliphatic esters RC*OOR′ (hereafter, C* means the carbon atom in a carbonyl group). All the results indicate that the dielectric absorption of these esters is dominated by intramolecular relaxation. However, in contrast to Crossley and Koizumi[1] who considered that the dipole orientation of the methoxyl and ethoxyl groups around their C*–O bonds is very important especially for a few esters, the present authors reached the conclusion that rotations of groups around the C–C bonds and/or the O–C bond play the dominant role in the dielectric absorption of the aliphatic esters.



Experimental

The apparatus and procedure used to determine dielectric constants (ε') and losses (ε'') at 100 GHz have been described previously.[2] Static dielectric constants (ε_0) were measured at 1 MHz and refractive indices (n) were determined at the frequency of Na–D line. The slopes a_0, a', a'', and a_D were obtained from ε_0, ε', ε'', and n_D^2 of the solvent and solutions as in the previous papers.[2,3] The units of weight fraction were used to express the concentration of the solute in solution.

Results

The values of a_0, a', a'', and a_D obtained for the aliphatic esters in cyclohexane solution at 25 °C are listed in Table 1. Two relaxation times $\tau(1)$ and $\tau(2)$ given by

$$\tau(1) = \frac{1}{\omega}\frac{a''}{a'-a_\mathrm{D}}; \quad \tau(2) = \frac{1}{\omega}\frac{a_0-a'}{a''}$$

are recorded in Table 1—ω denotes the angular frequency. The physical significance of $\tau(1)$ and $\tau(2)$ have been discussed in previous reports.[3,4] As a large error seems to arise from the bold assumption that a_D is equal to a_∞ (the slope at the extremely high frequency), we shall not place much reliance on values of $\tau(1)$.

For each of the esters Cole-Cole plots were made by use of a' and a'' of this experiment at 100 GHz together with those recalculated from Crossley and Koizumi's data obtained at *ca.* 35, 24, 16, 9, 6, 4, and 2 GHz. Crossley and Koizumi made the following remark concerning the highest frequency they employed. "In many cases the frequency of maximum loss is in the region of the highest experimental frequency, and thus the high frequency side of the dispersion is not well characterized." It may be added here that the high frequency side of the dispersion is examined first by the present experiment. The mean relaxation times (τ_0) and the distribution parameters (α) obtained in this way were compared with those given by Crossley and Koizumi using lower microwave frequency data alone (Table 2). We find our τ_0 values are slightly smaller than τ_0 obtained by Crossley and Koizumi in some esters but they compare well on the whole. Further we find values $\tau(2)$ to be sometimes smaller than our values for τ_0.

Discussion

If the Debye theory[5] of dielectric relaxation is correct, the relaxation times (τ_0) of all the rigid polar molecules measured in the same solvent at the same temperature should be proportional to the molecular volume of the solutes. This prediction is examined in Fig. 1 for a number of rigid molecules (code number 21—39; Table 3) in cyclohexane at 25 °C—the molecular volume is obtained by the ratio of the molecular weight (M) to the density (d). We find Debye's theory to be only qualitatively valid. The points for 21—39 scatter in a wide range and the fluctuation appears to be much larger than the error in estimating the molecular volume.[6] There exists a general tendency shown by curve A that the points for rigid molecules move upward with increasing molecular volume.

The relaxation times (τ_0) of seventeen aliphatic esters (code numbers 1—17) are also examined in a similar manner — as an exception, $\tau(2)$ is taken for methyl acetate since τ_0 is not available for this molecule. We can draw curve B through the points for esters. We notice that curve B is situated below curve A and is almost parallel to the abscissa for esters of large molecular volumes. This is a common feature of all flexible polar molecules.[7]

Two curves A and B intersect each other in the

TABLE 1. SLOPES, RELAXATION TIMES, AND DIPOLE MOMENTS FOR ALIPHATIC ESTERS IN CYCLOHEXANE SOLUTION AT 25 °C

Ester	a_0	a'	a''	a_D	$\tau(1)$/ps	$\tau(2)$/ps	μ/D
Methyl acetate	2.953	1.554	1.266	—	—	1.8	—
Methyl hexanoate	1.758	0.609	0.527	−0.092	1.2	3.6	1.68
Methyl octanoate	1.520	0.492	0.386	−0.059	1.1	4.4	1.71
Methyl decanoate	1.314	0.439	0.315	−0.034	1.1	4.5	1.71
Methyl hexadecanoate	0.875	0.337	0.209	0.016	1.1	4.2	1.64
Methyl octadecanoate	0.823	0.311	0.183	0.023	1.0	4.6	1.67
Methyl docosanoate	0.776	0.292	0.160	0.041	1.0	4.8	1.73
Methyl oleate	0.881	0.353	0.173	0.059	0.96	5.0	1.68
Ethyl acetate	3.086	1.058	0.985	−0.194	1.3	3.4	1.84
Ethyl hexanoate	1.742	0.452	0.414	−0.079	1.3	5.1	1.75
Ethyl octanoate	1.484	0.377	0.305	−0.049	1.2	5.9	1.75
Ethyl dodecanoate	1.155	0.310	0.221	−0.009	1.1	6.3	1.76
Ethyl octadecanoate	0.886	0.266	0.151	0.024	1.0	6.7	1.77
Ethyl linoleate	1.045	0.318	0.167	0.072	1.1	7.1	1.87
Ethyl lactate	5.020	1.001	0.782	−0.104	1.2	8.4	2.50
Pentyl acetate	2.211	0.621	0.512	−0.098	1.2	5.1	1.87
Diethyl tetradecanedioate	1.713	0.476	0.314	0.019	1.1	6.4	2.49

TABLE 2. CODE NUMBERS OF THE ALIPHATIC ESTERS AND THEIR COLE-COLE PARAMETERS τ_0 AND α

Code	Ester	This study		Crossley and Koizumi[1]	
		τ_0/ps	α	τ_0/ps	α
1	Methyl acetate	—	—	—	—
2	Methyl hexanoate	3.9	0.13	4.1	0.08
3	Methyl octanoate	5.0	0.13	5.1	0.12
4	Methyl decanoate	5.0	0.17	6.0	0.11
5	Methyl hexadecanoate	6.5	0.20	6.3	0.19
6	Methyl octadecanoate	5.5	0.26	6.3	0.17
7	Methyl docosanoate	5.8	0.21	6.4	0.16
8	Methyl oleate	6.7	0.16	7.0	0.13
9	Ethyl acetate	2.7	0.12	2.8	0.09
10	Ethyl hexanoate	5.1	0.12	6.0	0.07
11	Ethyl octanoate	6.5	0.12	7.0	0.09
12	Ethyl dodecanoate	7.8	0.18	8.6	0.10
13	Ethyl octadecanoate	8.7	0.18	9.4	0.13
14	Ethyl linoleate	11.1	0.27	12.1	0.19
15	Ethyl lactate	13.2	0.16	13.7	0.16
16	Pentyl acetate	6.3	0.24	6.9	0.18
17	Diethyl tetradecanedioate	9.5	0.13	10.0	0.09

region of molecules with small molecular volumes. One finds that point 1 for methyl acetate is quite close to point 23 for furan.[8] Does this mean that methyl acetate should be considered to have a rigid planar configuration? We have strong evidence from microwave spectroscopy that methyl acetate[9] as well as methyl and ethyl formates[10,11] have plane configurations. Perhaps we can say that rotation of the methyl group around the C*–O bond is not completely free and that it does not dominate the dielectric relaxation. At least we cannot refute the view from our evidence that this C*–O bond is strongly hindered and hence the molecule has a planar configuration. On the other hand, point 9 (ethyl acetate) and 16 (amyl acetate) are on curve B. That is, their relaxation process is the intramolecular one. If the acetyl group cannot rotate around the C*–O bond, rotation of the acetoxy group around the O–C bond should occur instead. And the latter rotation is supposed to be the dominant mechanism for these molecules since the main dipole moment of the ester originates from the carbonyl group.

TABLE 3. CODE NUMBERS OF THE RIGID MOLECULES

Code	Molecule	Code	Molecule
21	Acetone[a]	22	Chloroform[a]
23	Furan[b]	24	Chlorobenzene[a]
25	Bromobenzene[a]	26	Nitrobenzene[c]
27	*p*-Chlorotoluene[d]	28	*m*-Chlorotoluene[d]
29	*p*-Bromotoluene[d]	30	1-Bromonaphthalene[e]
31	1-Chloronaphthalene[f]	32	9-Bromophenanthrene[c]
33	*N*-Methylaniline[f]	34	*N*,*N*-Dimethylaniline[f]
35	*N*,*N*-Diethylaniline	36	*o*-Dichlorobenzene[d]
37	Tetralin[g]	38	*N*-Methylpyrrole[h]
39	Nitrocyclohexane[i]		

a) J. Crossley, S. P. Tay, and S. Walker, *Adv. Mol. Relax. Proc.*, **6**, 69 (1974). b) Ref. 8. c) O. Kiyohara and K. Higasi, *Bull. Res. Inst. Appl. Elect.*, **18**, 123 (1966). d) S. W. Tucker and S. Walker, *Can. J. Chem.*, **47**, 681 (1969). e) G. D. Martin and S. Walker, *Can. J. Chem.*, **50**, 707 (1972). f) S. W. Tucker and S. Walker, *J. Chem. Phys.*, **52**, 2547 (1970). g) J. Crossley, W. F. Hassell, and S. Walker, *J. Chem. Phys.*, **48**, 1261 (1968). h) S. W. Tucker and S. Walker, *Trans. Faraday Soc.*, **62**, 2690 (1966). i) Ref. 6.

Lastly attention must be paid to the fact that point 15 for ethyl lactate is on the curve A between points

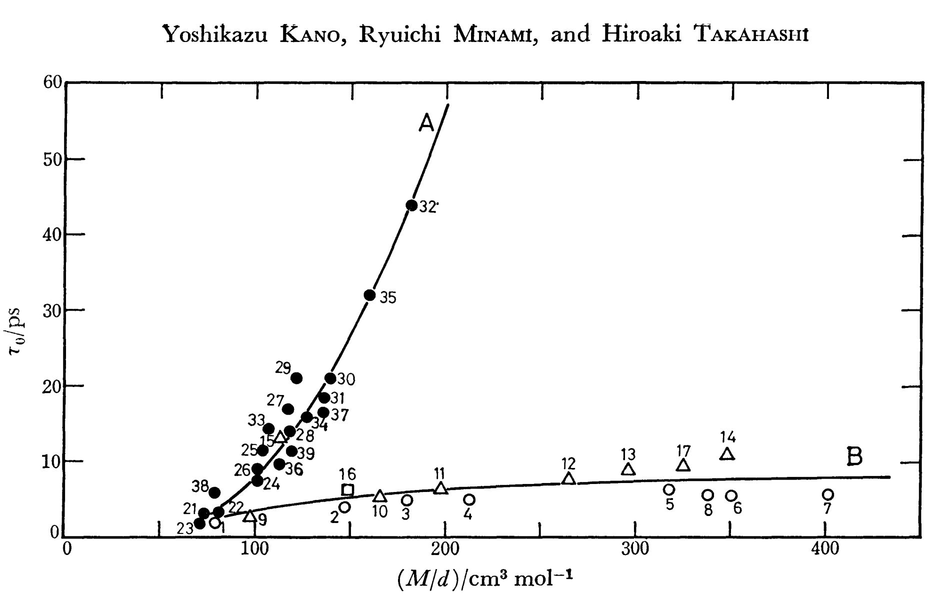
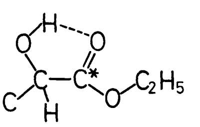


Fig. 1. Plot of relaxation time τ_0 in cyclohexane solution at 25 °C against the molecular volume: Code 1—17 aliphatic esters; 21—39 rigid molecules. M/d of esters 5, 7, and 17 are estimated values.

○: Methyl ester, △: ethyl ester, □: amyl ester, ●: rigid molecule.

Code: 1—17 see Table 2 and 21—39 Table 3.

25 (bromobenzene) and 28 (*m*-chlorotoluene) or between points 33 (*N*-methylaniline) and 39 (nitrocyclohexane). Planar configuration appears to be stabilized on account of formation of an intramolecular hydrogen bond in ethyl lactate.[12] Here, rotation of the groups around the central C–C* bond is hindered by the hydrogen-bond formation, and rotation of the ethoxyl group around the C*–O bond is also hindered on account of its partial double bond character. This phenomenon seems to be very important in understanding the nature of dielectric relaxation of flexible aliphatic esters.



In conclusion, it should be pointed out that dielectric relaxation of aliphatic esters is largely dominated by intramolecular rotation around the C–C bonds and/or the O–C bond rather than that around the C*–O bond.

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