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Dielectric Relaxation and Molecular Structure. II Dielectric Relaxation in Dibutyl Ether, Diphenyl Ether and Benzophenone in Various Nonpolar Solvents

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Measurements of dielectric constant and loss have been made at 1 Mc and 9.44 GHz for dibutyl ether and benzophenone in various solvents, *e.g.*, *n*-heptane, benzene, cyclohexane, carbon tetrachloride, decalin and Nujol. Whereas, diphenyl ether has only been studied in benzene and cyclohexane. The values of relaxation time and distribution parameter have been determined by using Cole-Cole's equation in terms of the so-called slopes, a_0, a', a'' and a_∞. The relaxation time values show a regular increase with the increase in viscosity of the medium both for dibutyl ether and benzophenone. The observations seem to suggest that dibutyl ether relaxes both by molecular and intramolecular mechanisms. The dipole moments in various solvents have also been calculated.

Several workers[1-6] have reported their findings about relaxation times for diphenyl ether and benzophenone and much has been said particularly about the anomalous behavior of the former.[7-10] However, no such data on relaxation study seems to be available for dibutyl ether. A study of this molecule may provide some information about the relaxation mechanism of aliphatic ethers in contrast to aromatic ones.

Experimental

Dibutyl ether, diphenyl ether and benzophenone (all of pure grade specifications) were imported from Dr. Theodor Schuchardt, West Germany, and were used without purification. The values of density, viscosity and refractive index for dibutyl and diphenyl ethers tallied[11] with their literature values. Melting point of benzophenone (48.0°C) agreed well with its literature value (48.1°C). All the solvents were purified by the processes described in our previous communication[12] which gives the measured values of their physical constants along with their literature values.

The dielectric constant, loss (at 1 Mc and 9.44 GHz) and refractive index measurements were made as per method already discussed.[12] All the measurements were made at 25°C. The accuracy in dielectric constant (at 1 Mc) is ±0.5%, in ε' and ε'' (at 9.44 GHz) 0.5 to 1% and 2 to 4%, respectively. The values of ε, ε', ε'' and n_D^2 were found to be linearly dependent upon weight fraction (w_2) for all the systems. The values of "the so-called slopes" a_0, a', a'' and a_D were determined and are presented in Table 1.

Method of Calculations. It has been shown by Higasi[13] that Cole-Cole[14] equation can be represented in terms of a_0, a', a'' and a_∞ which would take the form

$$a' - ja'' = a_\infty + \frac{a_0 - a_\infty}{1 + (j\omega\tau)^{1-\alpha}} \tag{1}$$

where τ is the most probable relaxation time and α is the distribution parameter. τ and α can be calculated from the measurements of a' and a'' at a single frequency[13,15] and their values are obtained from Eq. (1) in the manner given below:

$$\tau = \frac{1}{\omega}\left(\frac{A^2 + B^2}{C^2}\right)^{1/2(1-\alpha)} \tag{2}$$

and

$$1 - \alpha = \frac{2}{\pi}\tan^{-1}\frac{A}{B} \tag{3}$$

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1) J. Schneider, *J. Chem. Phys.*, **32**, 665 (1960).
2) F. Hufnagel, *Z. Naturforsch.*, **15a**, 723 (1960).
3) F. Hufnagel, G. Klages and P. Knoblock, *ibid.*, **17a**, 96 (1962).
4) W. E. Vaughan and C. P. Smyth, *J. Phys. Chem.*, **65**, 98 (1961).
5) W. E. Vaughan, W. S. Lovell and C. P. Smyth, *J. Chem. Phys.*, **36**, 535 (1962).
6) K. Chitoku and K. Higasi, This Bulletin, **36**, 1064 (1963).
7) D. M. Roberti, O. F. Kalman and C. P. Smyth, *J. Amer. Chem. Soc.*, **82**, 3523 (1960).
8) K. Higasi and C. P. Smyth, *ibid.*, **82**, 4759 (1960).
9) F. K. Fong, *J. Chem. Phys.*, **40**, 132 (1964).
10) K. Higasi, "Dipole, Molecule and Chemistry," Monograph series of the Research Institute of Applied Electricity, No. 13 (1965).
11) K. K. Srivastava, *J. Phys. Chem.*, **74**, 152 (1970).
12) K. K. Srivastava and J. K. Vij, This Bulletin, **43**, 2307 (1970).
13) K. Higasi, This Bulletin, **39**, 2157 (1966).
14) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).
15) G. L. Clark, *ibid.*, **25**, 125 (1956).

Table I. Values of a_0 (slope of ε *vs.* concn. curve), a' (slope of ε' *vs.* concn. curve), a''(slope of ε'' *vs.* concn. curve) and a_D (slope of n_D^2 *vs.* concn. curve)

	Medium	a_0	a'	a''	a_D
		Diphenyl ether			
1	Benzene	1.13_3	1.09	0.18	0.218
2	Cyclohexane	1.11	1.04	0.20	0.310
		Dibutyl ether			
1	*n*-Heptane	—	0.70_6	0.32	+0.02
2	Benzene	0.80	0.52	0.34	−0.357
3	Cyclohexane	1.02	0.68	0.40	−0.103
4	Carbon tetrachloride	1.75	1.07_5	0.90	−0.300
5	Decalin	1.16	0.64	0.47	−0.254
6	Nujol	0.96	0.42	0.36	−0.350
		Benzophenone			
1	*n*-Heptane	4.60	2.58	2.06	0.415
2	Benzene	5.90	2.47	2.42	0.281
3	Cyclohexane	4.78	2.10	2.54	0.374
4	Decalin	5.68	1.35	2.12	0.328
5	Nujol	5.62	0.78	0.85	0.270

where

$$A = a''(a_0 - a_\infty)$$
$$B = (a_0 - a')(a' - a_\infty) - a''^2$$
$$C = (a' - a_\infty)^2 + a''^2$$

The values of a_∞ are assumed to be approximately equal to a_D. This will not introduce much error in view of the inaccuracies involved in the measurements of a_0, a' and a''. Though this method has not been used by many workers, yet the authors feel that it would give reasonably accurate values of relaxation time for rigid molecules and the average values for molecular and intramolecular rotations in non-rigid molecules, depending upon their relative contributions to the overall relaxation process. The values of τ and α thus calculated are given in Table 2 along with the values of the dipole moment calculated by the method described earlier.[16]

Table 2. Values of relaxation time, distribution parameter and dipole moment for diphenyl ether, benzophenone and dibutyl ether

Solvent	τ(p.sec)	α	μ(D)
	Diphenyl ether		
Benzene	3.4	0.02	1.19
Cyclohexane	4.4	0.04	1.17
	Benzephenone		
n-Heptane	16.8	0.01	3.22
Benzene	20.1	~0	3.09
Cyclohexane	20.5	~0	3.04
Decalin	34.6	~0	3.05
Nujol	135.0	0.23	3.02
	Dibutyl ether		
Benzene	6.5	0.20	1.13
Cyclohexane	9.3	0.14	1.27
Carbon tetrachloride	11.4	0.04	0.98
Decalin	11.2	0.22	1.31
Nujol	14.2	0.40	1.25

Discussion

a) Diphenyl Ether. Values of relaxation time for diphenyl ether are 3.4 ps and 4.4 ps in benzene and cyclohexane respectively. The former compares favourably well with the literature values of 4.1[1] ps at 25°C and 4.0[3] ps at 20°C. The relaxation time for liquid diphenyl ether is 5.0 ps/30°C,[11] again in fair agreement with the value 5.1 ps/30°C as reported by Calderwood and Smyth.[17] Values of distribution parameter in both the solvents are nearly equal to zero which indicates one type of relaxation mechanism to be predominant.

The reason for a lesser value of τ for diphenyl ether as compared to a similar molecule (benzophenone) has been attributed to the internal rotations of the phenyl groups.[8] The possible mechanism responsible for giving lesser value of relaxation time is the mesomeric shift of charge due to changes in the interaction between the π-electrons in the phenyl rings and the unshared pairs on the oxygen as a function of ring twisting with respect to the C–O–C plane. However, Nelson and Smyth,[18] in a study of molecules similar in structure to diphenyl ether, seem to support Fong's[9] hypothesis that "double or coupled internal rotations, resembling a rowing motion with one oar feathered are

16) J. K. Vij and K. K. Srivastava, *Indian J. Pure Appl. Phys.*, **7**, 391 (1969).
17) J. H. Calderwood and C. P. Smyth, *J. Amer. Chem. Soc.*, **78**, 1295 (1956).
18) R. D. Nelson, Jr., and C. P. Smyth, *J. Phys. Chem.*, **69**, 1006 (1965).

Table 3. Relaxation times of benzophenone

Solvent	Present work		Literature	
	η(c.p.)	τ(ps)	η(c.p.)	τ(ps)
n-Heptane	0.408	16.8	—	—
Benzene	0.600	20.1	—	20.4/23°C[a)] 20.4/25°C[b)] 22/19°C[c)]
Cyclohexane	0.878	20.5	—	τ_1=27/20°C[d)] τ_2=3.5/20°C[d)]
Decalin	2.208	34.6	—	—
Nujol	147.6	135.0	137.8 197.0	238.0/25°C[b)] 295.0/19°C[e)]

a) E. Fisher, *Z. Naturforsch.*, **4a**, 707 (1949).
b) Ref. 6.
c) D.H. Whiffen and H.W. Thompson, *Trans. Faraday Soc.*, **42a**, 114 (1946).
d) Ref. 22.
e) Ref. 21.

responsible for the rapid relaxation mechanism". In the latter hypothesis, a fixed volume is always swept in rotation and it becomes difficult, on the basis of Debye's[19] concept of a rotating sphere in the viscous fluid characterized by its ordinary viscosity, to explain why the ratio of the rotating volume of diphenyl ether to benzophenone becomes only 2% in Nujol in comparison to 22% in benzene.[20] Indeed, some sort of internal rotation is definitely responsible for the rapid relaxation mechanism.

b) Benzophenone. Relaxation times for benzophenone along with the literature values (if available) are given in Table 3.

The value of 20.1 ps in benzene agrees fairly well with that of 20.4 ps/25°C determined by Chitoku and Higasi[6] from their study at low frequencies. However, a great disagreement appears in the case of Nujol. We found the τ value to be 135.0 ps as against 238.0 ps/25°C reported by Chitoku and Higasi.[6] and 295.0 ps/19°C reported by Jackson and Powels.[21] The reason for the large difference between the present and the literature values is perhaps due to the wide difference in frequencies at which the measurements have been carried out. Chitoku and Higasi determined the value from a study at low frequencies (~few Mc.) in which internal rotations may not have been taken into account.[6] The present value corresponds to the microwave frequency which accounts for both rotations, *i.e.*, molecular as well as intramolecular. The lesser value therefore indicates that the contributing factor of the rapid relaxation mechanism becomes predominant to the observed complex dielectric constant in the microwave range, which is obviously expected. This is further indicated by a comparatively higher value of distribution parameter (0.23) obtained in this solvent. Moreover, the existence of both processes is clearly established from the study of liquid benzophenone by Vaughan and Smyth[4,5] and from a recent study by Farmer and Walker[22] in cyclohexane. The values of τ_1 and τ_2 determined by the latter workers are also inserted in Table 3. It is interesting to note that the values of 3.0 ps[4,5] for liquid benzophenone and 3.5 ps for benzophenone in cyclohexane are nearly the same irrespective of the differences in the values of viscosity coefficients of the two media. The viscosity coefficent for liquid benzophenone is

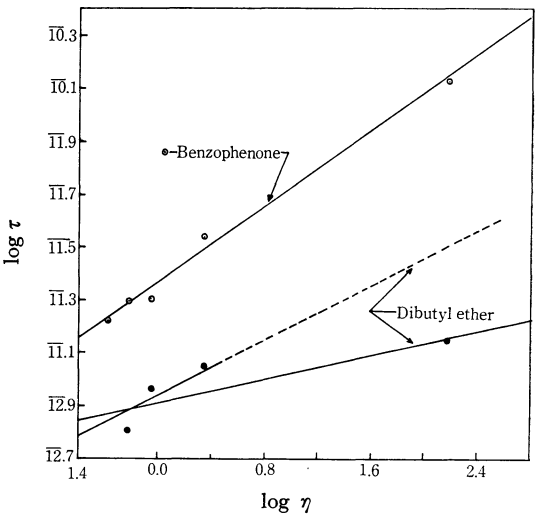

Fig. 1. Dependence of log τ upon log η.

19) P. Debye, *Trans. Faraday Soc.*, **30**, 679 (1934).
20) Ref. 10, p. 22.
21) W. Jackson and J. G. Powels, *Trans. Faraday Soc.*, **42a**, 101 (1946).
22) D. Farmer and S. Walker, *Tetrahedron*, **22**, 111 (1966).

4.19 c.p. whereas that of cyclohexane is 0.88 c.p. This suggests that the nature of rapid relaxation mechanism in this molecule is essentially the same as that of diphenyl ether. However, its contribution to the overall rotation is only about 6% in comparison to 74% for the diphenyl ether.[4,5]

The plot of log τ *vs.* log η gives a fairly reasonable linear curve and the value of x compares well with the value 0.46.[6] This confirms the viewpoint that semi-empirical equation[6] ($\tau=A\eta^x$) may replace Debye's formula[19] for a rigid sphere in a viscous fluid in which the coefficient of internal friction was taken to be the macroscopic measurable viscosity η. A systematic study of the coefficients A and X may provide a better insight into (i) the relaxation mechanism and (ii) internal rotations *vs.* overall rotations.

c) Dibutyl Ether. The relaxation time in benzene has been found to be 6.5 ps, whereas, for liquid dibutyl ether, the value (molecular relaxation time) is 5.0 ps/30°C as found by Srivastava.[11] Viscosity of dibutyl ether at 30°C is 0.58 c.p. which is almost the same as that of benzene (0.569 c.p.) A small difference between relaxation times hardly indicates any observable difference involved between the two systems.

Values of τ for this molecule, in solvents of low viscosity, show a usual trend. Ratio of relaxation times in carbon tetrachloride and cyclohexane is 1.23 as against their viscosity ratio of 1.03. This trend, possibly, is due to sticky nature[23,24] of carbon tetrachloride. Relaxation time in Nujol (having the largest viscosity coefficient) does not seem to be in accordance with its viscosity, if the molecules were considered to be of rigid structure. High value of α (0.40) in Nujol is interesting. Also a plot of log τ *vs.* log η hardly shows any trend towards linearity (see Fig. 1). This suggests intramolecular relaxation mechanism in dibutyl ether. The presence of internal rotation in the alkyl chains can also decrease the dependence of the relaxation time on the viscosity.

Considering the molecular volumes of dibutyl ether and benzophenone, one finds that these have similar values of 170.9 and 170.0 cc, but the relaxation times of these molecules in benzene are 6.5 ps and 20.1 ps respectively. This is possibly due to the reason that aliphatic groups (in comparison to phenyl groups) sweep lesser area of the solvent molecules while relaxing. This is further clear when we compare the relaxation time of this molecule with that of dipropyl ketone which has a similar molecular structure and nearly the same molecular volume (140 cc). The latter has the value of τ 5.4 ps in benzene at room temperature which compares well with that of dibutyl ether.[25]

The authors are grateful to Professor H. S. Hans, Head, Department of Physics and Professor V. B. Bhanot for their interest in the work and for providing the facilities.

23) K. Higasi, "Dielectric Relaxation and Molecular Structure," Monograph Series of the Research Institute of Applied Electricity, No. 9 (1961), p. 4.

24) K. Chitoku and K. Higasi, This Bulletin, **39**, 2160 (1966).

25) A. Vyas and H. N. Srivastava, *J. Sci. and Ind. Res.*, 399 (1959).