[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY]

Microwave Absorption and Molecular Structure in Liquids. XXIX. Dielectric Relaxation and Group Rotation in Some Aromatic Methoxy Compounds[1,2]

BY DOMINIC M. ROBERTI[3] AND CHARLES P. SMYTH

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The effect on dielectric relaxation of rotation of the methoxy group has been studied by a series of measurements on anisole, *o*-dimethoxybenzene, *m*-dimethoxybenzene, *p*-dimethoxybenzene, 1-methoxynaphthalene, 2-methoxynaphthalene and *p*-chloroanisole. Comparison of these values with those for the analogs, where a methyl group has been substituted for each methoxy group, shows that the presence of a methoxy group causes a lowering of the relaxation time below the expected value. Two distinct dispersion regions were indicated for *o*-dimethoxybenzene, as might be expected for a molecular rotation and a methoxy group rotation. The value for 1-methoxynaphthalene is higher than that for 2-methoxynaphthalene because of the hindrance to rotation of the methoxy group of the 1-isomer by the hydrogen on the 8-carbon. Mutual viscosities have been determined for benzene solutions of *o*-dimethoxybenzene, *p*-dimethoxybenzene, 1-methoxynaphthalene, 2-methoxynaphthalene, *p*-chloroanisole and 1-nitronaphthalene. Reduced relaxation times of the liquids have been compared with the solution values reduced by the solvent viscosity and by the mutual viscosity.

Dielectric Measurements

If a molecule contains a polar group which is able to rotate independently of the rest of the molecule, this rotation constitutes an alternative mode of orientation. There are then relaxation times corresponding to rotation of the whole molecule and to rotation of the polar group. Usually these relaxation times are seen as a broadening of the absorption peak and a lowering of the apparent most probable relaxation time below that expected for a comparable rigid molecule. Davies and Meakins[4,5] recently have noted instances of clearly separate dispersion regions. An indication of the same type of behavior had been previously obtained by Cole and Davidson[6] in alcohols at low temperatures.

In this study the dielectric relaxation times and losses are given for a series of compounds in which rotation of methoxy groups might be expected to lower the observed relaxation time.

Purification of Materials.—The substances were obtained from Brothers Chemical Company (B), or the Eastman Kodak Company (E), and were purified as noted in Table I. Boiling points, melting points and refractive indices are also given. The sample of 1-nitronaphthalene was obtained from Dr. R. W. Rampolla[7] and is identical with that used in his study.

Experimental Results.—The dielectric constants, ϵ', and losses, ϵ'', at 1.25, 3.22 and 10.0 cm. wave length and the static dielectric constant, ϵ_0, are listed in Table II, along with the densities and viscosities. In the case of *o*-dimethoxybenzene, it was possible to obtain measurements also at 0.312 cm. through the coöperation of Dr. R. W. Rampolla.

From the dielectric constant data Cole–Cole arc plots were drawn and used to determine the dielectric relaxation times, τ_M. Table III contains the values of the high-frequency or optical dielectric constants, ϵ_∞, the distribution parameters, α, the molecular relaxation times, τ_μ, which were obtained by applying the Powles internal field correction,[8] and the dipole moments, μ, calculated by the Onsager equation. Table IV contains the slopes a_0, a' and a'' for the dependence of dielectric constants and losses upon the mole fraction of *p*-dimethoxybenzene in benzene, whose dielectric constant, ϵ_1, is also listed. The relaxation times, as obtained by drawing arc plots of a' *vs.* a'', are listed in Table V.

Discussion of Results.—In order to compare the relaxation times of a series of liquids, it is necessary to correct for differences in viscosity. To this end, Table VI presents values of the reduced relaxation times, τ_μ/η, in which the molecular relaxation times have been divided by the macroscopic viscosity to give a quantity which should depend only on molecular size. The molar volumes, V, are also listed.

In parallel columns of Table VI are listed the reduced relaxation times and molar volumes of a previously measured[7,9] series of hydrocarbons. In this series, the methoxy groups of the compounds in the first column have been replaced by methyl groups. While the methyl groups may be capable of intramolecular rotation, they cannot cause dipole orientation by doing so, since the axis of rotation is along the dipole moment. They are used, therefore, as "rigid" molecules against which to compare the non-rigid molecules of similar size from the first column. Since they are slightly smaller than the non-rigid molecules, their relaxation times should be slightly shorter, in the absence of other effects. The hydrocarbon comparable to *p*-dimethoxybenzene, *p*-xylene, is non-polar and does not exhibit a relaxation time.

Anisole, with a slightly larger molar volume than toluene, shows a somewhat smaller reduced relaxation time. The same relationship is seen in comparing *m*-dimethoxybenzene and *m*-xylene. The lowered relaxation times of the methoxy compounds are evidence of some contribution to orientation by rotation of the methoxy groups. The major contribution seems to be from molecular rotation, however.

Both *p*-dimethoxybenzene and *p*-chloroanisole in comparison to *p*-chlorotoluene, show lowered reduced relaxation times. With *p*-chloroanisole, the lowering is very slight, however. The large fixed dipole moment of this compound puts greater emphasis on molecular rotation and reduces the effect of orientation by group rotation. In *p*-dimethoxybenzene, however, the entire moment

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(2) This paper represents a part of the work submitted by D. M. Roberti to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Gulf Oil Fellow in Chemistry, 1957–1958.

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(5) R. J. Meakins, *Trans. Faraday Soc.*, **54**, 1160 (1958).

(6) D. W. Davidson and R. H. Cole, *J. Chem. Phys.*, **19**, 1484 (1951); also R. H. Cole and D. W. Davidson, *ibid.*, **20**, 1389 (1952).

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TABLE I

PURIFICATION OF MATERIALS

	Source	Method of purif.	B.p., °C.	M.p., °C.	n^{20}_D
Anisole	B	[a]	153.0–153.5		1.51731
o-Dimethoxybenzene	E	[a]	208.5–208.7		1.53232(25°)
m-Dimethoxybenzene	B	[a]	212-213		1.52515
p-Dimethoxybenzene	B	[b]		55.2–55.7	
1-Methoxynaphthalene	E	[c]	268.4–268.5		
2-Methoxynaphthalene	E	[d]		73.0–73.6	
p-Chloroanisole	E	[c]	196.6		1.53465(22°)

[a] Fractionally distilled over barium oxide. [b] Fractionally distilled and dried in Abderhalden pistol. Fractionally distilled over calcium hydride. [d] Fractionally distilled, recrystallized from heptane and dried in Abderhalden pistol.

TABLE II

DENSITIES, VISCOSITIES, DIELECTRIC CONSTANTS AND LOSSES

				1.25		3.22		10.0 cm.	
t, °C.	d	η(c.p.s.)	ϵ_0	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
				Anisole					
20	0.9939	1.091	4.39	3.045	0.402	3.753	0.797	4.277	0.713
40	.9730	0.807	4.17	3.148	.274	3.801	.602	4.130	.734
60	.9495	0.626	3.99	3.246	.199	3.776	.492	3.976	.686
				o-Dimethoxybenzene[a]					
25	1.0819	3.281	4.09	3.419	0.449	3.674	0.317	3.874	0.218
40	1.0667	2.184	4.11	3.533	.482	3.787	.325		
60	1.0470	1.457	4.10	3.683	.455	3.908	.315		
				m-Dimethoxybenzene					
20	1.0684	2.54	5.46	3.036	0.577	3.503	1.06	4.754	1.21
40	1.0502	1.63	5.28	3.109	.717	3.811	1.10	4.898	0.900
60	1.0324	1.14	5.06	3.228	.867	4.118	1.05	4.954	0.658
				p-Dimethoxybenzene					
60	1.0343	2.75	5.53	3.790	1.30	4.901	1.05		
80	1.0155	2.67	5.14	3.944	1.21	4.889	0.757		
				1-Methoxynaphthalene					
20	1.0943	6.890	4.020	2.847	0.110	2.890	0.166		
40	1.0763	3.691	3.890	2.823	.114	2.897	.235		
60	1.0559	2.309	3.771	2.819	.152	2.921	.296		
				2-Methoxynaphthalene					
80	1.0327	1.498	3.587	2.891	0.298	3.134	0.374		
90.8	1.0207	1.280							
				p-Chloroanisole					
20	1.1721	1.675	7.84	2.955	0.761	3.430	1.42		
40	1.1499	1.193	7.39	3.007	0.835	3.737	1.72		
60	1.1244	0.900	6.87	3.093	1.08	3.976	1.76		

[a] Measurements at 0.312 cm. at 25° gave $\epsilon' = 2.96$, $\epsilon'' = 0.41$.

is resident in the rotating groups. As a result, molecular rotation would be expected to play little part in orientation, and it is found experimentally that the reduced relaxation time is much smaller than would be expected for its size, indicating the great contribution of the polar groups.

Since 2-methoxynaphthalene is a solid at 60°, the reduced relaxation time is given for 80°. The value for 2-methylnaphthalene is extrapolated to 80° from data at lower temperatures. In comparing the reduced relaxation times, one can conclude that there is a large contribution to orientation by the methoxy group, more than is the case with anisole. The reason is probably that, while the group relaxation time remains the same, the relaxation time for molecular rotation is larger for 2-methoxynaphthalene than for anisole and so the lowering effect of the group is more noticeable in the former. When the comparison is made between 1-methoxynaphthalene and 1-methylnaphthalene, however, it appears that there is no lowering. In marked contrast to the situation with 2-methoxynaphthalene, there is no contribution to orientation by rotation of the methoxy group. From an inspection of the Stuart–Briegleb models of the two methoxynaphthalene isomers, one can see clearly that the methoxy group can rotate freely in 2-methoxynaphthalene, whereas, in 1-methoxynaphthalene, it is blocked by the hydrogen atom on the 8-carbon. This restriction to rotation is reflected in the high relaxation time.

The situation with *o*-dimethoxybenzene is much more complex. It was impossible to draw a single Cole–Cole arc through the points. Instead, the data were represented by two arcs,[6] a high frequency Debye-type arc and a low frequency arc

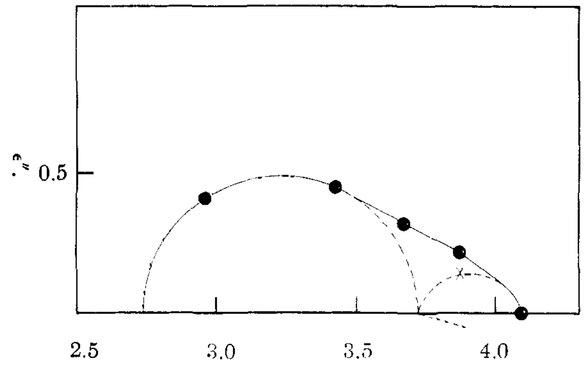

Fig. 1.—Plot of dielectric loss against dielectric constant for *o*-dimethoxybenzene at 25°.

with distribution. In Fig. 1, the solid line gives the locus of the experimental points, while the broken lines show the two arcs by which the data can be represented. For the 10 cm. point, the circle is the experimental point and the cross is the point obtained by subtracting the contribution due to the high frequency relaxation.[6] While it must be understood that there are not enough points for an accurate analysis of this kind, it is interesting to calculate approximate relaxation times for each arc. Table III shows the high frequency relaxation time as 0.37 × 10^{-11} sec., while the low frequency value is 6.9 × 10^{-11} sec. There seems to be no meaning in calculating a molecular relaxation time for a rotating group and so this calculation was not made for the high frequency arc. For the low frequency arc a molecular relaxation time was calculated, as well as the reduced relaxation time shown in Table VI.

TABLE III

HIGH FREQUENCY DIELECTRIC CONSTANTS, DISTRIBUTION PARAMETERS, RELAXATION TIMES AND DIPOLE MOMENTS

t, °C.	ϵ_∞	α	τ_M (× 10^{11})	τ_μ (× 10^{11})	μ (× 10^{18})
		Anisole			
20	2.60	0.05	1.23	1.06	1.08
40	2.58	.04	0.88	0.77	1.05
60	2.55	.02	0.69	0.61	1.06
		o-Dimethoxybenzene			
25	2.73	0	0.37		0.99
	3.72	0.13	6.9	6.2	
		m-Dimethoxybenzene			
20	2.82	0.06	3.12	2.62	1.35
40	2.80	.05	2.15	1.81	1.35
60	2.76	.05	1.57	1.34	1.34
		p-Dimethoxybenzene			
60	2.75	0.04	0.86	0.71	1.45
80	2.67	0.00	0.58	0.49	1.48
		1-Methoxynaphthalene			
20	2.84	0.13	14.0	12.7	0.97
40	2.81	.09	7.8	7.0	.97
60	2.78	.06	4.7	4.3	.98
		2-Methoxynaphthalene			
80	2.74	0	1.47	1.35	0.95
		p-Chloroanisole			
20	2.80	0.01	4.8	3.7	1.74
40	2.80	0.01	3.5	2.8	1.74
60	2.80	0	2.5	2.1	1.72

TABLE IV

SLOPES (a) FOR DEPENDENCE OF DIELECTRIC CONSTANT AND LOSS ON MOLE FRACTION OF *p*-DIMETHOXYBENZENE IN BENZENE

			1.25		3.22	
t, °C.	ϵ_1	a_0	a'	a''	a'	a''
20	2.2836	4.41	2.34	1.47	3.61	1.27
40	2.2436	4.06	2.68	1.41	3.93	0.92
60	2.2036	3.72	2.92	1.16	3.42	0.72

TABLE V

SLOPES (a_∞) OF HIGH FREQUENCY DIELECTRIC CONSTANT *vs.* MOLE FRACTION, DISTRIBUTION PARAMETERS AND RELAXATION TIMES OF *p*-DIMETHOXYBENZENE IN BENZENE

t, °C.	a_∞	α	τ (× 10^{11} sec.)
20	1.37	0	0.97
40	1.25	0	.64
60	1.12	0	.46

Because of limitations of the 3 mm. apparatus, it was impossible to obtain measurements at this frequency at higher temperatures. Since the 3 mm. point was essential in order to draw Cole–Cole arcs for this compound, the calculation of relaxation times for higher temperatures was impossible. For calculation of dipole moments, however, it is necessary to know only ϵ_0, which was measured over a temperature range, and ϵ_∞, which was estimated from the measured value at 25° and the temperature dependence of ϵ_∞, assumed to be the same as for *m*-dimethoxybenzene. These calculations showed values for the dipole moment of 0.99, 1.04 and 1.08 at 25°, 40° and 60°, respectively. The variation of dipole moment with structure was previously known[10] and is explained by assuming that the methoxy groups hinder one another as they rotate and that the hindrance is increasingly overcome with increasing temperature. This hindrance to rotation easily can be seen by inspecting the molecular model.

It is not clear why group rotation gives merely a lowering of the observed relaxation time in the other cases and results in two separate dispersion regions in the case of *o*-dimethoxybenzene. As evidenced by the above discussion of its dipole moment, *o*-dimethoxybenzene is an unusual molecule. Because of steric hindrance to rotation, each methoxy group influences the rotation of the other. Perhaps, their rotation becomes partly a coöperative motion, becoming similar to an oscillation about an equilibrium configuration. Such an oscillation would be expected to be different from the essentially free rotation shown by the other molecules of this series. In any event, it should be interesting to study the temperature dependence of the two relaxation times of *o*-dimethoxybenzene when suitable apparatus becomes available.

In Table VI the larger reduced relaxation time of *o*-dimethoxybenzene, corresponding to molecular rotation, may be compared with that for *o*-xylene.

(10) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, p. 373.

TABLE VI

REDUCED RELAXATION TIMES AND MOLAR VOLUMES AT 60°

	$\tau\mu/\eta$	V (cc.)		$\tau\mu/\eta$	V (cc.)
Anisole	0.97	114	Toluene	1.06	111
m-Dimethoxybenzene	1.18	134	*m*-Xylene	1.27	128
p-Dimethoxybenzene	0.64	134			
p-Chloroanisole	2.28	127	*p*-Chlorotoluene	2.32	123
1-Methoxynaphthalene	1.86	150	1-Methylnaphthalene	1.70	144
2-Methoxynaphthalene (80°)	0.90	153	2-Methylnaphthalene (80°)	1.84	145
o-Dimethoxybenzene (25°)	1.9	128	*o*-Xylene (20°)	0.98	121

In view of the approximate nature of the former value, the agreement may be considered satisfactory. The smaller relaxation time, 0.37, compares well with the estimate of 0.4 given by Fischer[11] for the relaxation time of the methoxy group. While Fischer's value is for solutions in benzene, the group relaxation time should be much less affected by the viscosity of the medium than the molecular relaxation time. Using the intercepts of the two arcs drawn in Fig. 1 as values of ϵ_0 and ϵ_∞, two approximate dipole moment values were calculated by means of the Onsager equation. The moment from the higher frequency region was found to be 0.86, while that from the lower frequency region was 0.45, not far from the approximate value, 0.32, calculated for the fixed moment of the molecule from the values of the bond moments.[12]

From the temperature dependence of the relaxation times and of the viscosities, activation energies have been calculated for dielectric relaxation, ΔH_ϵ, and for viscous flow, ΔH_v. These values are given in Table VII. The value $\Delta H_v - \Delta H_\epsilon$ is small and positive, as is usually found, except for *p*-dimethoxybenzene, which is uncertain because only two points are available for the calculation of ΔH_ϵ.

TABLE VII

ACTIVATION ENERGIES

	ΔH_ϵ (kcal.)	ΔH_v (kcal.)
Anisole	2.3	2.7
o-Dimethoxybenzene	. .	4.4
m-Dimethoxybenzene	2.7	3.2
p-Dimethoxybenzene	(3.9)	3.3
1-Methoxynaphthalene	4.7	5.2
2-Methoxynaphthalene	. .	4.0
p-Chloroanisole	2.5	3.1

Mutual Viscosity

In comparing relaxation times of liquids with those obtained for solutions in non-polar solvents, suitable corrections must be made for the internal field and for the viscosity of the surrounding medium. The internal field correction, which compensates for dipole–dipole interaction as it affects rotation, need be applied only to the pure liquid. Miller and Smyth[13] showed that the most nearly adequate form of this correction is that of Powles.[3] To reduce liquid and solution to a common viscosity, it has been usual to divide the liquid relaxation time by the liquid viscosity and compare the result with the solution relaxation time divided by the viscosity of the pure solvent. This latter quantity is not a satisfactory basis for comparison. In dilute solutions, the macroscopic viscosity emphasizes solvent–solvent interaction, whereas the relaxation process is concerned almost exclusively with solute–solvent interaction. In this study, the mutual viscosity described by Hill[14] is used instead of pure solvent viscosity to compare liquid and solution relaxation times.

Experimental Results.—The viscosities of dilute solutions were measured in an Ostwald–Fenske–Cannon[15] viscometer using a single viscometer for all determinations to assure internal consistency of results. The densities of the solutions were measured in an Ostwald–Sprengel type pycnometer.[16] Within the experimental error, the viscosities of the solutions were linear with the mole fraction of solute, x_2. The slopes, $d\eta_{12}/dx_2$, are given in Table VIII.

TABLE VIII

SLOPE OF SOLUTION VISCOSITY *vs.* MOLE FRACTION OF SOLUTE AND MUTUAL VISCOSITY COEFFICIENTS IN BENZENE

	$d\eta_{12}/dx_2$			η_m		
	20°	40°	60°	20°	40°	60°
o-Dimethoxybenzene	1.211	0.798	0.523	1.179	0.842	0.630
p-Dimethoxybenzene	2.353	1.707	1.289	1.104	.802	.606
1-Methoxynaphthalene	2.972	2.125	1.593	1.367	.978	.732
2-Methoxynaphthalene	1.699	1.268	0.962	1.378	1.036	.803
p-Chloroanisole	0.711	0.541	.418	0.956	0.728	.556
1-Nitronaphthalene	1.717	1.261	.919	1.403	1.046	.794

The concept of mutual viscosity was developed by Hill[1] according to the relation

$$n_{12} = x_1{}^2\eta_1\sigma_1/\sigma_{12} + 2x_1x_2\eta_m\sigma_m/\sigma_{12} + x_2{}^2n_2\sigma_2/\sigma_{12}$$

The quantities η are the respective viscosities in a mixture of mole fractions x_1 and x_2, and the σ values represent average intermolecular distances. These may be obtained from

$$\sigma_1 = (M_1/d_1N)^{1/3}$$

$$\sigma_2 = (M_2/d_2N)^{1/3}$$

$$\sigma_{12} = [(x_1M_1 + x_2M_2)/d_{12}N]^{1/3}$$

$$\sigma_m = (\sigma_1 + \sigma_2)/2$$

where M is the molecular weight, d is the density and N is the Avogadro number. The mutual viscosity is η_m.

The Hill relation may be put into an approximate form[17]

$$\eta_m = \sigma_1(d\eta_{12}/dx_2 + 2\eta_1)/2\sigma_m$$

This form of the equation is especially useful in dealing with solid solutes, since the viscosity of the pure solute does not appear. The mutual viscosities listed in Table VIII were calculated by means of this approximate equation.

As an experimental check on the validity of the approximate equation, mutual viscosities were calculated at three temperatures for *o*-dimethoxybenzene by the exact equation. Comparison with the values obtained from the approximate equation, as shown in Table IX, indicates that for *o*-dimethoxybenzene the approximate equation is valid within about 2%.

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(11) E. Fischer, *Z. Naturforsch.*, **4A**, 707 (1949).

(12) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, p. 244.

(13) R. C. Miller and C. P. Smyth, THIS JOURNAL, **79**, 3310 (1957).

(14) N. E. Hill, *Proc. Phys. Soc.* (*London*), **67B**, 149 (1954).

(15) M. R. Cannon and M. R. Fenske, *Ind. Eng. Chem.*, *Anal. Ed.*, **10**, 297 (1938).

(16) G. R. Robertson, *ibid.*, **11**, 464 (1939).

(17) D. A. Pitt and C. P. Smyth, THIS JOURNAL, **81**, 783 (1959).

TABLE IX

MUTUAL VISCOSITIES FOR *o*-DIMETHOXYBENZENE IN BENZENE

t, °C.	Approx. eq.	Exact eq.
20	1.179	1.154
40	0.842	0.838
60	0.630	0.643

TABLE X

COMPARISON OF REDUCED RELAXATION TIMES

t, °C.	τ_μ/η	τ/η_m	$\tau/\eta_{solv.}$
	p-Dimethoxybenzene		
20		0.88	1.48
40		.80	1.30
60	0.64	.77	1.17
80	0.58		
	1-Methoxynaphthalene		
20	1.84		
22		1.80	3.78
40	1.91		
60	1.86		
	2-Methoxynaphthalene		
22		1.12	2.37
80	0.90		
	p-Chloroanisole		
20	2.21		
22		1.76	2.57
40	2.31		
60	2.28		
	1-Nitronaphthalene		
20		1.62	3.50
40		1.60	3.37
60	1.41	1.64	3.30

Discussion of Results.—In Table X are presented a series of reduced relaxation times for comparison. The second column, τ_μ/η, gives the ratios of the corrected relaxation times to the macroscopic viscosities. These are the results of the measurements described in the first part of this paper.

The third and fourth columns represent values obtained from measurements of dilute solutions. The values for *p*-dimethoxybenzene are taken from the data presented in the first part of this paper. The values for 1-methoxynaphthalene, 2-methoxynaphthalene and *p*-chloroanisole were calculated from dielectric data obtained by Bergmann.[18] The data for 1-nitronaphthalene are taken from the measurements of Rampolla.[7]

In the third column, the mutual viscosity is used to obtain the reduced relaxation times. In the fourth column, the viscosity of the pure solvent is used to obtain the reduced relaxation time, as is commonly done. For *p*-dimethoxybenzene and 1-methoxynaphthalene, it is evident that the use of the mutual viscosity is much to be preferred. For 2-methoxynaphthalene, the comparison must be made at two widely different temperatures but it is still clear that the mutual viscosity is preferable. In the case of *p*-chloroanisole, it would appear that neither solution value agrees well with the pure liquid value. For 1-nitronaphthalene, while using the mutual viscosity gives only fair agreement, it is much better than is obtained using pure solvent viscosity.

It is notable that the two compounds for which poorest agreement is seen between liquid and solution reduced relaxation times are both highly polar and require a large internal field correction. It is probable that the disagreement merely reflects the approximate nature of the internal field correction.

It should be pointed out that for molecules which can orient by intramolecular motion, dividing by the mutual viscosity constitutes an over-correction. The reason is that mutual viscosity relates to solvent–solute molecule interaction but the solvent-rotating group interaction is less. On the other hand, dividing the pure liquid relaxation time by the macroscopic viscosity gives the same type of over-correction. If we make the reasonable assumption that both the solution and the liquid values are over-corrected to the same extent, the two values remain comparable.

The use of mutual viscosity to calculate reduced relaxation times of polar molecules measured in solution facilitates the comparison of measurements made in different solvents and in pure liquids. It is, however, only an approximation, which has been found inapplicable in the case of a solvent of high viscosity. There also seems to be a possibility of evaluating the internal field correction more exactly by comparing measurements made on liquids with those made in solution, assuming the mutual viscosity to be the correct reducing factor.

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[18] K. Bergmann, Doctoral Dissertation, Albert-Ludwigs-Universität, Freiburg, Germany.