Dielectric Properties of Liquid Isoamyl Bromide at Low Temperatures[1,2]

John G. Berberian and Robert H. Cole

Contribution from the Department of Chemistry, Brown University, Providence, Rhode Island 02912. *Received November 29, 1967*

Abstract: Dielectric relaxation was measured in the supercooled liquid from 122 to 107°K by steady-state ac measurements from 10^5 to 10^{-2} Hz and by transient measurements at times from 2 to 700 sec. Except for small differences at high frequencies, the ac data are described by a skewed arc relaxation function and the transient data by the incomplete γ function with values of the relaxation parameter β approaching 0.50 at the lowest temperatures. The temperature dependence of relaxation times is described by an empirical equation of the Vogel or Williams–Landel–Ferry form with characteristic temperature $T_\infty = 74$°K. Implications of the behavior in relation to the theories of Glarum, Adam and Gibbs, and Anderson and Ullman are discussed.

The work reported here was undertaken to extend previous measurements on isoamyl bromide by Glarum[3] and Denney[4] to lower temperatures and longer relaxation times of dipole reorientation. In the earlier work, the dielectric relaxation behavior was reasonably well defined in the normal liquid from 298°K to the melting point at 161.3°K, and in the supercooled liquid from 161.3 to 121°K by measurements in the frequency range 10^{10}–10^2 Hz. The present measurements were made over the narrow temperature range from 122 to 107°K in which the characteristic time scale changes from 6×10^{-4} to 470 sec, and the lowest temperature studied is very nearly the glass-transition temperature of the supercooled liquid (as inferred from the temperature at which the shear viscosity is estimated to be 10^{13} poise).

The principal reason for undertaking measurements of this particular liquid over such a wide range of times and temperatures is that isoamyl bromide, like other alkyl halides which supercool readily, is a reasonably simple polar liquid with dielectric properties remarkably similar to those of other liquids at low temperatures, including hydrogen-bonding alcohols and polymers. It therefore seemed worthwhile to extend the studies of both frequency and temperature dependence of the behavior in isoamyl bromide in order better to define and assess the common features for a hopefully simple and representative example.

Experimental Methods

Isoamyl bromide obtained from Matheson Coleman and Bell was distilled through a Vigreux column under a nitrogen atmosphere. The measured index of refraction of the distillate at 20° was n_D 1.4413, in good agreement with literature values 1.4415[5] and 1.4412.[6] A vapor-phase chromatogram showed no water present and a small amount of unidentified impurity in the starting material which was removed by the distillation. Preliminary measurements on the liquid as received were in agreement with results for the distillate.

The dielectric cell used in all measurements was a three-terminal capacitor with nickel-plated brass electrodes in the form of coaxial cylinders. The cell is described by Hassion and Cole[7] and was modified for the present work only in minor details. The direct geometrical capacitance was 1.00 pf (picofarad) at room temperature with a temperature coefficient of 14×10^{-6} pf deg^{-1}.

The thermostat used for the low temperatures consisted of two coaxial cylindrical containers surrounding the cell and immersed in liquid nitrogen, both being filled with lead shot to act as the heat transfer medium. Temperature control was accomplished by varying the heating current through a resistance wire winding on the inner container. A carbon 10-kohm resistor was used as a sensor for a proportional controller (Fisher Model 22) whose output supplies the power to the heater. With this arrangement, temperatures set near 115°K never changed by more than 0.25°K in 1 hr and usually changed considerably less over the duration of a complete series of measurements.

Two bridges were used to measure ac admittance of the liquid-filled cell as a function of frequency. For frequencies from 10^5 to 10^2 Hz, a transformer bridge built in our laboratory was employed to obtain direct measurements of equivalent parallel capacitance and conductance of isoamyl bromide (details of the instrument have not been published, but a description of the circuits and operation is available on request). For frequencies from 10^3 to 0.02 Hz, measurements were made with a low-frequency bridge recently developed in this laboratory. This instrument, to be described in more detail elsewhere, employs operational amplifier circuits to provide variable capacitance and conductance currents in known ratios and of opposite sign to the components of current through the unknown. These currents are summed at the input of the current detector (a tuned amplifier for frequencies above 20 Hz and high-speed picoammeter at lower frequencies). The balancing currents are adjusted for zero resultant current, the unbalance being indicated by an oscilloscope display.

The time variation of polarization for times too long for bridge measurements was determined by transient measurements of the sample current in response to an applied voltage rising linearly in time. This method is basically that described by Davidson, Auty, and Cole[8] with improved circuits for generating the ramp voltage and recording the current. With this arrangement, currents were measured to times 700 sec after initiation of the voltage rise.

The precision of ac capacitance and conductance measurements is better than 0.1% for both bridges except at the lowest frequencies in their ranges, and the accuracy of derived dielectric parameters from these data is limited by errors of temperature measurement and control. Values of time-dependent polarization from the transient data are accurate to 2% except at the longest times, for which drift and noise limit accuracy to 5%.

Experimental Results

Although relaxation behavior was of principal interest in this work, the values of static dielectric constant ϵ_0 should be mentioned briefly. These were found to in-

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(2) This work was supported by the Advanced Research Projects Agency, U. S. Department of Defense.

(3) S. H. Glarum, *J. Chem. Phys.*, 33, 639 (1960).

(4) D. J. Denney, *ibid.*, 27, 259 (1957).

(5) W. O. Baker and C. P. Smyth, *J. Am. Chem. Soc.*, 61, 2063 (1939).

(6) "International Critical Tables of Numerical Data Physics, Chemistry and Technology," McGraw-Hill Book Co., Inc., New York, N. Y., 1926.

(7) F. X. Hassion and R. H. Cole, *J. Chem. Phys.*, 23, 1756 (1955).

(8) D. W. Davidson, R. P. Auty, and R. H. Cole, *Rev. Sci. Instr.*, 22, 678 (1951).

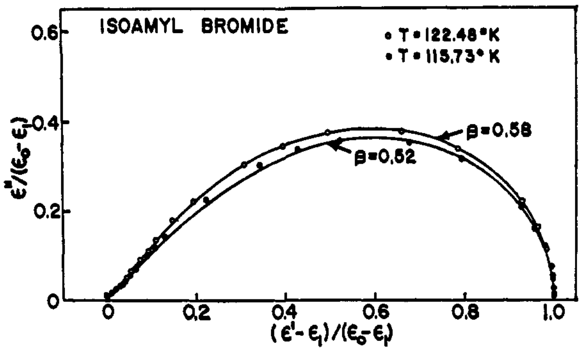

Figure 1. Complex plane loci of the normalized dielectric constant $(\epsilon^* - \epsilon_1)/(\epsilon_0 - \epsilon_1)$ for isoamyl bromide at 122.5 and 115.7°K. The curves are calculated from eq 1 for values of the parameters given in the text.

crease smoothly and nearly linearly with decreasing temperature from 13.26 at 122.8°K to 14.1 at 109.8°K. The data overlapped previous results of Denney[4] and showed a systematic difference of 5% which we presume to be the result of error in cell calibration in the earlier work. This difference has no effect on derived relaxation parameters, which are in excellent agreement.

Analysis of the frequency dependent values of complex dielectric constant $\epsilon^* = \epsilon' - i\epsilon''$ showed that, except for small deviations at the extreme high-frequency end of the dispersion range, the data could be presented within experimental error by the "skewed-arc" empirical relaxation function. This function was proposed by Davidson and Cole[9,10] to fit data for glycols at low temperatures and has since been used to give a good representation of the data for a variety of other liquids and high-temperature phases of some molecular solids.[11] The "skewed-arc" function has the form

$$\epsilon^* = \epsilon' - i\epsilon'' = \epsilon_1 + (\epsilon_0 - \epsilon_1)/(1 + i\omega\tau_0)^\beta \quad (1)$$

where ϵ_1 is the limiting high-frequency value of ϵ', ω is the angular frequency $2\pi f$, and β is an empirical parameter in the range $0 < \beta < 1$, the limiting value $\beta = 1$ giving the familiar Debye function. The parameter τ_0 is the characteristic relaxation time for the temperature of measurement. The relaxation properties of the liquid are thus defined by the values of ϵ_0, ϵ_1, τ_0, and β if eq 1 is an adequate representation of the data.

Representative plots of the normalized complex dielectric constant $(\epsilon^* - \epsilon_1)/(\epsilon_0 - \epsilon_1)$ for isoamyl bromide at 122.5 and 115.7°K are shown in Figure 1, the points being experimental values and the solid curves being the loci for values of the parameters in eq 1 giving the best fit to the data. (At 122.5°K, $\epsilon_0 = 13.35$, $\epsilon_1 = 2.76$, $\tau_0 = 7.08 \times 10^{-4}$ sec, $\beta = 0.51$; at 115.7°K, $\epsilon_0 = 13.88$, $\epsilon_1 = 2.78$, $\tau_0 = 6.94 \times 10^{-2}$, $\beta = 0.53$.) The deviations just visible in these plots at the high-frequency limit are first recognizable in the data for frequencies f greater than about $50\tau_0^{-1}$, corresponding to times less than $\tau_0/300$. These deviations are shown more clearly in Figure 2, which is a plot to a larger scale of the high-frequency region of the data at 111.7 and 106.7°K, the solid line being the extension of the skewed arc locus best fitting the lower frequency data. Also indicated on the plot is the value $(n\text{D})^2 = 2.37$ (at 120°K) for optical refraction estimated from higher temperature data. It is seen that the difference $\epsilon_1 - (n\text{D})^2 = 0.40$ at 120°K is only partly accounted for by dispersion at frequencies below 10^5 Hz; this difference is about 4% of the difference $\epsilon_0 - \epsilon_1 = 10.85$ at 120°K.

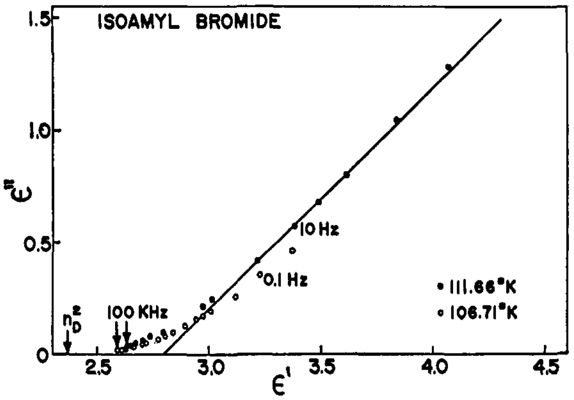

Figure 2. High-frequency portions of the complex dielectric constant loci for isoamyl bromide at 111.7 and 106.7°K. The straight line is the extension of the skewed arc loci fitting the data at lower frequencies.

Because of the high-frequency deviation, the values of ϵ_1 do not correspond to a directly measurable quantity but are simply values for best fit of eq 1 to the data. They depend only slightly on temperature, increasing from 2.76 at 122.8°K to 2.82 at 110.4°K with an estimated uncertainty of ±0.01. We have no molecular interpretation of the high-frequency effect but suspect that it is a specific one involving internal rearrangements of neighboring bonds which lead to small changes in dipole moment. Measurements of other alkyl halides should throw light on this question.

The transient measurements below 112.7°K give values of current $I(t)$ at times t following application of a linearly rising voltage $V(t) = V_0t/T$. For systems such as the present one which have linear response in the sense of the superposition principle, this current has the same time dependence as the charge $Q(t)$ following application of a step voltage of magnitude V_0 at $t = 0$, $Q(t) = I(t)T$. The normalized charge $Q(t)/C_gV_0$, where C_g is the geometric capacitance of the sample cell, is conveniently, if loosely, described as a time-dependent dielectric constant $\epsilon(t)$. From the superposition principle, it follows (as discussed by Davidson, Auty, and Cole[8]) that this quantity is given by the inverse Laplace transform of $\epsilon^*(i\omega)$. If eq 1 is valid, one obtains

$$\epsilon(t) = \epsilon_1 + (\epsilon_0 - \epsilon_1)\gamma(t/\tau_0,\beta) \quad (2)$$

where $\gamma(t/\tau_0,\beta)$ is the normalized incomplete α function. Tables of this function given by Pearson[12] extend to $t/\tau_0 = 0.1414$ for $\beta = 0.50$; values for shorter times are easily calculated from the series expansion of $\gamma(t/\tau_0,\beta)$ for $t/\tau_0 < 1$.

The adequacy of eq 2 as a representation of the transient data was tested by trial-and-error fitting curves calculated from eq 2 to plots of $\epsilon(t)$ against log t. It was found that agreement with experimental data could be obtained with uncertainty of less than 10% in τ_0 and 0.02 in β, and that the values of τ_0 and β obtained at the highest temperatures of the transient measurements

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(9) D. W. Davidson and R. H. Cole, *J. Chem. Phys.*, **18**, 1417 (1950).

(10) D. W. Davidson and R. H. Cole, *ibid.*, **19**, 1484 (1951).

(11) P. P. M. Groenewegen and R. H. Cole, *ibid.*, **46**, 1067 (1967).

(12) K. Pearson, "Tables of the Incomplete Gamma-Function," His Majesty's Stationary Office, London, 1922.

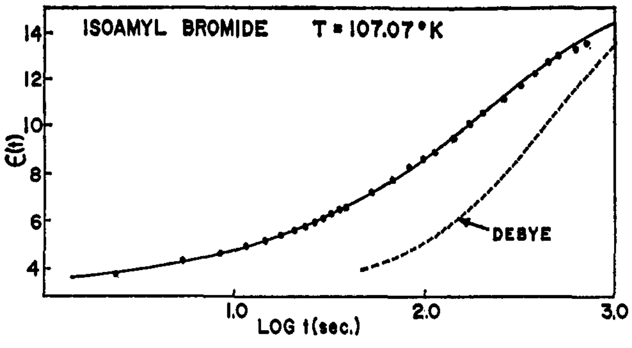

Figure 3. Plot of transient capacitance $\epsilon(t)$ of isoamyl bromide at 107.1°K against log t (sec). The solid curve is calculated from eq 2 for $\beta = 0.50$ and $\tau_0 = 469$ sec. The dashed curve is the exponential (Debye) response function for the same value of τ_0.

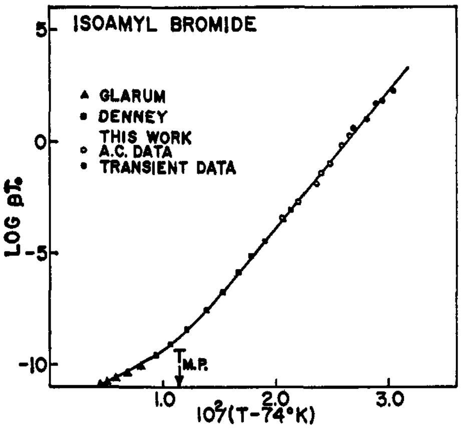

Figure 4. Plot of log $\beta\tau_0$ against $10^2/(T - 74°\text{K})$ for isoamyl bromide. Data of Glarum[3] and Denney[4] are also plotted for comparison.

were in good agreement with those derived from fitting eq 1 to ac data at the same temperature.

A representative plot of transient data at 107.1°K is shown in Figure 3. The short time resolution of the transient data was inadequate to show the counterpart of the high-frequency deviations found in the ac measurements.

Because nearly all of the observed relaxation effects are adequately described by eq 1 or eq 2, the results can be compactly presented in terms of the temperature dependence of the derived parameters τ_0 and β. We choose to do this by appropriate plots rather than a table (available in the Ph.D. thesis of J. G. B.), because this permits comparison with the previous results at higher temperatures, and because a simple but adequate analytic representation for the temperature dependence of τ_0 has been established.

The temperature dependence of $\beta\tau_0$, rather than τ_0, was analyzed, as some measurements of absorption conductance $\omega\epsilon''$ made by Denney[4] yield only values of the product $\beta\tau_0$. It was found, as expected, that an Arrhenius plot of log $\beta\tau_0$ against reciprocal temperature showed increasing curvature at low temperature, but that the data could be fitted by a modified rate expression of the form

$$\log \beta\tau_0 = A + B/(T - T_\infty) \tag{3}$$

where the constants B and T_∞ have the values 620 and 74°K and $A = 7.1 \times 10^{-17}$ sec.

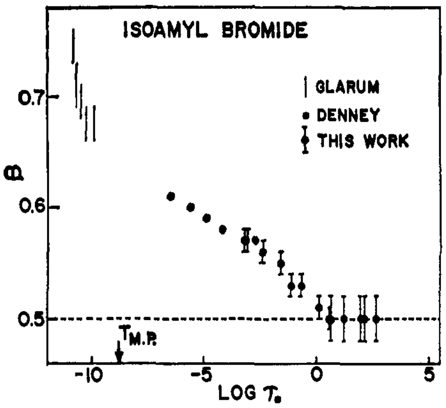

Figure 5. Plot of the parameter β for isoamyl bromide as a function of log τ_0.

This fit is shown by the plot in Figure 4 of log $\beta\tau_0$ against $10^2/(T - 74°\text{K})$, in which the data of Denney[4] and Glarum[3] are also plotted. Equation 3 is valid from 145°K to the lowest temperature of measurement; on the other hand, significant deviations from an Arrhenius rate law of the form log $\beta\tau_0 = A' + B'/T$ become apparent below 200°K.

The variation of the parameter β, which defines the time dependence of the relaxation process in the liquid, is best shown by the plot in Figure 5 of β as a function of the characteristic time τ_0 of the dispersion. From this plot, the value of β best fitting the data is seen to change from 0.7, as derived from Glarum's microwave measurements from 298 to 198°K, to numbers in the range 0.57–0.50 below 122°K as determined in the present work. It should be pointed out that the best values of β are somewhat uncertain at both ends of the temperature range for the following reasons: in Glarum's results because of the limited number and accuracy of measurements in the frequency range 10^9–10^{10} Hz, and in the present work because of circuit noise in measurements at times greater than 10^2 sec. Even so, the course of the variation of β with increasing characteristic time τ_0 is clear: a gradual decrease with indications of approaching a limiting value $\beta = 0.50$ (dotted line in Figure 5). A possible significance of this behavior is discussed later. In presenting the results over this very wide range of relaxation times in terms of a single parameter β, it should be pointed out that the data of Glarum are not represented within their experimental error by eq 1, there being systematic errors exceeding the estimated accuracy of the data. These differences are discussed by Glarum;[13] we have chosen values of β for best average fit of these data. Detailed examination of the suggested changes in behavior at temperatures above 200°K will have to await more complete measurements at frequencies above 10^9 Hz.

Discussion

The temperature dependence of the static dielectric constant ϵ_0 is interesting in that the values are of the magnitude expected for a normal polar liquid and show no signs of an approach to a Curie point or "$^4/_3\pi$ catastrophe"[14] at lower temperatures. Such usual criteria as melting point, entropy of melting, and other

[13] S. H. Glarum, Ph.D. Thesis, Brown University, Providence, R. I., 1959.

[14] J. H. Van Vleck, *Ann. N. Y. Acad. Sci.*, **40**, 293 (1940).

equilibrium properties given no indication that isoamyl bromide is anything but a normal polar liquid. More immediately relevant is the value of dipole moment calculated from Onsager's equation[15] at 122°K using the measured ϵ_0 of the liquid, the estimated value of the index of refraction, and the extrapolated value of the liquid density. This calculated dipole moment is 1.90 D, which is in excellent agreement with the value 1.95 D obtained from benzene solution measurements[16] when the assumptions involved both in Onsager's equation and in the theory of solution dipole moment measurements are considered.

We may further note that the measured values of ϵ_0 show no signs of the sort of behavior inferred by Reddish[17] from transient charge measurements on poly(vinyl chloride) as the glass temperature was approached: namely, that the static dielectric constant increased rapidly with decreasing temperature, indicating a possible infinite value, or "Curie point" at finite temperature as predicted by Lorentz field theories (for a review of these theories, see Cole[18]) or at lower temperatures by Pirenne's extension of the Onsager model.[19]

The relaxation behavior of isoamyl bromide as defined over 13 decades of time by this and earlier work is striking in two respects. The first is that the temperature dependence of τ_0 is so well described by eq 3 down to the glass temperature. The second is that the change in the frequency or time dependence of the relaxation gives strong indications of a limiting low-temperature behavior characterized by the value $\beta = 0.50$ in eq 1 and 2.

Empirical rate equations of the form of eq 3 were introduced many years ago by Vogel[20] to describe viscosities of liquids at low temperatures; these equations are also similar in form to the Williams–Landel–Farry (WLF) equation[21] which is widely used to describe rates of viscoelastic processes in polymer systems. This form of equation was also found to describe dielectric relaxation times of aliphatic alcohols[9,10] and of other alkyl halides[4] at low temperatures; these data, however, did not extend to as long times as the present results.

The close relation between rates of dielectric relaxation and viscous flow is shown by the fact that Denney's data for viscosity of isoamyl bromide[22] in the range 10^2–10^9 poise at temperatures from 137 down to 113°K can be fitted within their accuracy by the equation $\log \eta = A_\eta + B_\eta/(T - T_\infty)$ with values $B_\eta = 622°\text{K}$ and $T_\infty = 74°\text{K}$ which are very nearly the same as the corresponding values in eq 3 to fit the dielectric data. Such a close connection at the molecular level was of course proposed by Debye in his classic model of dipole reorientation by rotational diffusion damped by viscosity η of a surrounding continuous medium.[23] This theory gives the relation $\tau = 3\eta V/kT$, where V is the volume of the molecule, assumed spherical. This relation predicts essentially the observed proportionality (variations of the extra factor kT are insignificant compared to exponential changes of τ_0 and η), but fails quantitatively as the molecular volume V to satisfy the τ–η relation has the unrealistically small value 5.7×10^{-24} cm^3, as pointed out by Denney.[22] Numerous authors have emphasized the real need for a theory in which both viscosity and relaxation are accounted for in terms of intermolecular forces.

Two types of relaxation time theory have been proposed to account for functions having the form of eq 3 or the related WLF equation. The first type makes use of free-volume concepts; the difficulties with the concept and theories based on it have been discussed by Adam and Gibbs.[24] These authors have proposed an alternative explanation in terms of cooperative rearrangements of interacting molecules with the supposition that there is a minimum size of cooperative region which can rearrange independently of its environment. The temperature dependence of this size, and of activation energy for reorientations which is assumed proportional to the size, is then evaluated in terms of the configurational entropy of the liquid. As in the Gibbs–DiMarzio theory,[25] based on a quasi-lattice calculation of polymer configurations, this entropy monotonically increases from essentially zero at a transition temperature T_2 (corresponding to the temperature T_∞ in eq 3) and can be estimated from specific heats of the equilibrium melt and the glassy state. The model is conceptually attractive in its emphasis on the cooperative aspect of molecular reorientations at low temperatures and has led to remarkably accurate predictions for several systems for which results of adequate specific heat measurements are available. Unfortunately, such an application is not possible in our case as we have been unable to find any specific heat data for isoamyl bromide in the temperature range of interest. Such data would be very useful, as they would permit a test of the theory in terms of a simple polar liquid rather than polymers for which the theory was primarily developed.

Neither of the theories for the temperature dependence of τ_0 makes any prediction of the frequency dependence of the relaxation function, or what is equivalent, the time-dependent correlations of dipole orientations. Such correlation functions as developed for dielectrics by Kubo,[26] Glarum,[3] and Cole [27] are directly related to the "transient dielectric constant" or response function $\epsilon(t)$ and, by Laplace transformation, to the complex dielectric constant $\epsilon^*(i\omega)$.

Although deviations from the familiar Debye equation (obtained by setting $\beta = 1$ in eq 1) are often attributed to a distribution of relaxation times or activation energies for reorientations of individual molecules, satisfactory molecular explanations of the necessary form of such distributions are usually lacking, particularly when, as in the present case, a continuous distribution of times shorter than a maximum value τ_0 must be accounted for in terms of the dynamics of motion of small molecules. A different kind of approach was proposed by Glarum,[3] who assumed two concurrent mechanisms of relaxation: an exponential decay of dipole correlation with characteristic time τ_r and a

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(15) L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).

(16) A. Parts, *Z. Physik. Chem.*, **B12**, 312 (1931).

(17) W. Reddish in "Transitions and Relaxations in Polymers," R. F. Boyer, Ed., Interscience Division of John Wiley and Sons, Inc., New York, N. Y., 1966, pp 123–137.

(18) R. H. Cole, *Progr. Dielectrics*, **3**, 49 (1961).

(19) J. Pirenne, *Helv. Phys. Acta*, **22**, 479 (1949).

(20) H. Vogel, *Physik. Z.*, **22**, 645 (1921).

(21) M. L. Williams, R. L. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).

(22) D. J. Denney, *J. Chem. Phys.*, **30**, 159 (1959).

(23) P. Debye, "Polar Molecules," Dover Publications, Inc., New York, N. Y., 1945.

(24) G. Adam and J. H. Gibbs, *J. Chem. Phys.*, **43**, 139 (1965).

(25) J. H. Gibbs and E. A. DiMarzio, *ibid.*, **28**, 373 (1958).

(26) R. Kubo, *J. Phys. Soc. Japan*, **12**, 570 (1957).

(27) R. H. Cole, *J. Chem. Phys.*, **42**, 637 (1965).

mechanism in which otherwise unspecified defects cause complete loss of correlation whenever one reaches a molecular site. By assuming that the motion of these defects has the nature of one-dimensional diffusion with time constant τ_d, Glarum[18] showed, for suitable values of the ratio τ_d/τ_r, this model to predict relaxation functions closely resembling the empirical skewed-arc function for β in the range $0.5 < \beta < 1$. In particular, his result gives exactly the function $(1 + i\omega\tau_0)^{-1/2}$ for $\beta = 0.5$ if the reorientation and diffusion times are the same, $\tau_d = \tau_r = \tau_0$, and the Debye function $(1 + i\omega\tau_0)^{-1}$ for $\tau_r = \tau_0 \ll \tau_d$.

Although Glarum's model is admittedly crude and highly simplified, it has two important features: first, the observed behavior can be reproduced without invoking distributions of exponential decay functions, the deviations from the simple Debye behavior arising from the fact that the diffusive or random-walk mechanism of cooperative interactions has a nonexponential time dependence; and, second, a limiting low-temperature behavior with $\beta = 0.50$ corresponds to equal time of the assumed local molecular reorientations and cooperative loss of correlation. A proper molecular interpretation of the significance of the second result obviously requires a more fundamental justification of the model from molecular dynamics of liquids.

Anderson and Ullman[28] have recently developed a modified treatment of molecular relaxation in the spirit of Glarum's approach, in which the probability of molecular reorientations is assumed to vary with fluctuations in the environment and to satisfy an Ornstein–Smoluchowski equation[29] for Brownian motion of a bound particle as a function of a fluctuation variable. This variable is called a free volume without implying that this description or connotation is to be taken too literally. As for Glarum's result, their development leads, for appropriate values of somewhat similar parameters, to predictions of relaxation functions resembling the skewed arc function; for details, their interesting paper should be consulted.

From the discussion above, characteristic features of the observed relaxation in isoamyl bromide have intriguing and suggestive similarities to recent theories which have the common feature that they invoke cooperative interaction effects. These theories are still far from explaining both temperature and frequency dependence of the observed relaxation effects within a single framework having a reasonably direct connection with molecular dynamics, but they suggest viewpoints and directions of attack for further developments of theory. The fact that the present results are broadly similar to those for other "cold" liquids of quite different molecular composition suggests the need for a quite general form of explanation.

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(28) J. E. Anderson and R. Ullman, *J. Chem. Phys.*, 47, 2178 (1967).

(29) G. E. Uhlenbeck and L. S. Ornstein, *Phys. Rev.*, **36**, 823 (1930).

The Quadrupole Moments of Some Simple Molecules

A. D. Buckingham,[1a] R. L. Disch,[1b] and D. A. Dunmur[1a]

Contribution from the School of Chemistry, University of Bristol,
Bristol 8, England, and from the Department of Chemistry, Columbia University,
New York, New York 10027. *Received November 29, 1967*

Abstract: The birefringence induced in a number of simple gases by an electric field gradient has been measured. In general, this birefringence is composed of two terms, a temperature-dependent one due to the orientation of quadrupolar molecules, and a small temperature-independent term B. Values are derived for the quadrupole moments of carbon dioxide, nitrogen, oxygen, ethane, and ethylene by neglecting contributions from B. For isotropically polarizable molecules, only B contributes to the birefringence; it has been measured for methane, argon, and sulfur hexafluoride. The importance of contributions from B to the induced birefringence in anisotropic molecules is considered, and an experimental value of B is obtained for H_2. Values are recorded for the effective quadrupole moments of the dipolar molecules COS, CO, and N_2O. These values are compared with center-of-mass quadrupole moments calculated from rotational g factors and magnetic susceptibility anisotropies. The differences between these quadrupole moments yield values for some new polarizabilities describing the behavior of molecules in electromagnetic fields.

In one of his classic early papers,[2] Debye showed how measurements of the static dielectric constant ϵ of a gas at low pressure lead to molecular dipole moments μ

$$\epsilon - 1 = 4\pi N[\alpha + \mu^2/(3kT)] \tag{1}$$

where N is the number of molecules in unit volume and α is the mean molecular polarizability. The polarizability contribution represents distortion of the electronic and nuclear arrangement by the applied electric field, and the term in $\mu^2(kT)^{-1}$ describes the effect of dipolar orientation (*i.e.*, distortion of the molecular rotation).

The dipole is the first moment of the electric charge

$$\mu = \sum_i e_i z_i \tag{2}$$

where z_i is the average distance of the ith charge e_i along the z axis fixed in the molecule. Molecular dipole moments have the magnitude of the Debye unit (1 D =

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(1) (a) University of Bristol, Bristol, England; (b) Columbia University, New York, N. Y.

(2) P. Debye, *Physik. Z.*, 13, 97 (1912).