

The Mechanism of Orientation in iButyl and iAmyl Bromide Glasses

William O. Baker and Charles P. Smyth

Citation: *The Journal of Chemical Physics* **7**, 574 (1939); doi: 10.1063/1.1750494

View online: <http://dx.doi.org/10.1063/1.1750494>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/7/8?ver=pdfcov>

Published by the **AIP Publishing**

Articles you may be interested in

[Frontside versus backside reactivity in electron transfer to oriented tert butyl bromide and methyl bromide](#)

J. Chem. Phys. **117**, 4220 (2002); 10.1063/1.1496477

[Electron transfer to oriented molecules: Surprising steric effect in t-butyl bromide](#)

J. Chem. Phys. **114**, 10569 (2001); 10.1063/1.1380233

[Oriented molecule beams: Focusing and orientation of tbutyl bromide with analysis by polarized laser photofragmentation](#)

J. Chem. Phys. **91**, 3477 (1989); 10.1063/1.456877

[Dielectric and Viscous Behavior in the iAmyl Bromide–2Methylpentane System](#)

J. Chem. Phys. **44**, 4621 (1966); 10.1063/1.1726682

[Hydrates of the Tetra nbutyl and Tetra iamyl Quaternary Ammonium Salts](#)

J. Chem. Phys. **31**, 1231 (1959); 10.1063/1.1730574



The Mechanism of Orientation in *i*-Butyl and *i*-Amyl Bromide Glasses

WILLIAM O. BAKER AND CHARLES P. SMYTH

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

(Received June 2, 1939)

The relaxation times of two typical, unassociated polar molecules have been calculated from experimental dispersion data. Both Stokes' law and absolute reaction rate theories have been applied to show that the inner friction constant in the usual Debye relaxation formula must be considered in terms of a mechanism involving higher activation energies than those obtaining in ordinary viscous flow. Hence, the macroscopic viscosity will generally be inadequate as an inner friction constant for relaxation. Slight alterations in the structure of these molecules

are found apparently to change their relative orientations and hence energies of interaction. Rotational motion in viscous flow of lesser degree but similar kind to that of relaxation is indicated by the parallelism between the respective energies in *i*-butyl and *i*-amyl bromides. Possible generalizations have been extended to relaxation and flow phenomena in liquid crystals, where effectively the co-existence of phases derived from a single component over a temperature range makes the structure considerations simpler than in the usual case of solutions.

EXPERIMENTS over a range of temperature have provided complete dispersion data at three frequencies for the simple polar molecules of *i*-butyl bromide and *i*-amyl bromide in the vitreous state.¹ These results are considered in terms of the theories of dielectric relaxation, and the mechanisms of molecular motions during rotation and viscous flow. Dielectric loss related to the polar structure of matter has been comprehensively reviewed by Müller.²

Debye³ applied Stokes' expression for the rotation of a sphere in a viscous medium to obtain a relation between the relaxation time, τ , of the molecules, and their radii, a , in which

$$\tau = 4\pi\eta a^3/kT,$$

where η is the inner friction constant, k is the Boltzmann constant, and T is the absolute temperature. This equation is sometimes moderately well obeyed for dilute solutions of polar molecules, where η is taken as the viscosity of the solvent, but must be modified when there is pronounced intermolecular action, such as obtains in a pure polar substance, as Debye⁴ and others have recognized. Then, η can no longer be a simple macroscopic viscosity, and we shall consider the relaxation time in terms of molecular processes. For comparison with this latter treatment, however, the classical relaxation times of

the bromides have been calculated. By a graphical extrapolation from the data reported, ϵ_1 , the dielectric constant at zero frequency is evaluated, and ϵ_0 , that at infinite frequency, is, with sufficient accuracy, given by the low temperature solid value, or the square of the refractive index. The calculation of τ then follows from Debye's⁵ equation

$$\omega\tau = \frac{\epsilon_0 + 2}{\epsilon_1 + 2} \left[\frac{1}{2} \{ y + (4 + y^2)^{1/2} \} \right]^{1/2},$$

where $\omega = 2\pi f$, f = frequency in cycles per second, $y = (\epsilon_1 - \epsilon_0)/(\epsilon_1 + \epsilon_0)$. The relaxation times, in each case at a temperature corresponding to maximum dispersion for 50 kc., are:

i-butyl bromide, $\tau = 0.9 \times 10^{-6}$ sec. at 118.6°K;
i-amyl bromide, $\tau = 1.2 \times 10^{-6}$ sec. at 131.1°K.

Rough estimates of kinetic theory radii from Sutherland's constant data (Landolt-Börnstein's "Tabellen") may be used to calculate η values: *i*-butyl bromide, for $a^3 = 16.64 \times 10^{-24}$ cm³, $\eta = 0.68 \times 10^2$ poise at 118.6°K; *i*-amyl bromide, for $a^3 = 20.91 \times 10^{-24}$ cm³, $\eta = 0.79 \times 10^2$ poise at 131.1°K. Lillie⁶ showed that there is no discontinuity in η at the vitrification point, while Eyring⁷ has theoretically justified a linear relation between $\ln \eta$ and $1/T$ which permits extrapolation of the viscosity data of Thorpe and

¹ Baker and Smyth, J. Am. Chem. Soc. 61 (1939).

² Müller, *Ergebnisse der Exakten Naturwissenschaften* (Julius Springer, Berlin, 1938), Vol. XVII, pp. 164-228.

³ Debye, *Polar Molecules* (Chemical Catalog Co., Inc., New York, 1929), p. 85.

⁴ P. Debye and W. Ramm, Ann. d. Physik 28, 28 (1937).

⁵ Reference 3, p. 94.

⁶ H. R. Lillie, J. Am. Ceram. Soc. 16, 619 (1933).

⁷ H. Eyring, J. Chem. Phys. 4, 283 (1936). See also, E. N. Andrade, Nature 125, 580 (1930); S. E. Sheppard, J. Rheology 1, 349 (1930).

Rodger⁸ for *i*-butyl bromide to the temperature at which the relaxation time was measured. Although the value thus obtained, $\eta = 0.90$ poise at 118.6°K, is very approximate, it demonstrates, by being 100 times too small, the inadequacy of the simple macroscopic viscosity in specifying the rotational hindrance in a pure polar medium. Of course, the linear extrapolation of the liquid viscosity values into the glass region is made uncertain by the possibility that the mechanism of viscous flow has changed, but even this would probably not account for the discrepancy between the extrapolated and calculated values.

A method for considering the relaxation phenomenon as a molecular process has been suggested by Eyring,^{7, 9} and further developed by Frank,¹⁰ who made calculations for ice, some solid solutions in paraffin wax, and for a composite commercial insulator, Permitol. We propose to extend this treatment to the simple, homogeneous bromide glasses. The quantal basis for the theory of absolute reaction-rates¹¹ gives an expression for the rate at which an activated complex formed at the top of a potential hump decomposes to give the products. In the case of a unimolecular reaction, this is effectively the surmounting of a potential barrier, which may readily be considered as that imposed by its neighbors to restrict the rotation of a given molecule. The standard Arrhenius form for a unimolecular reaction will yield an activation energy for the process, since $\log \tau$ is found to be practically a linear function of T , and $1/\tau = k' = Ce^{-A/RT}$, where k' = specific reaction rate, A = activation energy, C = "steric factor," later to be explicitly defined. The τ to be used above is most accurately found by regarding it as the mean relaxation time for the temperature of maximum dielectric loss. That is, considering the decay of orientation as an exponential function of time, Debye⁵ has derived the relations

$$\epsilon' = \epsilon_0 + \frac{\epsilon_1 - \epsilon_0}{1 + x^2},$$

$$\epsilon'' = \frac{\epsilon_1 - \epsilon_0}{1 + x^2} x,$$

in which the quantities preserve their already defined meanings, and

$$x = \frac{\epsilon_1 + 2}{\epsilon_0 + 2} \omega \tau,$$

while ϵ'' is the loss component of the dielectric constant as indicated by the equation $\epsilon = \epsilon' - i\epsilon''$. Clearly, ϵ'' reaches a maximum when $x = 1$, and the temperatures of these maxima are obtained from the experimental work quite independently of the absolute values of ϵ'' , since the graphs of ϵ'' against temperature are symmetrical.¹ We now find that

$$-d \ln \tau / dT = A / RT^2,$$

or, since $\omega = 2\pi f$, and $\tau = 1/\omega$ at the critical frequency, then

$$d \ln f / dT = A / RT^2.$$

Thus, A/R values result from the slope of the straight line obtained by plotting $\ln f$ against $1/T$, where T is the temperature of maximum ϵ'' for the given frequency f . Further, a mean T of ϵ''_{\max} may be found, and from it a mean f , which may be then used to calculate the specific rate, a mean $1/\tau$, from

$$1/\tau = \frac{\epsilon_1 + 2}{\epsilon_0 + 2} \cdot 2\pi f.$$

The fundamental equation $k' = \kappa kT / h e^{-\Delta F^\ddagger / RT}$, where κ = transmission coefficient, taken as 1, k = Boltzmann's constant, h = Planck's constant, and ΔF^\ddagger = free energy of activation, may now be used to calculate ΔF^\ddagger . It may also be rewritten as

$$k' = \kappa kT / h e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT},$$

where ΔS^\ddagger is the activation entropy, and ΔH^\ddagger is the heat of activation taken as the activation energy A for the rotation process. The factor C thus includes the terms $\kappa kT / h e^{\Delta S^\ddagger / R}$. The mechanism of the rotation of vitreous *i*-butyl and *i*-amyl bromides may now be interpreted from the results given in Table I.

It is evident from the large entropy terms that many molecules surrounding a given one able to orient in the field must cooperate in permitting its orientation. Probably, they undergo, by thermal fluctuations, slight rearrangements, a very definite combination of these

⁸ Landolt-Börnstein, *Tabellen* (Julius Springer, Berlin, 1935), 5th ed., Vol. I.

⁹ A. E. Stearn and H. Eyring, *J. Chem. Phys.* **5**, 113 (1937).

¹⁰ F. C. Frank, *Trans. Faraday Soc.* **32**, 1634 (1936).

¹¹ H. Eyring, *Chem. Rev.* **17**, 65 (1935).

TABLE I.

	T_{MEAN} °K	f_{MEAN}	A (CAL./MOLE)	C	ΔF^\ddagger (CAL./MOLE)	ΔS^\ddagger (E.U./MOLE)
<i>i</i> -Butyl bromide	115.6	5.6×10^3	23,108	7.86×10^{48}	3796	167.1
<i>i</i> -Amyl bromide	128.0	5.0×10^3	18,007	5.21×10^{38}	4425	106.1

being necessary for a single molecule to be able to rotate. In the liquid state, this entropy factor is small. Hence, this direct evidence explains the great difference in solid and liquid values of properties involving rotational motion, as viscosity and diffusion. The activation energy for viscous flow in glass or even in steel may not differ greatly from that in the molten state, but high entropy terms will vastly retard the processes concerned in the solid state. These results should also be applied to the mechanical properties of rigid mixtures, such as plastics and resins, where elasticity or resiliency as well as dielectric properties may depend on the effect of cross linkages and foreign ingredients upon the orientation entropies of the molecules.

Although the additional methylene group in *i*-amyl bromide somewhat dilutes the dipoles, this alone is not sufficient to account either for the lower activation energy for rotation, 18 kcal., or for the reduced maximum dielectric constant, 12.3, of the larger molecule as compared to values of 23 kcal. and 17.3, respectively, for *i*-butyl bromide. However, this difference would be expected if the elongated pear shape of the *i*-amyl as contrasted to the compressed pear shape of the *i*-butyl compound had introduced sufficient anisotropy to make the former molecule rotate preferably only about its long axis. Independent evidence that this slight structural change has indeed produced such an effect, and, conversely, independent support from the dielectric measurements for the rotating couple concept of viscous flow^{7, 12} arise from examination of the activation energies of viscosity for these compounds. These energies, given in Table II, were calculated from the data of Thorpe and Rodger.⁸ According to the Eyring theory of viscosity, the flow process occurs in a fashion requiring the least use of extra volume, for to make a hole the size of a molecule requires the

energy of vaporization of the molecule. For nearly spherical, or quite symmetrical molecules, no preferred orientations of the molecules forming the rotating couple are possible, and the ratio of the energy of vaporization to the activation energy for viscous flow, $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$, is generally found to be about 3.¹² However, rod-like molecules will align along their long axes, and then the ratio $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$ is 4 or even larger. If, then, *i*-amyl bromide is tending to behave as an extended molecule, while the *i*-butyl bromide is more isotropic, the ΔE_{vis} values should be in the same order as, although of quite different magnitudes from, the activation energies for orientation. This is confirmed by Table II, in which the activation energy for rotation, A , is again given, and, further, the $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$ ratio of 3.5 for *i*-butyl bromide differs from the value 4.3 for the longer *i*-amyl bromide. Thus, the interrelation of the previously unconnected mechanisms of the kinetic processes of dielectric relaxation and viscous flow is seen to be consistent with the structure of the molecules. Such a method of deciding about the mode of orientation processes should prove general.

It has been noted in a discussion of the swarm theory of liquid crystals¹³ that the relaxation time of para-azoxyanisole groups, as measured by the region of maximum dispersion for a given frequency, varies rapidly with temperature. However, the experimental viscosity shows a normal slow change with temperature. It is also shown from optical studies that the groups are altered in size only very gradually with temperature. These relaxation time-viscosity phenomena, anomalous in the classical theory, would seem to be explained by the previous evidence that the process of viscous flow requires an activation energy which is only a fraction of that required for rotation of the particles orienting in a field.

TABLE II.

	ΔE_{VIS} (CAL./MOLE)	A (CAL./MOLE)	$\Delta E_{\text{VAP}}/\Delta E_{\text{VIS}}$ (CAL./MOLE)
<i>i</i> -Butyl bromide	1990	23,108	3.5
<i>i</i> -Amyl bromide	1759	18,007	4.3

¹² R. H. Ewell and H. Eyring, J. Chem. Phys. **5**, 726 (1937).

¹³ L. Ornstein and W. Kast, Trans. Faraday Soc. **29**, 931 (1933).

Hence, the temperature coefficient of the relaxation rate would exceed that of the viscosity change, as observed.

The viscosity of liquid crystalline systems is also found to show a maximum with increasing temperature in the anisotropic region¹⁴ instead of the uniform decrease found with normal liquids. Too, the Hagen-Poiseuille law is not obeyed, and liquid crystal mixtures appear to have a disproportionately high viscosity for low pressures.¹⁴ Ostwald has termed this a "structure viscosity" effect, without further explanation. The structure sensitivity is quantitatively illustrated in the bromides discussed above. If the difference of a methylene group so alters the flow orientation of the molecules, as here indicated, it is understandable that the liquid crystalline groups may, by relatively small changes in shape, engage in a variety of flow processes. These changes in shape may be effected by temperature. Thus, at certain temperatures, the activation energy for viscous flow may change so much as to produce temporarily an apparent increase of viscosity over that found for a lower temperature. Also, the local group orientation will be influenced by the rate of flow through a capillary, and, again, the activation energies and hence apparent viscosities as well as actual flow mechanism may change as they would not do in the normal case of the passage through a capillary of a liquid whose flow units are of molecular size too small to be oriented by the streaming through the tube. Further, as expected, it is found that the plot of $\ln \eta$ against $1/T$ for a liquid crystalline substance has not only a different slope from that of the isotropic liquid, but often deviates from linearity in the region where the swarms are changing, presumably in shape and size. This is again possible evidence for a varying activation energy in the absolute reaction rate theory of viscosity.⁷ It may be concluded that at least qualitatively this theory is applicable to systems exhibiting viscosities often considered anomalous. There is prob-

ably, of course, the additional factor that other terms besides the energy exponential in the specific rate expression for viscosity^{7, 12} change in the cases considered above, but the dielectric relaxation results have shown how sensitive potentials involving rotational interaction are to the shape of the interacting units.

A somewhat different theoretical approach to the viscosity of anisotropic liquids, in which the rotational motion is represented in terms of the center of mass and the turning moment has been offered.¹⁵ It has not been applied to the effects here discussed. Bingham¹⁶ also suggested, without further detail, that a new molecular arrangement was probably formed at the clarifying point of a crystalline liquid. The viscosity-temperature relation of *p*-azoxyanisole resembles significantly that for liquid sulfur¹⁷ in the region of its anomaly. A change of structure has been proposed to explain the sulfur behavior.¹³

Oncley and Williams¹⁸ have noted the deficiencies of the macroscopic viscosity in relaxation time calculations in reporting that the measured viscosity of a solution might be increased a thousand-fold without changing significantly the value of the inner friction constant in the Debye formula. They varied the viscosity by using mixtures of hydrocarbon oils or waxy compounds. On the present scheme of regarding orientation as the surmounting by the polar solute molecules of potential barriers created, at least in moderately dilute solutions, chiefly by the solvent molecules, lengthening of the solvent molecules would presumably not alter the average environment of the solute. Hence, just the results of Oncley and Williams would be expected, as in the rotation of the polar molecule in the field in contrast to the viscous flow of the solution, the solvent molecules need not themselves rotate.

¹³ R. O. Herzog and H. Kuder, *Trans. Faraday Soc.* **29**, 1006 (1933).

¹⁶ E. C. Bingham, *Fluidity and Plasticity* (McGraw-Hill Book Co., Inc., New York, 1922), p. 210.

¹⁷ L. Rotinjan, *Zeits. f. physik. Chemie* **62**, 609 (1908).

¹⁸ J. L. Oncley and J. W. Williams, *Phys. Rev.* **43**, 341 (1933).

¹⁴ Wo. Ostwald, *Trans. Faraday Soc.* **29**, 1002 (1933).