The Influence of Molecular Shape upon Dielectric Relaxation Times.

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Measurements are recorded of the relaxation times τ at infinite dilution of 32 different solutes, including methyl, *tert.*-butyl, phenyl, diphenylyl, and naphthyl derivatives. Carbon tetrachloride is the solvent most frequently concerned. Correlations between τ and a number of properties of the solute are mentioned; the relationship of τ with mean polarisability multiplied by a " shape factor " is illustrated graphically.

As is well known, Debye's original formula (1) only very roughly forecasts the

$$\tau = 4\pi\eta r^3/kT \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

relaxation time τ of a molecule from the radius r and a coefficient of inner friction η. Practical attention has been given much more to the dependence of τ on η than to τ on r (cf. " Dielectrics," *Trans. Faraday Soc.*, 1946, **42**, *A*, for references and details). However, the model assumed for the derivation of (1), *viz.*, a spherical polar molecule in a homogeneous uniform medium, is obviously too simple. Perrin (*J. Physique*, 1934, **5**, 497) considered an ellipsoid to be a better approximation to reality and replaced r^3 by products of appropriate half-axes; the idea has been further elaborated by Budo, Fischer, and Miyamoto (*Physikal. Z.*, 1939, **40**, 337). For another problem (cf. Barclay and Le Fèvre, *J.*, 1950, 556; Holland and Le Fèvre, *J.*, 1950, 2166; Angyal, Barclay, and Le Fèvre, *J.*, 1950, 3370; Buckingham and Le Fèvre, *J.*, 1952, 1932), the degrees by which molecules depart from spherical symmetry have been represented by " shape factors." It seemed possible that these might be introduced in an empirical amendment or altern- ative to (1). Accordingly, a preliminary survey has been made of the values of τ of about 30 different species, selected to have extensions along or across the directions of their resultant dipole moments.

EXPERIMENTAL

Measurements have been made on solutions in carbon tetrachloride or benzene, the majority in the former. Power from an oscillator (incorporating a reflex Klystron, type CV-35), operating at 3109 Mc., was fed to an E_{010} cavity resonator. This was made from 4″-diameter brass rod, its depth being 4·5 cm. and internal radius 3·56 cm. It was fitted with a brass lid through the centre of which was a guide-hole (diameter 0·8 cm.). All surfaces were silver- plated. Half-way down the wall were two diametrically opposed holes through which were inserted two silver-plated " magnetic " probes, each fixed in orientation by a counter-sunk screw adjustable from the top of the resonator when the lid (itself held by six screws) was removed. The energy from the oscillator to the resonator and that from the resonator to the detector was controlled by small rotations of the probe loops. The solution to be examined, in a silica tube, stood vertically through the guide-hole in the centre of the resonator lid. Power was taken from the resonator to a detector consisting of a silicon–tungsten rectifier (Sylvania Electric Co.) in series with a galvanometer. The frequency was progressively increased from below to above that for resonance, and the current–frequency curve recorded. As the width of this curve at

half-height, i.e., Δf, was 1—2 Mc., a beat method was employed to obtain Δf: power from the above oscillator was fed into a mixer with power from a similar oscillator adjusted to give a beat frequency within the range 13·5—18·5 Mc. The frequency of the main oscillator was adjusted to the two half-height frequencies in turn, and the beat frequencies were measured. Their difference gave Δf. Since the detector crystal on calibration had been found to follow the " square law," the Q factor of the circuit was $f_{\text{resonance}}/\Delta f$; Q was determined successively for the pure solvent and for the solutions. The incremental loss tangent, $\Delta \tan \delta$, was $A(1/Q_2 - 1/Q_1)$, where suffix 1 refers to the solvent, 2 to the solute, 12 to the solution, and A is a constant determined by the properties of the resonator.

The computation of τ has been based on the following argument, starting with Debye's equation (2) :

$$\Delta \tan \delta = \frac{(\varepsilon_{12} + 2)^2}{\varepsilon_{12}} \cdot \frac{2\pi f \tau}{(1 + 4\pi^2 f^2 \tau^2)} \cdot \frac{4\pi \mu^2 N c_2}{27kT} \quad . \quad . \quad . \quad (2)$$

in which c_2 is measured in moles of solute per c.c. and other symbols have their usual meanings. Since solutions have been made up by weight, concentrations are conveniently given as weight fractions of solute, w_2. Appropriate transformation of c_2 into w_2 allows (2) to be rewritten as (3) :

$$\Delta \tan \delta = (\varepsilon_{12} + 2)^2 w_2 d_{12} K / \varepsilon_{12} M_2 \quad . \quad . \quad . \quad . \quad (3)$$

where $K = 8\pi^2 f \mu^2 N \tau / 27kT(1 + 4\pi^2 f^2 \tau^2)$ and M_2 is the molecular weight of the solute. It is not necessary to know the dielectric constants and densities of the mixtures used. At the dilutions used in this work ε_{12} and d_{12} may be each taken as rectilinear with w_2. Insertion of $\varepsilon_{12} = \varepsilon_1(1 + \alpha w_2)$ and $d_{12} = d_1(1 + \beta w_2)$ into (3), and differentiation with respect to w_2, etc., gives

$$[d(\Delta \tan \delta)/dw_2]_{w_2=0} = Kd_1(\varepsilon_1 + 2)^2/M_2\varepsilon_1 \quad . \quad . \quad . \quad . \quad (4)$$

The left-hand side of (4) can be obtained from experiment (either by calculating the " line of best fit " of $\Delta \tan \delta$ against w_2, or as the mean $\Sigma(\Delta \tan \delta)/\Sigma w_2$); calling it ψ, we have ultimately (since f is always ca. $3\cdot109 \times 10^9$ cycles/sec.) :

$$\tau = \frac{5\cdot1993 \times 10^{28} D \mu^2}{M_2 T \psi} \pm \left[\frac{2\cdot7032 \times 10^{57} D^2 \mu^4}{M_2{}^2 T^2 \psi^2} - 2\cdot6204 \times 10^{-21} \right]^{\frac{1}{2}} \quad . \quad . \quad (5)$$

D in (5) is $d_1(\varepsilon_1 + 2)^2/\varepsilon_1$; around room temperature it has the following values for the two solvents now used :

T, °K	ε	d	D	T, °K	ε	d	D
	Carbon tetrachloride				*Benzene*		
295	2·2323	1·5900	12·758	295	2·2784	0·8770	7·046
293	2·2360	1·5940	12·792	293	2·2825	0·8791	7·063₅
291	2·2398	1·5979	12·824	291	2·2866	0·8812	7·081
289	2·2435	1·6019	12·857	289	2·2905	0·8834	7·100
288	2·2454	1·6039	12·874	288	2·2925	0·8844	7·108

The various solutes had the m. p.s or b. p.s recorded for pure specimens in Beilstein's " Handbuch." Methyl chloride and bromide were prepared and dissolved as indicated respectively by Barclay and Le Fèvre (*loc. cit.*) and Buckingham and Le Fèvre (*J.*, 1953, 3432).

Essential observations are recorded in Table 1; sub-headings give. in order, solute, solvent, and temperature. The variations in Q for $w_2 = 0$ shown in Table 1 are due to the fact that the value of Q of the resonator system seemed to be dependent upon the state of polish of the internal surfaces of the cavity : Q was greatest immediately after silvering and decreased with age. Measurements were not taken chronologically in the order shown. However, the value of $\Delta \tan \delta$, derived from the differences of the values of $1/Q$ for a given solution and its solvent, is independent of the actual magnitude of $1/Q_1$, since $1/Q_{12}$ and $1/Q_1$ are equally affected.

Results, calculated by eqn. (5), are set out in Table 2. Experience, gained by repetitions and redeterminations at different dates, suggests that the smaller relaxation times (τ) may vary by about $\pm15\%$ and the larger (those over 10×10^{-12} sec.) by $\pm10\%$; these ranges are indicated by the diameters of the circles surrounding the points on the Figure.

Three of these solute–solvent systems have been examined by other authors, who report values of τ not differing seriously from those now found (see Table 3).

TABLE 1. *Dependence of incremental* tan δ *on concentration.*

Methyl chloride, carbon tetrachloride, 20°

$10^5 w_2$	Δf (Mc.)	$10^1/Q_{12}$	$10^3(\Delta \tan \delta)$
0	0·71	2·28	—
922	1·17	3·76	1·83
971	1·18	3·80	1·87
1184	1·28	4·12	2·27

Methyl bromide, carbon tetrachloride, 22°

$10^5 w_2$	Δf (Mc.)	$10^1/Q_{12}$	$10^3(\Delta \tan \delta)$
0	1·28	4·12	—
370	1·34	4·31	0·236
494	1·36	4·37	0·310
864	1·52	4·89	0·955
0	0·94	3·02	—
859	1·11	3·57	0·682
0	0·91	2·93	—
1866	1·28	4·12	1·48

Methyl iodide, carbon tetrachloride, 22°

$10^5 w_2$	Δf (Mc.)	$10^1/Q_{12}$	$10^3(\Delta \tan \delta)$
0	0·94	2·99	—
5970	1·82	5·85	3·55
8930	2·24	7·20	5·23

Nitromethane, carbon tetrachloride, 22°

$10^5 w_2$	Δf (Mc.)	$10^1/Q_{12}$	$10^3(\Delta \tan \delta)$
0	0·77	2·48	—
187	1·17	3·76	1·59
236	1·27	4·08	1·98

Acetonitrile, carbon tetrachloride, 22°

$10^5 w_2$	Δf (Mc.)	$10^1/Q_{12}$	$10^3(\Delta \tan \delta)$
0	1·26	4·05	—
366	2·48	7·98	4·87
485	2·90	9·33	6·55

Toluene, carbon tetrachloride, 22°

$10^5 w_2$	Δf (Mc.)	$10^1/Q_{12}$	$10^3(\Delta \tan \delta)$
0	0·82	2·64	—
2883	0·93	2·99	0·43
4774	1·00	3·22	0·72
7205	1·09	3·51	1·08

Fluorobenzene, carbon tetrachloride, 14°

$10^5 w_2$	Δf (Mc.)	$10^1/Q_{12}$	$10^3(\Delta \tan \delta)$
0	1·16	3·73	—
1156	1·74	5·60	2·32
1458	1·90	6·11	2·95
1602	2·00	6·43	3·35
1729	2·09	6·72	3·71
1853	2·04	6·56	3·51

Chlorobenzene, carbon tetrachloride, 14°

$10^5 w_2$	Δf (Mc.)	$10^1/Q_{12}$	$10^3(\Delta \tan \delta)$
0	1·23	3·96	—
379	1·54	4·95	1·23
737	1·78	5·73	2·20
1493	2·51	8·07	5·10

Bromobenzene, carbon tetrachloride, 24°

$10^5 w_2$	Δf (Mc.)	$10^1/Q_{12}$	$10^3(\Delta \tan \delta)$
0	1·20	3·86	—
2131	2·70	8·68	5·98
4271	4·26	13·70	12·20

Iodobenzene, carbon tetrachloride, 14°

$10^5 w_2$	Δf (Mc.)	$10^1/Q_{12}$	$10^3(\Delta \tan \delta)$
0	1·18	3·80	—
988	1·69	5·44	2·04
0	1·30	4·18	—
1497	2·22	7·14	3·67
1806	2·33	7·50	4·12

Benzonitrile, carbon tetrachloride, 14°

$10^5 w_2$	Δf (Mc.)	$10^1/Q_{12}$	$10^3(\Delta \tan \delta)$
0	1·19	3·83	—
86	2·10	6·75	3·62
317	4·86	15·63	13·96
400	6·14	19·75	19·07
417	6·25	20·10	19·50
788	10·09	32·45	34·82
0	1·36	4·37	—
926	10·50	33·77	36·46

Nitrobenzene, benzene, 20°

$10^5 w_2$	Δf (Mc.)	$10^4/Q_{12}$	$10^3(\Delta \tan \delta)$
0	2·02 *	6·50 *	—
145	2·34 *	7·53 *	1·67
290	2·61 *	8·39 *	3·06
1344	5·39 *	17·33 *	17·54
0	1·10	3·54	—
292	2·11	6·79	4·03
553	2·86	9·20	7·02
721	3·45	11·10	9·37

o-Xylene, carbon tetrachloride, 14°

$10^5 w_2$	Δf (Mc.)	$10^4/Q_{12}$	$10^3(\Delta \tan \delta)$
0	1·13	3·63	—
2465	1·39	4·47	1·04
8097	2·01	6·47	3·52
8299	1·97	6·34	3·36

m-Xylene, carbon tetrachloride, 14°

$10^5 w_2$	Δf (Mc.)	$10^4/Q_{12}$	$10^3(\Delta \tan \delta)$
0	1·29	4·15	—
9839	1·56	5·02	1·08
9970	1·57	5·05	1·12
16,138	1·81	5·82	2·07
18,980	1·83	5·89	2·16

4-Chlorodiphenyl, benzene, 20°

$10^5 w_2$	Δf (Mc.)	$10^4/Q_{12}$	$10^3(\Delta \tan \delta)$
0	1·16	3·73	—
666	1·57	5·05	1·64
1657	2·25	7·24	4·35
0	1·14	3·67	—
614	1·54	4·95	1·59

4-Nitrodiphenyl, benzene, 22°

$10^5 w_2$	Δf (Mc.)	$10^4/Q_{12}$	$10^3(\Delta \tan \delta)$
0	1·07	3·44	—
272	2·32	7·47	5·05
369	2·89	9·30	7·26
0	1·02	3·28	—
257	2·29	7·37	5·07
317	2·59	8·33	6·26

α-Nitronaphthalene, carbon tetrachloride, 20°

$10^5 w_2$	Δf (Mc.)	$10^4/Q_{12}$	$10^3(\Delta \tan \delta)$
0	1·22	3·92	—
116	1·95	6·27	2·91
0	1·25	4·02	—
217	2·62	8·43	5·47

α-Nitronaphthalene, benzene, 15°

$10^5 w_2$	Δf (Mc.)	$10^4/Q_{12}$	$10^3(\Delta \tan \delta)$
0	1·22	3·93	—
68	1·42$_5$	4·58	0·81
225	1·95	6·27	2·90
320	2·24	7·22	4·08

p-Chloronitrobenzene, carbon tetrachloride, 20°

$10^5 w_2$	Δf (Mc.)	$10^4/Q_{12}$	$10^3(\Delta \tan \delta)$
0	1·23	3·96	—
418	2·72	8·75	5·94
433	2·74	8·81	6·02

p-Nitrotoluene, benzene, 22°

$10^5 w_2$	Δf (Mc.)	$10^4/Q_{12}$	$10^3(\Delta \tan \delta)$
0	0·95	3·06	—
147	1·80	5·78	3·37
0	1·15	3·70	—
231	2·50	8·04	5·38

tert.-Butyl chloride, carbon tetrachloride, 24°

$10^5 w_2$	Δf (Mc.)	$10^4/Q_{12}$	$10^3(\Delta \tan \delta)$
0	0·81	2·61	—
670	1·22	3·92	1·64
1020	1·50	4·83	2·75
1483	1·80	5·79	3·95
2067	2·12	6·82	5·23
2394	2·33	7·49	6·06

* The quartz tube in these observations was different from that used for all the others now reported.

TABLE 1. (*Continued.*)

$10^5 w_2$	Δf (Mc.)	$10^4/Q_{12}$	$10^3 (\Delta \tan \delta)$	$10^5 w_2$	Δf (Mc.)	$10^4/Q_{12}$	$10^3 (\Delta \tan \delta)$
tert.-Butyl bromide, carbon tetrachloride, 20°				α-*Bromonaphthalene, carbon tetrachloride,* 12°			
0	1·01	3·25	—	0	1·06	3·41	—
570	1·34	4·31	1·31	737	1·65	5·31	2·36
1957	2·12	6·82	4·43	981	1·81	5·82	2·99
tert.-Butyl iodide, carbon tetrachloride, 20°				β-*Bromonaphthalene, carbon tetrachloride,* 14°			
0	0·78	2·51	—	0	1·27	4·08	—
567	1·07	3·44	1·16	172	1·43	4·60	0·65
1734	1·62	5·21	3·35	305	1·55	4·99	0·77
2048	1·90	6·11	4·47	0	1·16	3·73	—
2651	2·20	7·08	5·66	311	1·45	4·66	1·15
α-*Fluoronaphthalene, carbon tetrachloride,* 14°				α-*Iodonaphthalene, carbon tetrachloride,* 12°			
0	1·10	3·54	—	0	1·03	3·31	—
561	1·58	5·08	1·91	1161	1·71	5·50	2·72
1728	1·93	6·21	3·31	0	1·06	3·40	—
β-*Fluoronaphthalene, carbon tetrachloride,* 15°				1595	2·00	6·43	3·76
				0	1·15	3·70	—
0	1·14	3·67	—	2338	2·51	8·07	5·42
747	1·89	6·08	2·99				
1413	2·54	8·17	5·58	β-*Iodonaphthalene, carbon tetrachloride,* 12°			
α-*Chloronaphthalene, carbon tetrachloride,* 20°				0	1·06	3·40	—
0	1·10	3·54	—	276	1·27	4·08	0·84
271	1·33	4·28	0·92	706	1·58	5·08	2·08
1724	2·60	8·36	5·98	*Camphor, benzene,* 15°			
2005	2·79	8·97	6·73	0	1·11	3·57	—
				1201	2·66	8·56	6·19
β-*Chloronaphthalene, carbon tetrachloride,* 12°				0	1·19	3·83	—
0	1·05	3·38	—	1768	3·58	11·52	9·53
322	1·46	4·70	1·64	2203	4·06	13·07	11·46
634	1·84	5·92	3·15				

TABLE 2. *Calculation of relaxation times.*

Solute	ψ	Temp.	M_2	μ, D	$10^{12}\tau$, sec.	Solute	ψ	Temp.	M_2	μ, D	$10^{12}\tau$, sec.
CH_3Cl	0·192	22°	50·5	1·79	1·8	1-$C_{10}H_7 \cdot NO_2$	2·52	20°	173	3·88	19
CH_3Br	0·082	20	94·9₅	1·70	1·8	,,	1·28	15	173	3·88	17 *
CH_3I	0·059	22	142	1·48	2·5	*p*-$ClC_6H_4 \cdot NO_2$	1·40	20	157	2·6	25
$CH_3 \cdot NO_2$	0·84	22	61	3·14	3·1	*p*-$CH_3 \cdot C_6H_4 \cdot NO_2$	2·31	22	137	4·44	19 *
$CH_3 \cdot CN$	1·35	22	41	3·38	2·8	CMe_3Cl	0·253	24	92·5	2·14	3·0
$C_6H_5 \cdot CH_3$	0·015	22	92	0·35	6·7	CMe_3Br	0·226	20	137	2·19	3·7₅
C_6H_5F	0·203	14	96·5	1·44	5·4	CMe_3I	0·214	20	184	2·14	5·0
C_6H_5Cl	0·33	14	112·6	1·58	8·6	α-$C_{10}H_7F$	0·30	14	146	1·35	15
C_6H_5Br	0·285	24	157	1·51	12	β- ,,	0·40	15	146	1·43	18
C_6H_5I	0·23	14	204	1·39	15	α-$C_{10}H_7Cl$	0·34	14	163	1·42	18
$C_6H_5 \cdot CN$	4·25	14	103	4·02	17	β- ,,	0·50	12	163	1·62	20
$C_6H_5 \cdot NO_2$	1·30	20	123	3·95	11 *	α-$C_{10}H_7Br$	0·31	12	207	1·41	21
o-Xylene	0·041	14	106	0·53	9·0	β- ,,	0·37	14	207	1·55	21
m-Xylene	0·012	14	106	0·26	11	α-$C_{10}H_7I$	0·232	12	254	1·32	23·5
4-$C_6H_4Ph \cdot Cl$	0·26	20	189	1·56	32 *	β- ,,	0·30	12	254	1·42	27
4-$C_6H_4Ph \cdot NO_2$	1·97	22	199	4·17	35 *	Camphor	0·52	15	152	2·94	9·7 *

* Determined in benzene.

TABLE 3. *Previous determinations relevant to Table 2.*

Solute	Solvent	$10^{12}\tau$, sec.	Source
CMe_3Cl	CCl_4	3·4	Curtis, McGeer, Rathmann, and Smyth, *J. Amer. Chem. Soc.*, 1952, **74**, 644
Camphor	C_6H_6	9·5	Whiffen, *Trans. Faraday Soc.*, 1950, **46**, 130
$C_6H_5 \cdot NO_2$	C_6H_6	12·0	Spengler, *Physikal. Z.*, 1941, **42**, 134
,,	,,	11·6	Jackson and Powles, *Trans. Faraday Soc.*, 1946, **42**, *A*, 106
,,	,,	13·0	Cripwell and Sutherland, *ibid.*, p. 151
,,	,,	11·5	Whiffen and Thomson, *ibid.*, p. 118
,,	,,	12·8	Whiffen, *loc. cit.*
,,	,,	12·7	Curtis *et al.*, *loc. cit.*

DISCUSSION

The results illustrate the general tendency for τ to increase with increasing molecular size or weight. Such behaviour has been noted before, particularly for certain homologous series (cf. Böttcher, " Theory of Dielectric Polarisation," Elsevier Publ. Co., 1952, Chap. 10, for references). Table 2, however, shows no smooth variation of τ with M_2. Since many of the solutes are solid at room temperature, the relation between τ and molar volume, taken as M_2/d_2, cannot be completely considered, although signs of a rough dependence may be seen for those compounds which are liquid. Various empirical and other properties of the substances listed have been plotted against τ; *e.g.*, the curve of parachor (P) versus τ included all the values of τ within a rather wide " corridor." This was of interest since parachors provide relative measures of molecular volumes and can be computed with fair accuracy from known atom and bond " constants " (the figures in parentheses in Table 4 were estimated in this way from Vogel's Table XXII of *J.*, 1948, 1833; the remainder are measurements given in Vogel's various papers). Neither the plot of the product ABC (see later) nor that of the quotient $\mu^2/3kT$ against τ was at all satisfactory; they were tried because they had the same order of magnitude (*viz.*, 10^{-24} c.c.) as has r^3 in equation (1). A graph of R_2 against τ was suggestive : it contained all points in a band no

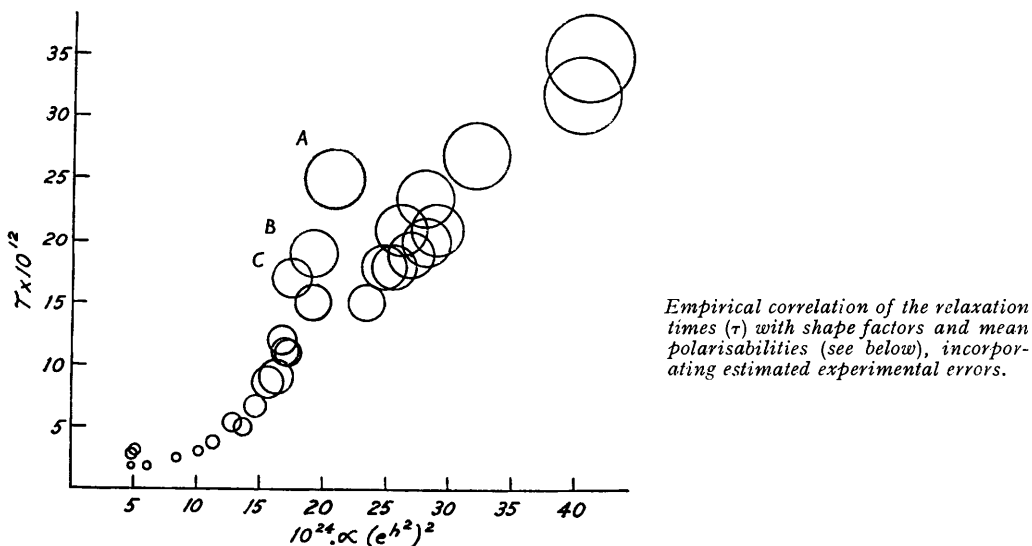TABLE 4. *Molecular dimensions, parachors, and refractivities.*

	A	B	C	P	R_D (c.c.)	$10^{24}\alpha_{mean}$	$10^3 h^2$
CH_3Cl	5·27	3·80	3·80	(111)	11·5	4·53	26·1
CH_3Br	5·54	3·80	3·80	(124)	14·5	5·71	35·1
CH_3I	5·92	3·80	3·80	(146)	19·4	7·64	49·2
$CH_3\cdot NO_2$	5·20	4·50	3·80	132	12·5	4·93	16·1
$CH_3\cdot CN$	5·95	3·80	3·80	122	11·1	4·37	50·4
$C_6H_5\cdot CH_3$	8·25	6·05	3·80	247	31·1	12·2$_5$	90·7
C_6H_5F	7·33	6·05	2·90	214	26·0	10·2	118
C_6H_5Cl	8·08	6·05	3·16	244·5	31·1	12·2$_5$	123
C_6H_5Br	8·20	6·05	3·40	261	33·9	13·4	111
C_6H_5I	8·58	6·05	3·64	282	39·1	15·4	110
$C_6H_5\cdot CN$	8·95	6·05	2·90	259	31·4	12·4	171·5
$C_6H_5\cdot NO_2$	8·00	6·05	2·90	264·5	32·7	12·9	138
o-Xylene	7·50	6·80	3·80	283	35·8	14·1	70·7$_5$
m-Xylene	6·80	8·70	3·80	284	35·9	14·1	98·3
$4\text{-}C_6H_5\cdot C_6H_4\cdot Cl$	12·40	6·05	3·16	(419)	57·8	22·8	287
$4\text{-}C_6H_5\cdot C_6H_4\cdot NO_2$	12·32	6·05	2·90	(435)	56·4	22·2	305
$1\text{-}C_{10}H_7\cdot NO_2$	8·00	8·70	2·90	(369)	50·0$_5$	19·7	156·5
p-$Cl\cdot C_6H_4\cdot NO_2$	9·41	6·05	3·16	(303)	37·5	14·8	169
p-$CH_3\cdot C_6H_4\cdot NO_2$	9·57	6·05	3·80	303	37·4	14·7	135
CMe_3Cl	6·80	6·88	6·88	(225)	25·8	10·2	0·0
CMe_3Br	7·05	6·88	6·88	(239)	28·9	11·4	0·1
CMe_3I	7·46	6·88	6·88	(260)	34·6	13·6	1·5
$\alpha\text{-}C_{10}H_7F$	7·34	8·70	2·90	321	43·7	17·2	154
$\beta\text{-}\quad,,$	9·79	7·30	2·90	(321)	43·7	17·2	183
$\alpha\text{-}C_{10}H_7Cl$	8·00	8·70	3·16	(350)	49·2	19·4	138
$\beta\text{-}\quad,,$	10·44	7·30	3·16	(350)	49·4	19·5	183
$\alpha\text{-}C_{10}H_7Br$	8·28	8·70	3·40	(363)	51·6	20·3	125
$\beta\text{-}\quad,,$	10·71	7·30	3·40	(363)	51·8	20·4	175
$\alpha\text{-}C_{10}H_7I$	8·60	8·70	3·64	(386)	56·5	22·3	114·5
$\beta\text{-}\quad,,$	11·02	7·30	3·64	(386)	57·9	22·8	169

wider than that of the parachor–τ plot, and placed related molecules (*e.g.*, fluoro-, chloro-, bromo-, and iodo-benzenes) on individual straight lines having different inclinations to the τ-axis.

When either parachors or refractivities were used, however, the three *tert.*-butyl halides stood on the lower fringe of the " corridor," as though their τ's were abnormally low. Now, the small relaxation times of certain molecules of a near-spherical form have been noted by several workers (*e.g.*, Smyth, *Trans. Faraday Soc.*, 1946, **42**, *A*, 175; Böttcher, *op. cit.*, Chap. 10); it seemed, therefore, that multiplication of the parachors or refractivities by " shape factors" would improve the curves in question.

The dimensions given in Table 4 have been used as a basis. Their derivations from scale-drawings, etc., are explained in the papers by Le Fèvre and his colleagues cited on

p. 2873. Of various ratios and combinations of A, B, and C, that denoted as h^2 by Holland and Le Fèvre (*J.*, 1950, 2166) seemed to be most suitable (numerical values of h^2 are quoted in Table 4).

Empirical correlation of the relaxation times (τ) with shape factors and mean polarisabilities (see below), incorporating estimated experimental errors.

The figure depicts the best relationship, *viz.*, $10^{12}\tau$ plotted against the product 10^{24} (α_{mean}) (exp h^2)^2, so far extracted from the present data. (The average polarisability (α_{mean}) is directly calculable from the molecular refraction R.) The closeness of the points makes provision of a key difficult; A, B, and C, which are most out-of-line, refer respectively to *p*-chloronitrobenzene in carbon tetrachloride, *p*-nitrotoluene in benzene, and benzonitrile in carbon tetrachloride. In addition to experimental errors, and to the use of non-uniform temperatures, its imperfections must be, in part, due to neglect of solvent effects. The work of, *inter al.*, Whiffen (*Trans. Faraday Soc.*, 1950, **46**, 130) indicates that a given medium will not influence the τ's of all molecules alike (*e.g.*, the relaxation times of nitrobenzene and camphor are slightly greater in carbon tetrachloride than in benzene; for chloroform the reverse is true). Hill (*Nature*, 1953, **171**, 836) has plotted τ against the " mutual viscosities " for solute–solvent pairs made by six solutes and three solvents; an approximation to a straight line through the origin resulted. However, the Figure embraces a wider range of relaxation times and a greater number of solutes than were considered by Hill; further, it appears to do so more smoothly.

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