

## Dielectric Relaxation Time, a Non-linear Function of Solvent Viscosity

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By extending the Debye and Wirtz treatments to the case where the frictional force opposing rotation of the molecule differs from that of the bulk liquid, the relaxation time ( $\tau$ ) is found to depend non-linearly upon the macroscopic viscosity ( $\eta$ ). The resulting expression is of the form  $\tau = \tau' \eta / (\eta + \eta')$ . When  $\eta \ll \eta'$  it reduces to a Debye-like equation but when  $\eta$  increases  $\tau$  does not increase in proportion but eventually approaches a constant value. Relaxation time data for a large number of solutions are found to conform to this relationship over the viscosity range 0.3 to 200 cP.

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Using a simple hydrodynamic model in which the molecule is regarded as a sphere rotating in a continuous viscous medium, Debye found <sup>1</sup> that the molecular relaxation time ( $\tau$ ) should be linearly dependent upon the viscosity ( $\eta$ ) of the medium. He went on to show that, in general, this is not true. Other workers have proposed modified relationships which fall broadly into two categories, those based upon a theoretical model and those which are purely empirical. Some of the empirical equations <sup>2</sup> are quite successful in predicting the magnitude of relaxation times under some conditions, but most of them retain the linear dependence of  $\tau$  upon  $\eta$  which is not obeyed in practice. Of the theoretical relationships, Hill's <sup>3</sup> is the most fundamental. Beginning with Andrade's theory of viscosity and extending it to the case of mixtures of liquids, she extracts a local viscosity effective between species at the molecular level. It is upon this "mutual viscosity" that the relaxation time depends.

Hill's theory satisfactorily explains the observed five-fold increase in relaxation time of chlorobenzene in liquid paraffin solutions compared with benzene solutions, whereas the Debye relationship predicts a 350-fold increase. Evaluation of the mutual viscosity, however, requires a good deal of information not yet readily available and therefore much additional work is needed. Approximations <sup>4</sup> to Hill's equations again reduced to linear relationships between  $\tau$  and  $\eta$ . Various expressions <sup>2</sup> predict that the ratio of microscopic to macroscopic viscosity should fall as the volume of the solvent molecule rises relative to that of the solute molecule, but of these only the Wirtz equation is well founded.<sup>5</sup> For solutes and solvents of similar molecular volume Wirtz's equation differs from Debye's equation only by a numerical factor. This gives a closer agreement with the magnitude of observed relaxation times and attributes the low relaxation time in viscous solvents to the difference in molecular size between solvent and solute. But the explanation of the unusually low values in liquid paraffin is unlikely to be simply a molecular volume effect, since the paraffin is not the rigid molecule required by theory but a mixture of flexible hydrocarbons, each segment of which is likely to behave like a much smaller molecule. Overall, macroscopic viscosity is discredited as a pointer to the behaviour of relaxation times.<sup>6</sup>

The object of this paper is to show that the macroscopic viscosity is still useful for predicting relaxation times providing that the non-linearity of the relationship is acknowledged.

### THE DEBYE APPROACH

That the molecular relaxation time depends upon macroscopic viscosity implies that dielectric relaxation involves regions of the liquid and not just rotation of single molecules. This argument,<sup>7</sup> seemed to be confirmed experimentally by Schallamach.<sup>8</sup> Under certain conditions, the separate relaxation regions of the components of a binary mixture of polar liquids coalesce into a single region, even when the separate relaxation times are sufficiently far apart to yield bimodal absorption. The tentative explanation is that the volume undergoing relaxation contains at least four, and perhaps many more molecules. When the relaxing region is sufficiently large that its composition is that of the bulk liquid, then a single absorption is obtained, otherwise separate relaxation peaks occur. Later work<sup>9</sup> contradicted Schallamach's conclusion, the loss curves of mixtures being separable into relaxation times characteristic of each individual molecule. Schallamach's results were attributed to the structure-making influence of the low temperatures he used. However, these two approaches are not mutually exclusive. A molecule trapped in a partially structured region of the liquid may lose its orientation by rotation of the whole region as well as by rotation of the individual molecule within the region. In each case resistance to rotation is provided by quasifrictional forces and, neglecting local fields, the externally applied field  $E$  may be taken to be that which acts upon the dipoles in the liquid. The orientations  $(\phi_i, \theta_i)$  of the molecules may be represented by points on a sphere, and the rate  $(J_\theta)$  at which the molecules pass through a unit length of an arbitrary latitude ( $\theta = \text{constant}$ ) of the sphere in the direction of increasing  $\theta$ , yields the rate of the reorientation of the dipoles under the joint influence of the Brownian movement and the applied field. If  $\theta$  is referred to the direction of the applied field, then  $J_\theta$  is given by

$$J_\theta = K \frac{\partial f}{\partial \theta} + f \bar{v}_\theta.$$

The first term represents the contribution of the diffusional process, the second that of the applied field,  $f(\theta, t)$  is the distribution function of points on the sphere and  $\bar{v}_\theta$  the mean terminal angular velocity of the points under the influence of the field.  $\bar{v}_\theta$  is obtained by equating the applied torque ( $M = -dU/d\theta$ ) with the resistive couple  $\xi \bar{v}_\theta$  (where  $\xi$  is the resistive constant). The value of  $K$  is then obtained as  $\tau = 1/\omega = \xi/2kT$ .

The difference in *this* treatment is that  $\bar{v}_\theta$  is generated by summing two relative velocities; that of the dipolar molecule with respect to its immediate surroundings  $(\bar{v}_\theta)_M$  and that of the structured surrounding region with respect to the bulk of the liquid  $(\bar{v}_\theta)_R$ . Neglecting any additional couples which might arise (unlikely in non-polar solvents), in the steady state the torques on the dipolar molecule and on the neighbouring region are equal so that

$$M = \xi_M (\bar{v}_\theta)_M = \xi_R (\bar{v}_\theta)_R$$

where  $\xi_M$  is the frictional constant of the molecule and  $\xi_R$  is that of the structured region. It follows that

$$\bar{v}_\theta = -M \left[ \frac{1}{\xi_M} + \frac{1}{\xi_R} \right],$$

an expression identical to that of Debye except that  $\xi = \xi_M \xi_R / (\xi_M + \xi_R)$ . Therefore we find

$$\tau = \frac{1}{2kT} \frac{\xi_M \xi_R}{\xi_M + \xi_R}. \quad (1)$$

The frictional constant between the structured region and the bulk liquid may be set equal to the Stokes value i.e.  $\xi_R = 8\pi a_R^3 \eta$  where  $\eta$  is the solvent viscosity and  $a_R$  is the radius of the structured region. An equivalent expression for  $\xi_M$  is not strictly valid but may be used to define a microscopic viscosity ( $\eta_M$ ) between the rotating molecule and its nearest neighbours,

$$\xi_M = 8\pi a_M^3 \eta_M.$$

Here  $a_M$  is the radius of the spherical molecule.

Using eqn (1) we can obtain

$$\tau = \frac{4\pi a_R^3 \eta'}{kT} \frac{\eta}{\eta + \eta'}. \quad (2)$$

$\eta' = (a_M^3 \eta_M) / a_R^3$  is a limiting viscosity. This expression is similar to Debye's but incorporates a non-linear viscosity term. It reduces to Debye's expression under conditions for which a hydrodynamic expression is expected to hold i.e. for a macroscopic particle rotating in an effectively continuous medium with no slipping. In such a case the particle and the adjacent layer of solvent move with the same angular velocity and therefore  $\eta_M$  is infinite. The structured region, consisting of the solvent layer adjacent to the particle, may be several solvent molecules thick but since the solvent molecules, for an effectively continuous medium, are very much smaller than the particle it follows that  $a_M \approx a_R$  and eqn (2) regenerates Debye's equation. More generally, the viscosity dependence of the relaxation time in eqn (2) depends upon the relative magnitudes of  $\eta$  and  $\eta'$ . When  $\eta \ll \eta'$  the relaxation time varies linearly with macroscopic viscosity

$$\tau(\eta/\eta' \rightarrow 0) = \frac{4\pi a_R^3 \eta}{kT}.$$

Conversely, when  $\eta \gg \eta'$  the relaxation time is independent of macroscopic viscosity

$$\tau(\eta/\eta' \rightarrow \infty) = \frac{4\pi a_M^3 \eta_M}{kT}.$$

Behaviour of this sort might be observed in highly viscous media such as Nujol and also in rotator phase solids.

#### INFLUENCE OF THE SOLVENT SIZE

The effect of the size of the solvent molecules may be included by a modification of the Wirtz approach.<sup>5</sup> The polar molecule is treated as a sphere of radius  $a_M$  rotating in a medium consisting of molecules of radius  $a_S$ . The zone surrounding the molecules consists of a series of concentric shells of solvent molecules, the thickness of each shell being the diameter of the solvent molecules. For the polar molecule rotating with average angular velocity  $\bar{v}_\theta$  the  $m$ th shell rotates with angular velocity  $(\bar{v}_\theta)_m$  with respect to the  $(m+1)$ th shell. In the steady state the angular velocity of the central molecule with respect to the bulk of the medium is the sum of the increments in angular velocity for each shell. Because of the discontinuous nature of the medium on this scale, the viscous drag  $F$  is not given by  $F = \eta_A (dv/dr)$  but by  $F_m = \eta_m A_m$

$(\Delta\bar{v}/\Delta r)_m$  where  $\Delta\bar{v}$  is the difference in linear velocity between adjacent layers. Consider an element at an angle  $\phi$  to the axis at the surface between the  $m$ th and  $(m+1)$ th layers. The interface is a sphere of radius  $r_m = r_0 + m\Delta r$  and the force acting on the element between  $\phi$  and  $(\phi + d\phi)$  is

$$dF_m = \eta_m(2\pi r_m^2 \sin \phi d\phi) r_m \sin \phi (\Delta\bar{v}_\theta)_m \Delta r^{-1}.$$

The couple acting on the interface is therefore

$$\begin{aligned} M_m &= (2\pi\eta_m r_m^4 (\Delta\bar{v}_\theta)_m \Delta r^{-1}) \int_0^\pi \sin \phi d\phi \\ &= 8\pi\eta_m r_m^4 (\Delta\bar{v}_\theta)_m \Delta r^{-1}. \end{aligned}$$

The angular velocity of the polar molecule is the sum of the velocity increments between shells

$$\bar{v}_\theta = \sum_{m=0}^{\infty} (\Delta\bar{v}_\theta)_m.$$

Using the fact that in the steady state the torque exerted on each of the shells is the same

$$\bar{v}_\theta = \frac{3M\Delta r}{8\pi} \sum_{m=0}^{\infty} \frac{1}{\eta_m r_m^4}$$

so that the resistive constant ( $\xi = M/\bar{v}_\theta$ ) is given by

$$\xi = \frac{8\pi}{3} \left( \sum_{m=0}^{\infty} \frac{\Delta r}{\eta_m r_m^4} \right)^{-1},$$

i.e.

$$\xi^{-1} = \frac{3}{8\pi} \left( \sum_{m=0}^{\infty} \frac{\Delta r}{\eta_m r_m^4} \right). \quad (3)$$

The assumption usually made here is that  $\eta_m = \eta$  (for all  $m$ ) enabling  $\eta$  to be removed from the summation. If, in addition,  $\Delta r$  is small relative to  $r_0$  then the summation may be replaced by an integral and the Stokes approximation for  $\xi$  is obtained. Or, if  $\Delta r$  is not small relative to  $r_0$ , the first term can be separated and by replacing the subsequent terms by an integral, eqn (3) yields the Wirtz equation. But when the assumption is made that  $\eta_0$  is different from  $\eta_1, \eta_2$ , etc. and that

$$\eta_m = \eta (m \neq 0)$$

then the zeroth term may be separated from the summation. Replacing the remaining term by an integral, we obtain

$$\begin{aligned} \xi^{-1} &= \frac{3}{8\pi} \left( \frac{\Delta r}{\eta_0 r_0^4} + \frac{1}{\eta} \int_{r_1}^{\infty} \frac{dr}{r^4} \right) \\ &= \frac{3}{8\pi} \left( \frac{\Delta r}{\eta_0 r_0^4} + \frac{1}{3\eta r_1^3} \right). \end{aligned}$$

Now  $\Delta r$  is the diameter of the solvent molecules ( $2a_s$ ),  $r_0$  is the radius of the polar molecule ( $a_M$ ) and  $r_1$  is to be identified with the radius ( $a_R$ ) of the structured region surrounding the polar molecule. Inserting the new symbols, using

$$\tau = \xi/2kT$$

and re-arranging gives

$$\tau = \frac{4\pi a_M^3 \eta_M}{kT} \frac{\eta}{\eta + \eta'} \quad (4)$$

with

$$\eta' = \eta_M(a_M/a_R)^3$$

and

$$\eta_M = \eta_0(a_M/6a_s).$$

The relationship is identical to eqn (2) with  $\eta_M$  more thoroughly defined. Eqn (4) is bivariate with respect to solvent, depending upon both  $\eta$  and the ratio  $a_M/a_s$ . (i) When  $a_s \ll a_M$  then  $\tau = 4\pi a_M^3 \eta / kT$ , i.e. Debye behaviour is obeyed. (ii) When  $a_s \gg a_M$  then  $\tau$  approaches zero, i.e. there are no frictional forces and the rate of rotation will be inertially controlled. (iii) When  $\eta \ll \eta'$  then  $\tau = 4\pi a_R^3 \eta / kT$ , i.e. the polar molecule is effectively held rigidly in the solvent cage for a time which is long relative to the relaxation time of the structured zone. (iv) When  $\eta \gg \eta'$  then  $\tau = 4\pi a_M^3 \eta_M / kT$ , i.e.  $\tau$  becomes independent of viscosity and assumes a value which depends upon the size of the solvent molecules. (v) Finally, when  $\eta_0 = \eta$  then  $\tau$  is given by

$$\tau = \frac{4\pi a_M^3 \eta}{kT} \left( \frac{6a_s}{a_M} + \left( \frac{a_M}{a_R} \right)^3 \right)^{-1}$$

and since  $a_R = a_M + 2a_s$  this is, of course, the Wirtz equation.

## RESULTS

The derived expressions, (2) and (4), are of the form

$$\tau = \tau' \eta / (\eta + \eta'). \quad (5)$$

For solvents in which there are no strong solute-solvent interactions  $\tau'$  and  $\eta'$  should not be strongly solvent dependent and eqn (5) can be recast as

$$\frac{1}{\tau} = \frac{\eta'}{\tau'} \frac{1}{\eta} + \frac{1}{\tau'}. \quad (6)$$

A graph of  $\tau^{-1}$  against  $\eta^{-1}$  should, therefore, be a straight line. The graph serves to test both the severity of the final assumption and the adequacy of the treatment.

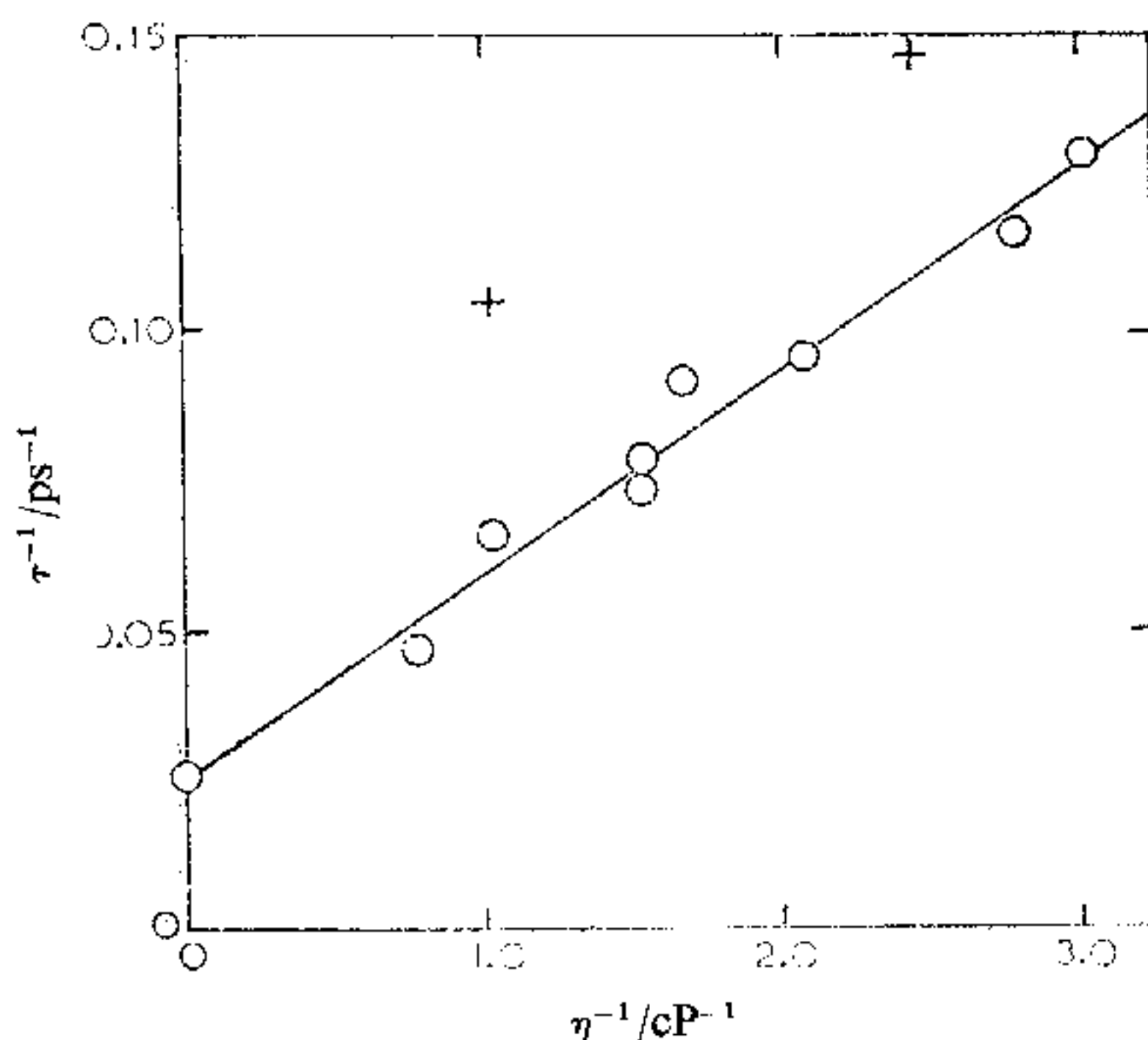


FIG. 1.—Plot of  $\tau^{-1}$  against  $\eta^{-1}$  for nitrobenzene in several solvents at 293 K.



In fig. 1 data for nitrobenzene <sup>2, 10</sup> in a series of solvents are plotted according to eqn (6). Fig. 2 shows a  $\tau$  against  $\eta$  plot for the nitrobenzene solutions. The solid curve is the theoretical curve corresponding to eqn (5) with  $\tau' = 39.2$  ps and  $\eta' = 1.34$  cP. Fig. 3 shows a  $\tau^{-1}$  against  $\eta^{-1}$  plot for some solutions of camphor.<sup>10</sup>

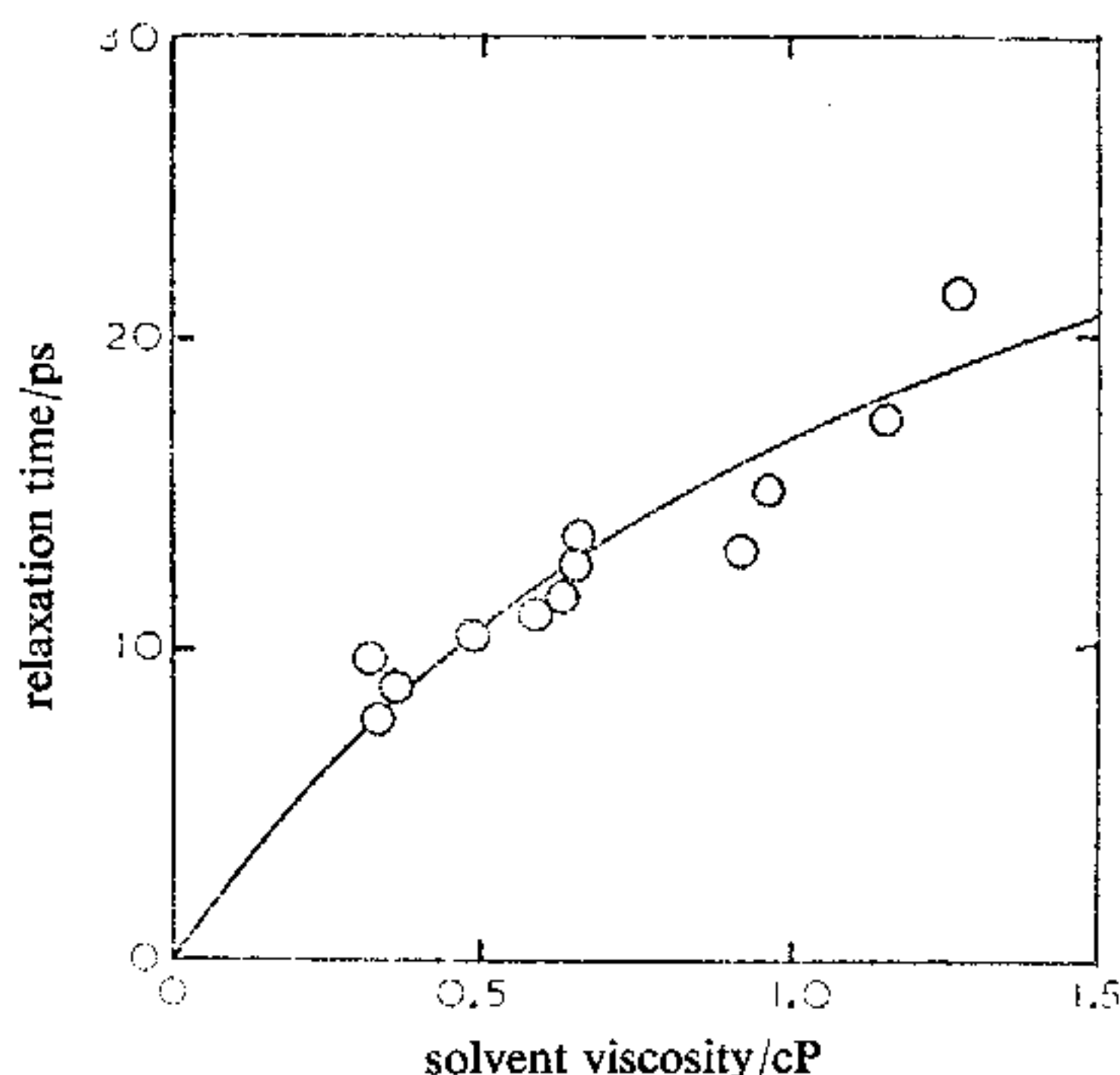


FIG. 2.—Plot of relaxation time against solvent viscosity for nitrobenzene. Solid curve is the computed curve for  $\tau' = 39.4$  ps and  $\eta' = 1.34$  cP.

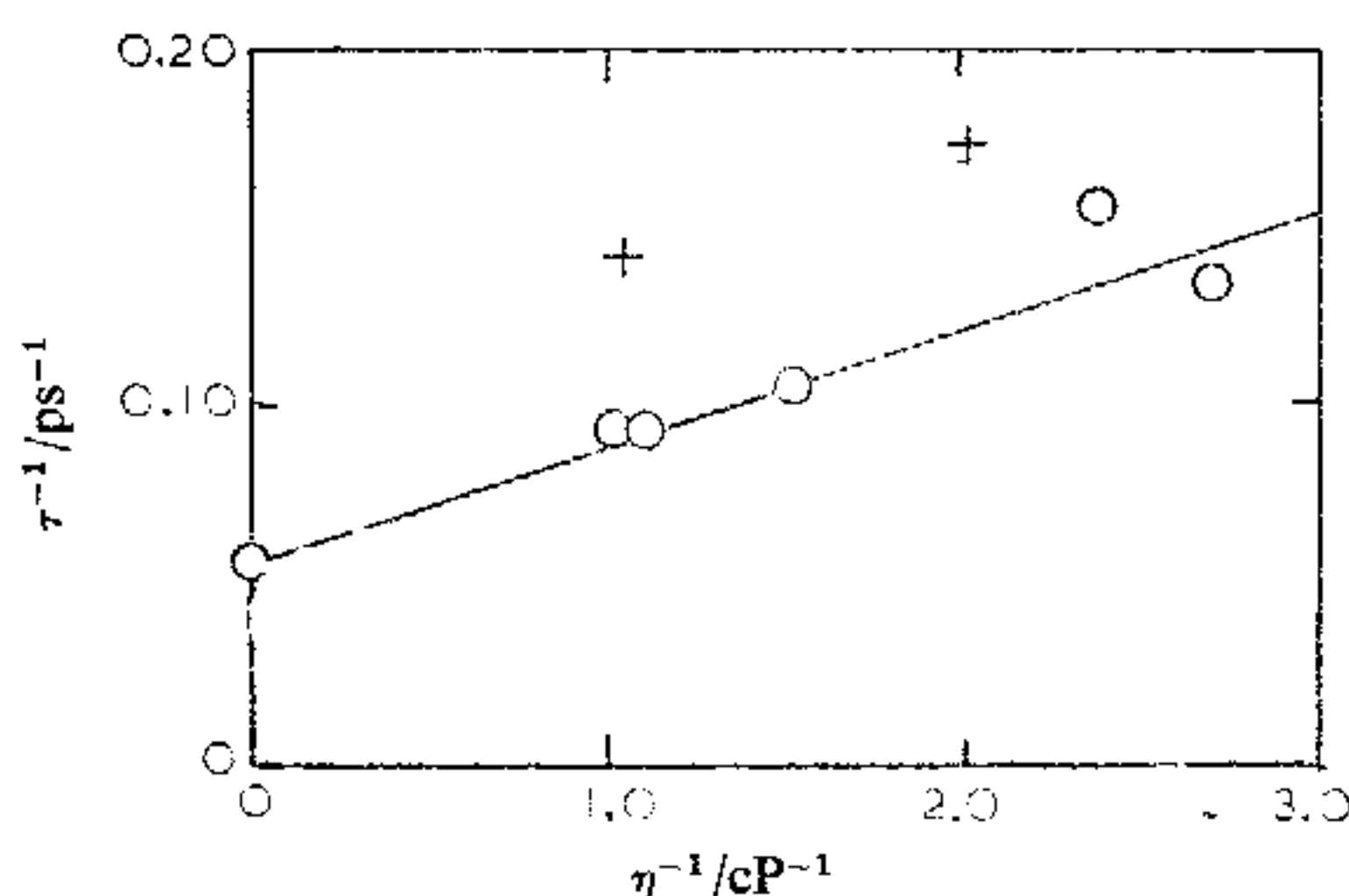


FIG. 3.—Plot of  $\tau^{-1}$  against  $\eta^{-1}$  for camphor in several solvents at 293 K.

## DISCUSSION

Despite the apparently severe assumption that  $\tau'$  and  $\eta'$  are essentially independent of solvent for the nitrobenzene solutions, only two points in fig. 1 fall conspicuously off the line and are marked by crosses. The line of regression of  $\tau^{-1}$  on  $\eta^{-1}$  obtained from all the data points yields a limiting relaxation time of 31 ps and a limiting viscosity of 1.07 cP. If the two anomalous points represent some unusual phenomena at a molecular level and are therefore omitted the regression line yields a  $\tau'$  of 39.2 ps and  $\eta'$  of 1.34 cP. The relaxation time of nitrobenzene in Nujol ( $\eta = 137$  cP) at 25°C is 40.2 ps, in remarkable agreement with the extrapolated values especially in view of the 100-fold range of the extrapolation.

In fig. 2 the data point for liquid paraffin lies well beyond the range of the abscissa but, bearing this in mind, the  $\tau$  against  $\eta$  curve is revealed as a gentle curve in the low viscosity region and not the straight line of Debye's equation.

Fig. 3 includes Kalman and Smyth's value<sup>12</sup> of 17.9 ps for camphor in Nujol at 25°C. Again two solutions are anomalous but the regression line lies near the other low viscosity points as well as the Nujol point and yields 14.7 ps for  $\tau'$ . In view of the long extrapolation, the limiting relaxation time is again in satisfactory agreement with Nujol measurements. Omission of the deviant points yields 0.62 cP for  $\eta'$  and 18.5 ps for  $\tau'$ , the limiting relaxation time now being very close to the observed value in liquid paraffin and even approaches the relaxation time of 19.8 ps obtained by Clement and Davies for solid camphor.<sup>13</sup>

A still more stringent test of eqn (6) is to make use of the reduced form,

$$\frac{\tau}{\tau'} = 1 - \frac{\tau\eta'}{\tau'\eta} \quad (7)$$

which shows that, for any solute, a plot of  $\tau/\tau'$  against  $\tau\eta'/\tau'\eta$  should be a straight line of slope  $-1$ , and intercepting ordinate and abscissa at  $+1$ . Fig. 4 shows such a plot

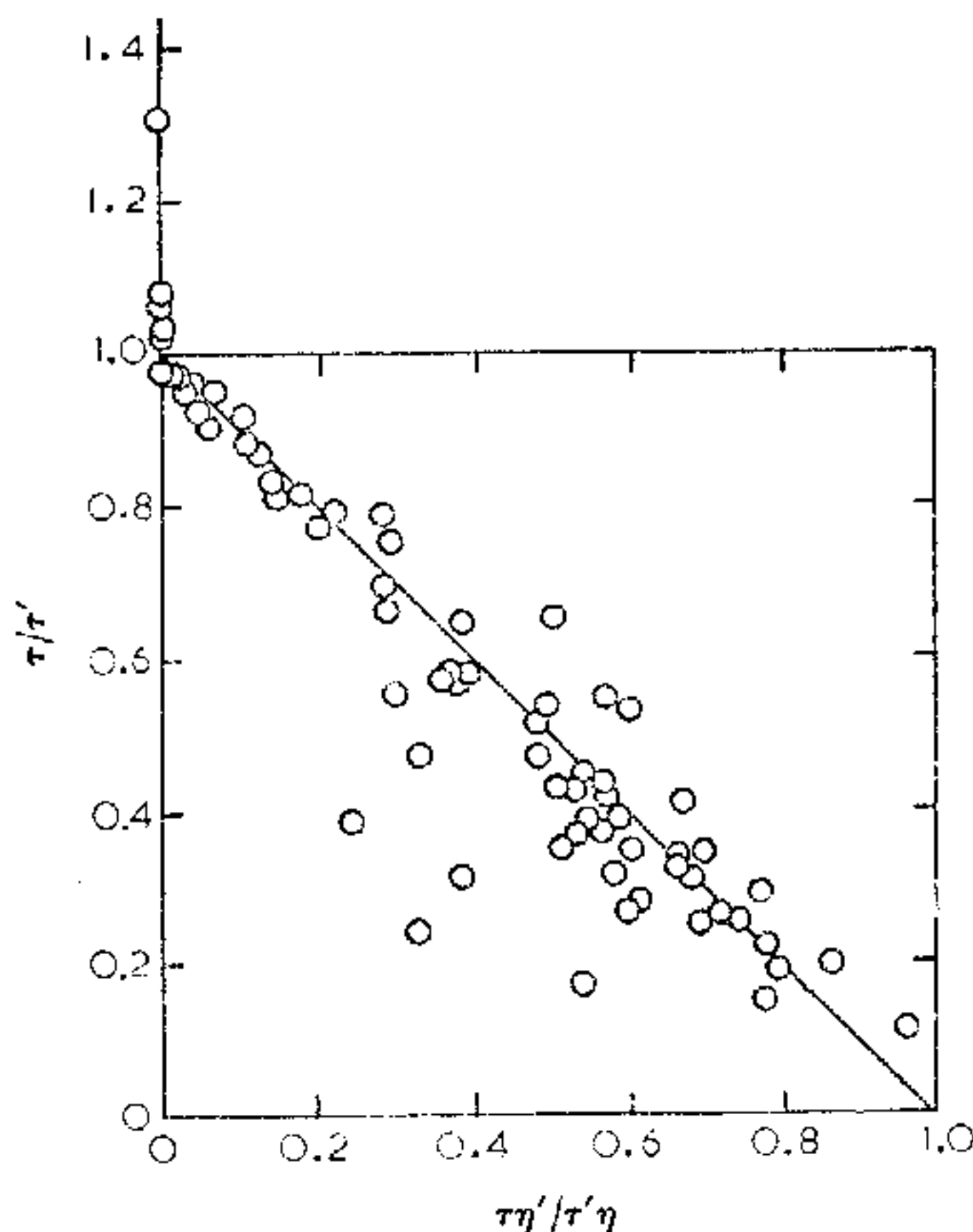


FIG. 4.—Plot of  $\tau/\tau'$  against  $\tau\eta'/\tau'\eta$  for 72 solutions in a variety of solvents and solvent mixtures. The points are expected to lie close to the solid line obtained according to eqn (7). The degree of negative correlation is very high ( $-0.93$ ).

for 72 solutions involving 14 different solutes and a variety of solvents and solvent mixtures. The solutes and their limiting relaxation times and viscosities are given in table 1. The points in fig. 4 are highly negatively correlated, correlation coefficient  $= -0.93$ , all but seven of them lying within  $\pm 20\%$  of the expected line. If these solutions are untypical owing to an anomalous microscopic viscosity then the correlation coefficient for the remainder becomes  $-0.98$ .

The anomalous solutions merit some attention. Most of them are in cyclohexane or similar solvents such as methylcyclopentane. Cyclohexane has a viscosity much

the same as tetrachloromethane but consistently furnishes shorter relaxation times. Higasi,<sup>14</sup> for example finds that the ratio of the relaxation times of many solutes in tetrachloromethane and in cyclohexane is between 1.5 and 2.1. From the graphs it seems that it is tetrachloromethane which behaves normally. The inference might be that the molecular viscosities of solutes in cyclohexane solutions are unusually

TABLE 1.—THE LIMITING RELAXATION TIME ( $\tau'$ ), THE LIMITING VISCOSITY ( $\eta'$ ) AND THE VOLUME OF THE RELAXING REGION ( $V_R$ ) FOR SOME SOLUTES AT AMBIENT TEMPERATURES. WHERE AVAILABLE THE OBSERVED RELAXATION TIME IN NUJOL IS GIVEN FOR COMPARISON

solute	$\tau'$ /ps	$\eta'$ /cP	$10^{30} V_R/\text{m}^3$	$\tau(\text{Nujol})/\text{ps}$	ref.
nitrobenzene	39.4	1.34	40	40	2, 10, 11
camphor	18.5	0.62	41	17.9	10, 12
2-cyano-2-methylpropane	4.2	0.36	16	4.5	16
2,2-dimethylpropanal	3.5	0.09	53	3.6	16
trichloronitromethane	3.1	0.19	22	3.3	16
tribromonitromethane	4.7	0.59	11	4.8	16
4-nitromethylbenzene	100	2.60	53	138	11
1,3-dinitrobenzene	42	0.92	63	—	11
benzophenone	43.5	0.63	95	135	11, 17
benzil	71	1.06	92	—	11
4-nitrodiphenyl	227	1.77	175	—	11
trichloromethane	8.8	0.78	16	—	10, 15
pyridine	5.9	0.88	10	6.5	11
diphenyl ether	5.5	0.0	—	5.5	11

small, perhaps because of co-operative flexing of the solvent molecules. The molecular viscosity should be a good pointer to phenomena at a molecular level such as molecular interactions. An example is provided by trichloromethane<sup>10, 15</sup> which forms weak hydrogen bonds in benzene and 1,4-dioxan solutions. Points on the  $\tau^{-1}$  against  $\eta^{-1}$  plot fall below the general trend for these solutions suggesting that  $\eta_0$  is exceptionally large.

The accuracy of the data fit provided by eqn (5) is clearly illustrated by fig. 5. Graphs of  $\tau$  against  $\eta$  are shown for solutions of 2-cyano-2-methylpropane, 2,2-dimethylpropanal, trichloronitromethane and tribromonitromethane in mixtures of benzene and liquid paraffin.<sup>16</sup> The solid curves are calculated from optimum values of  $\tau'$  and  $\eta'$  (see table 1) and closely represent the experimental data over a wide viscosity range.

Table 1 summarises analyses of data for some solute-solvent systems taken from the literature. In most instances  $\tau'$  agrees with the relaxation time determined in viscous solutions. A long molecule with an axial dipole like 4-nitrobiphenyl has a high molecular viscosity because solvent molecules must be displaced for it to undergo single molecule relaxation. Small, essentially spherical, molecules like pyridine and trichloromethane have low  $\tau'$  values. Diphenyl ether, although not spherical, has an unusually small limiting viscosity, apparently close to zero. Thus the molecular relaxation mechanism seems independent of the solvent. Evidently an intramolecular relaxation process is overwhelmingly dominant in diphenyl ether solutions. The most severe disagreement in the table occurs for benzophenone for which the high viscosity relaxation time is predicted to be 43.5 ps whereas the minimum observed relaxation time<sup>17</sup> is 135 ps. There seems to be a relationship between  $\tau'$  and  $\eta'$  as expected since both are proportional to  $\eta_0$ . In fact the ratio  $\tau'/\eta'$  should be a measure of the volume of the structured region. The volumes thus evaluated and listed in table 1 broadly follow the sizes of the molecules but are rather smaller than expected.



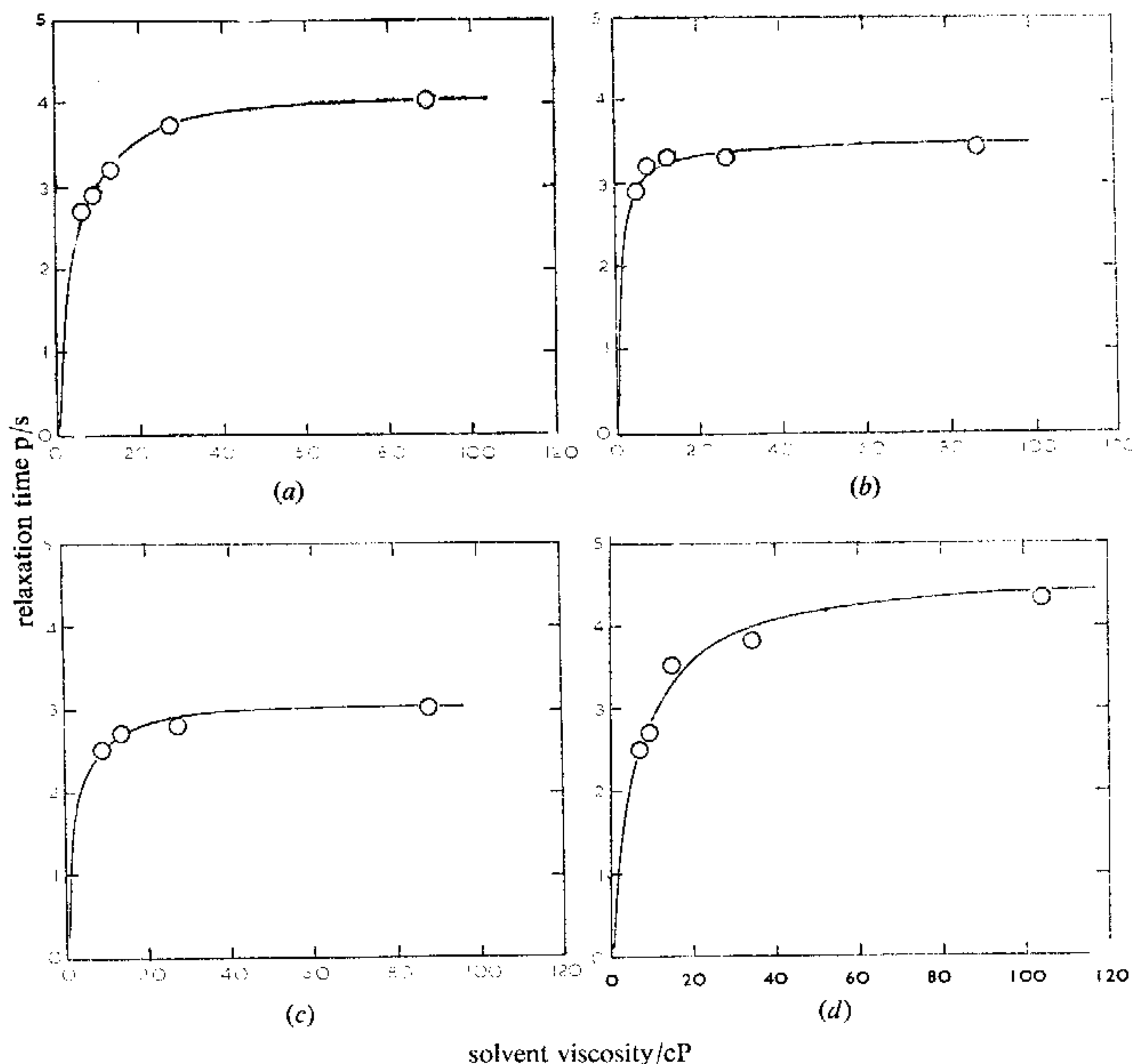


FIG. 5.—Plots of relaxation time against solvent viscosity for (a) 2-cyano-2-methylpropane, (b) 2,2-dimethylpropanal, (c) trichloronitromethane, (d) tribromonitromethane in mixtures of benzene and liquid paraffin, (data from ref. (16)). Solid lines are theoretical curves derived from the empirical parameters in table 1 and eqn (5).

### CONCLUSION

The equation  $\tau = \tau' \eta / (\eta + \eta')$  is found empirically to represent the viscosity dependence of relaxation times very well for 65 of 72 solutions tested. The form of the equation can be accounted for by a model incorporating zonal as well as individual molecule relaxation.

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