mole % a second complex is making its appearance although still at a low concentration.

We have one reservation to make with regard to these deductions. It is possible although not likely that the spectrum of a polynuclear anion, such as $Ni_2Cl_6^{2-}$ or $Ni_2Cl_7^{3-}$ in which each nickel retains a tetrahedral coordination geometry, might be indistinguishable from that of the mononuclear $NiCl_4^{2-}$ anion.

Temperature Effects. The results presented here for the effect of temperature on the $^3T_1(F) \rightarrow {}^3T_1(P)$ absorption of a 33.3 mole % mixture are in agreement with Morrey's rule[3] for the behavior of a one-entity system; namely, A varied linearly with temperature at every wavelength.

Although we do not believe that Morrey's rule has general validity,[11] we propose that the small changes in spectral profile observed in the present case are reasonably consistent with the view that absorption was due to a single species of molecule ion. The most conspicuous changes were a small band broadening accompanied by a decrease in the intensity of maximum absorption. The band energies changed very little, but the direction of this small change—a blue shift with increasing temperature—was contrary to that expected from elementary considerations in terms of a Franck–Condon model.

Concluding Remarks. In summary we conclude that over the range 0.1–33.3 mole % $NiCl_2$ all of the nickel in $NiCl_2$–Bu_3BzPCl melts was present as $NiCl_4^{2-}$ to within a small uncertainty.

We are led to the following point of view. Upon dissolution of $NiCl_2$ in molten Bu_3BzPCl virtually every mole of $NiCl_2$ reacts with 2 moles of chloride ions from Bu_3BzPCl to form 1 mole of $NiCl_4^{2-}$ molecule anions. At 33.3 mole % $NiCl_2$ the free chloride ions are consumed and the melt may be regarded as the liquid compound $(Bu_3BzPCl)_2NiCl_4$. For homogeneous mixtures containing somewhat more than 33.33 mole % $NiCl_2$, a second nickel-containing entity must be present in addition to $NiCl_4^{2-}$. Undoubtedly this second entity is present in equilibrium with $NiCl_4^{2-}$ at all concentrations, but the equilibrium must strongly favor $NiCl_4^{2-}$ except at very small free chloride ion concentrations.

The fact that the Bouguer–Beer law is obeyed at all compositions not only implies that the coordination sphere of nickel remains unchanged over the entire composition range, it also implies that the surroundings of the chloronickel complex do not change sufficiently to perturb the intraconfigurational states of nickel in any different way at high concentrations than at low concentrations. This invariance of the effect of the surroundings, one might suppose, may be associated with the large size of the phosphonium cations so that the $NiCl_4^{2-}$ anions are primarily in contact with phosphonium cations at all compositions. Only the anionic composition is altered by changing the nickel content, and anion–anion contacts are presumably infrequent. The latter pictorial details cannot, however, be formulated quantitatively because there is very little systematic information on the effect which changes in the surroundings have on the states of halonickel complexes.

Acknowledgments. We gratefully record our thanks to C. R. Boston and W. M. Ewing for generous aid during this investigation, and to H. L. Holsopple for preparing the phosphonium salt.

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[11] An analysis of Morrey's rule will be published by J. Brynestad and G. P. Smith.

Relation of the Relaxation Time of Electric Dipoles in Condensed Phase to Molecular Structure

A. Bondi

Contribution from the Shell Development Company, Emeryville, California.
Received January 3, 1966

Abstract: The relaxation rate of polar molecules in the condensed phase is treated as proportional to the frequency of a torsional oscillator in the periodic force field of its neighbors. Hence a reduced relaxation time $\tau_i^* \equiv \tau(E^\circ/I_i)^{1/2}$ can be defined, where E° is the appropriate lattice energy and I_i is the applicable principal moment of inertia of the dipole molecule. A corresponding states plot of log τ_i^* *vs.* the inverse of the common reduced temperature T^* leads to bands characteristic of structurally related "families" of compounds rather than a universal correlation. A simple geometrical structure parameter (characterizing the surface roughness of molecules) is proposed as a third correlating parameter. Typical of the correlation within a given band is the wide range of normal haloalkanes for which log τ^* *vs.* $(T^*)^{-1}$ falls on a single curve, regardless whether as pure liquid or admixed with solvents including solution in viscous paraffin oil. It appears that replacement of E° by the geometric mean lattice energy, etc., suffices to correlate relaxation times of solutions. Reference to the solvent viscosity (or any other viscosity), long recognized as unsatisfactory, is thereby obviated.

The present work has been undertaken as part of an effort to develop correlations of rotational and mass diffusion in the condensed phase without reference to viscosity. Macroscopic viscosity has been a moderately successful descriptor of liquids for predicting rotational and mass diffusion in simple systems but has become increasingly unsatisfactory for systems where small solute molecules diffuse in liquids com-

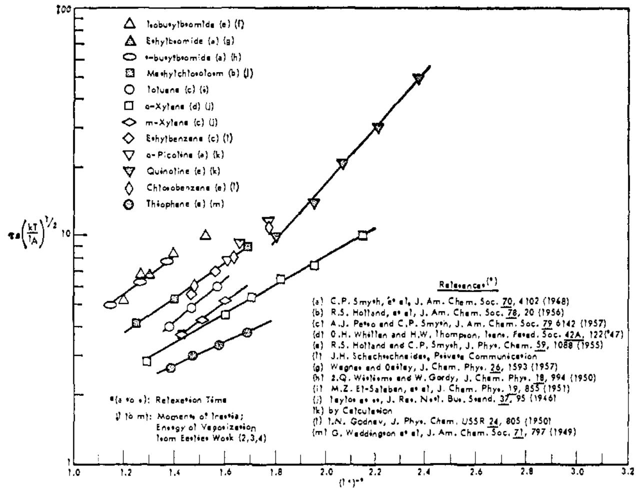

Figure 1. Electric dipole relaxation time of rigid molecules as a measure of hindered external rotation in the liquid phase.

posed of larger molecules[1] and is entirely useless for the description of their movement in high-polymer melts.

The increasing scientific and technological interest in polymer systems suggested a completely new approach to the problem using rotational diffusion as a comparatively simple first example. Earlier experience with the correlation of transport properties of liquids[2-4] suggested that here too the medium could be characterized by its Prigoginian energy and kinetic parameters. The rotating molecules on the other hand were to be treated as torsional oscillators in the periodic force field of their neighbors. The scope of the present phase of the work is best characterized as exploratory, *i.e.*, concerned with the demonstration of the feasibility and inherent limitations of the method rather than with the development of a finished engineering tool. Even at this stage the treatment yields sufficient new insights to encourage its application by others.

Rigid Hindered Rotors

The average rotation rate of classical free rotors in moderately dense gases is given by kinetic gas theory[5] as $1.47(kT/I_i)^{1/2}$, where I_i is the appropriate principal moment of inertia. In the case of dipole molecules rotating in resonance with an alternating electric field, "appropriate" means that moment of which the axis is normal to the field producing maximum coupling with the permanent electric dipole. If the polar molecules in a liquid were rotating freely, the product $\tau(kT/I_i)^{1/2}$ should be near unity, where τ is the well-known dipole relaxation time.[1] (The field correction from macroscopic to microscopic relaxation time has been omitted in the present order of magnitude argument because it changes τ only by a factor ranging between 0.5 and 1.[1]) A plot of $\tau(kT/I_i)^{1/2}$ *vs.* the Prigoginian reduced temperature T^* $(=5cRT/E°)$ defined earlier[2,3] for several liquids composed of small rigid molecules is shown in Figure 1.

It is evident that $\tau(kT/I_i)^{1/2}$ approaches unity asymptotically at high temperatures ($T^* \approx 1$ at about the atmospheric boiling point). However, at the low reduced temperatures of primary interest in the present work the relaxation time is many times longer than corresponds to free rotation.

A reasonable rule of thumb is that a slowdown by a factor of five makes a rotor resemble a torsional oscillator. The observed retardation of dipole relaxation is connected with the reduction of intermolecular distances as $T < T_b$ to the point that the rotating molecule begins to experience a nonuniform force field.

A theory of the rotation rate of a polar molecule in the periodic force field of its neighbors proposed by Bauer[6] can be used as point of departure. Assuming that the shape of the barrier experienced by the molecule during a rotation on the crystal-like lattice is $W = W_0(1 - \cos\alpha)$, where α is the angle relative to its starting (equilibrium) position, and that the transmission coefficient of the barrier equals unity, Bauer obtains

$$\tau\left(\frac{W_0}{I_i}\right)^{1/2} = A\left(\frac{kT}{W_0}\right)^{1/2}\exp(W_m/kT) \qquad (1)$$

where W_m is the value of W at the angle corresponding to the bottom of the potential energy well, I_i is the appropriate principal moment of inertia of the molecule, and A is a numerical constant that varies between 1.8 and 4.4 depending on the details of the models chosen.

In spite of its attractive simplicity, this theory has not been applied to liquids and has remained dormant for 20 years. The appropriate axis of rotation and therefore I_i can generally be chosen by inspection. The calculation of moments of inertia is a bit tedious, but many are now available from the literature so that only W_0 and W_m remain to be estimated. With rigid molecules one could obtain W_0 by application of the same periodic barrier assumption to the interpretation of the heat capacity of the liquid under consideration.[7]

When heat capacity data are not available, one might make the assumption that $W_0 \sim E°$, the standard energy of vaporization.[2] Then one can define a reduced molecular relaxation time for external rotation

$$\tau_i^* = \tau_r(E°_m/I_i)^{1/2}$$

Since numerator and denominator in $(E°_m/I_i)^{1/2}$ rise generally in parallel with increasing molecule size and variations are damped by the $^1/_2$ power, this reducing parameter does not vary over a very wide range ($E_m = E°/N_A$, where N_A = Avogadro's number).

Both ratios kT/W_0 and kT/W_m should then be proportional to the reduced temperature T^* mentioned earlier. They might even be of the same order as T^*. The reasonableness of the theory can be tested by examining the absolute value of τ^* predicted and the linearity of log $(\tau^*/T^{*1/2})$ *vs.* $1/T^*$. Taking $kT/W_0 \approx kT/W_m \approx T^*$ one obtains with $A = 4$ for $T^* = 0.7$ (in the middle of the liquid range) $\tau^* \approx 16$, while the observed values are $\sim 30 \pm 10$, at least in the right order of magnitude. Over the usual short temperature ranges $T^{1/2}$ is unimportant and log $\tau \sim 1/T$ is well established.

The possibility of a universal relation log τ^* *vs.* $1/T^*$ hinges upon the universality of the ratios $W_m/E°$. One can expect these ratios to be constant only within

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(1) C. P. Smyth, "Dielectric Behavior and Molecular Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(2) A. Bondi, *A.I.Ch.E. J.*, 8, 610 (1962).

(3) A. Bondi, *Ind. Eng. Chem. Fundamentals*, 2, 95 (1963).

(4) A. Bondi in "Rheology," Vol. 4, F. R. Eirich, Ed., Academic Press Inc., New York, N. Y., 1966.

(5) K. F. Herzfeld and H. M. Smallwood in "Treatise on Physical Chemistry," Vol. II, H. S. Taylor and S. Glasstone, Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1951.

(6) E. Bauer, *Cahiers Phys.*, 20, 1 (1944).

(7) A. Bondi, "Physical Properties of Molecular Crystals and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1966.

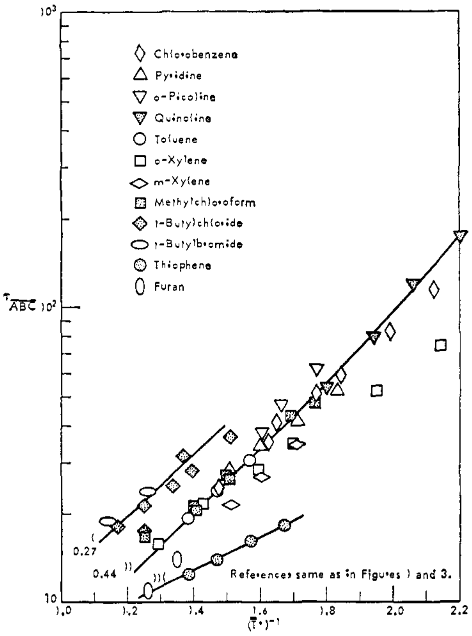

Figure 2. Generalized dipole relaxation time of liquids composed of rigid molecules (random rotation).

fixed families of compounds, depending upon the relative role played by dipole orientation energies, dispersion energy, and molecular geometry in determining the magnitudes of W_0, W_m, or $E°$.

The somewhat disappointing spread of curves on the plot of τ_i^* *vs.* $1/T^*$ in Figures 2 and 3, is therefore, not surprising. Uniformity is improved somewhat by the choice of the largest principal moment of inertia of a molecule for the reducing parameter. Close inspection of the curves suggests the existence of three distinct groups of compounds. The least hindered rotors at the bottom of the graph are the heteroaromatics with smooth molecular surface; the most hindered rotors, high on the graph, are large (branched) alkyl halides with very bumpy molecule surface and an intermediate band, largely composed of moderately substituted aromatic ring compounds. A suitable measure of molecule smoothness should then serve as third parameter for the characterization of molecular rotation.

Roughness of Molecule Surfaces

The roughness of plane surfaces is conventionally expressed as the root-mean-square deviation from the location of a hypothetical "average plane" surface. A second number is required to describe the average width of the roughnesses, unless one assumes a regular shape, such as a hemisphere, for the average roughness, which is characterized by a single length.

Characterization of the surface roughness of molecules also starts with the establishment of a hypothetical average surface, the deviation from which is a measure of the average height of the roughness. The total range of van der Waals radii is so small that a second number to characterize the average width of the surface roughness does not seem to be necessary.

The molecular model for making the roughness estimate is identical with that used for estimating the van der Waals volume of molecules.[8] An obvious

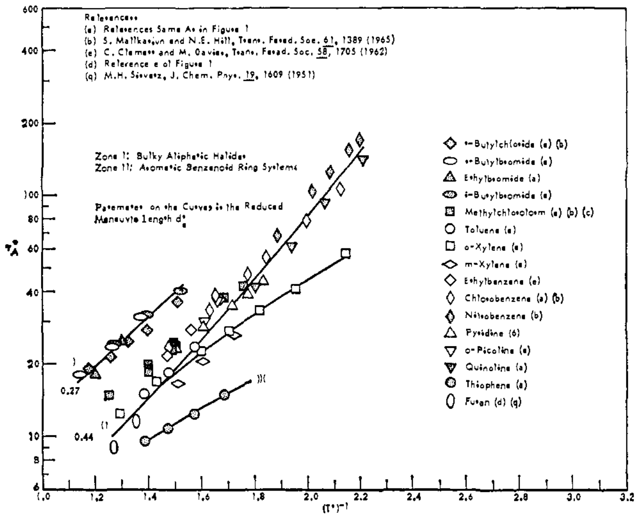

Figure 3. Generalized dipole relaxation time of liquids composed of rigid molecules (rotation around shortest axis).

measure of roughness d_r is

$$d_r = \bar{r} - (r_2^2 - m^2)^{1/2}$$

where

$$\bar{r} = \frac{1}{n}\sum_{i=1}^{i=n} r_i$$

is the average van der Waals radius of the atoms on the molecule under consideration and

$$m = \frac{r_2^2 - r_1^2 + l^2}{2l}$$

where the r_i's are the van der Waals radii of neighboring bonded atoms, taking $r_2 > r_1$, and l is the chemical bond length between atoms 1 and 2. The roughness corrected ("effective") average distance between molecules $d_e = d_s - d_r$, where the average distance between molecules is taken as

$$d_s = \frac{V_w}{A_w}(V^* - 1)$$

where V_w and A_w are the volume and surface area, respectively, per mole of molecules.[8] In the molecular weight range of interest in the present context the reduced volume $V^* \equiv V/V_w$ is essentially a universal function of T^*.[9] A convenient dimensionless form of d_e is

$$d_e^* = V^* - (d_r A_w/V_w) - 1$$

Typical values of d_e^* for the middle of the liquid range ($V^* = 1.8$) have been entered in Table I and as the third parameter in Figure 3. It is apparent that d_e^* serves as the ordering parameter for the reduced relaxation time of pure liquids composed of rigid molecules.

The foregoing should be regarded primarily as a suggestion for further research. Reasoning from macroscopic mechanics to events on molecular scale is unsafe if not backed up by careful analysis on the basis of first principles. Since an analysis has not yet been carried out, further elaboration of the effect of molecule roughness on rotation in the liquid state would be premature.

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(8) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

(9) A. Bondi and D. J. Simkin, *A.I.Ch.E. J.*, **6**, 191 (1960).

Table I. Surface Roughness of Molecules

Type	Bond	d_r, A	Typical compounds	d_r, A	d_e^* at V^* = 1.8	d_{min}^*
Alkanes	C–C (side)	0.26	n-C_7H_{16}	0.31	0.37	
	C···C (side ╲╱ C	0.57	n-$(CH_2)_x$	0.33	0.37	0.11
	C–H	0.27	Neopentane	0.36	0.27	−0.04
Perfluoroalkanes	C–F	0.18	n-C_7F_{16}	0.31	0.32	
	F···F (or CF_2) ╲╱ C	0.47	n-$(CF_2)_x$	0.32	0.33	0.09
Chloroalkanes	C–Cl	0.30	EtCl	0.31	0.34	0.1
	Cl···Cl ╲╱ C	0.75	t-BuCl	0.37	0.27	−0.15
	C···Cl ╲╱ C	0.66	$MeCCl_3$	0.47	0.14	−0.17
Bromoalkanes	C–Br	0.29	EtBr	0.31	0.35	−0.04
	Br···Br ╲╱ C	0.92	t-BuBr	0.37	0.27	−0.04
	C····Br ╲╱ C	0.58				
Aromatic rings	C_{ar}–C_{ar}	0.14	Benzene	0.34	0.38	0.14
	C_{ar}–H	0.53	Chlorobenzene	0.29	0.44	0.15
	C_{ar}–N_{ar}	0.16	Pyridine	0.30	0.44	0.16
	C_{ar}–O_{ar}	0.16	Furan	0.28	0.44	0.12
	C_{ar}–S_{ar}	0.22	Thiophene	0.33		

External Rotation of Flexible Molecules

The relaxation-time distribution of long chain molecules with a permanent electric dipole at one end has been determined sufficiently well to permit at least approximate resolution into two primary relaxation times: that for rotation around the long axis, τ_1, and that for end-over-end tumbling, τ_2.[10] Owing to the absence of data in the corresponding high-frequency region, τ_1 can be estimated only with limited accuracy, while τ_2 is probably quite reliable.

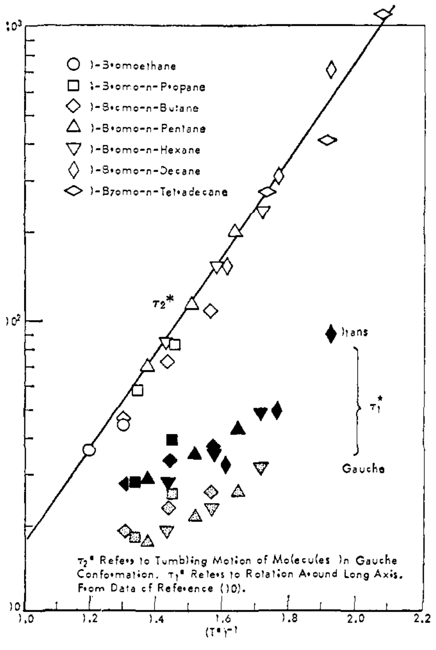

Figure 4. Resolved generalized dipole relaxation times of 1-bromo-n-alkanes.

The data in Figure 4 reveal a striking difference between the two types of rotation. Rotation relaxation time τ_1 (around the long axis of the molecules) rises only very slowly with decreasing temperature, especially for the series n-propyl to n-hexyl bromide. The data for ethyl bromide cannot be incorporated into this series because the two types of rotation cannot be separated very well. It is doubtful whether the slightly smaller scatter obtained with the moment of inertia of the *gauche* conformation in the reducing parameter for τ_1 has physical significance. The end-over-end tumbling motion τ_2, by contrast, can be correlated on a single curve from ethyl through hexyl bromide only if the *gauche* conformation (at the polar end) is assumed as predominant.

The coincidence of all points on a single curve suggests that n-alkanes in the liquid at $T < T_b$ rotate like rigid rods at least up to $N_c = 14$. Their molecular flexibility should become important in rotational motion at $N_c \geq 16$. There should be a chain length beyond which only the terminal segment containing the dipole participates in rotational motions, *i.e.*, beyond which τ (at a given value of T^*) becomes essentially independent of chain length. This "critical" chain length, which should be a function of T^*, can only be established by further experiments.

Rotation in Solutions and Mixtures

The rotational relaxation time of polar substances in nonpolar solvents is of greater scientific and technological interest than that in pure liquids because of the elimination of the complication of extensive dipole–dipole interaction and because of the technical im-

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(10) K. Higasi, K. Bergmann, and C. P. Smyth, *J. Phys. Chem.*, **64**, 881 (1960).

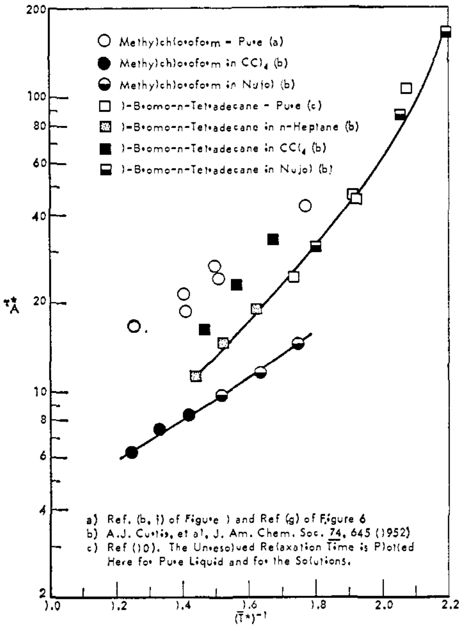

Figure 5. Generalized dipole relaxation time of polar molecules in solutions.

portance of dielectric energy losses due to polar substances in insulating liquids and polymers.

At infinite dilution each polar molecule is completely surrounded by solvent molecules. Only if solvent and solute molecule are of equal size is the interaction energy between solvent and solute given by

$$E^\circ = (E_i{}^\circ E_2{}^\circ)^{1/2} - F^{\mathrm{E}}$$

In the more general case of different molecule size the averaging should be carried out on the energy per unit surface area (per molecule)

$$\bar{E}^\circ = \left[\frac{E_1{}^\circ}{A_{\mathrm{w}}(1)}\frac{E_2{}^\circ}{A_{\mathrm{w}}(2)}\right]^{1/2} A_{\mathrm{w}}(2) - F^{\mathrm{E}}$$

where index (2) refers to the solute, and F^{E}, the excess free energy of mixing (from phase equilibrium data), is a measure of the specific interaction energy between molecules of solute and solvent.

At finite concentration of solute one must also consider the molecules of solute contained in the "cage" wall surrounding the test molecule. Then

$$\bar{E}^\circ = A_{\mathrm{w}}(2)\left\{\frac{E_2{}^\circ}{A_{\mathrm{w}}(2)}\left[x_1{}^2\frac{E_1{}^\circ}{A_{\mathrm{w}}(1)} + x_2{}^2\frac{E_2{}^\circ}{A_{\mathrm{w}}(2)} + 2x_1x_2\left(\frac{E_1{}^\circ}{A_{\mathrm{w}}(1)}\frac{E_2{}^\circ}{A_{\mathrm{w}}(2)}\right)^{1/2}\right]\right\}^{1/2} - F^{\mathrm{E}}$$

In either case the reduced relaxation time of the solute is $\tau(E^\circ/I_i)^{1/2} \equiv \bar{\tau}^*$.

The appropriate reduced temperature is

$$\bar{T}^* \equiv 5\bar{c}RT/\bar{E}^\circ$$

where the property c equals one-third of the number of external degrees of freedom, $\bar{c} = (c_1 + c_2)/2$ in dilute solution, and $\bar{c} = [(1 + x_1)c_1 + (1 - x_1)c_2]/2$ for concentrated solutions. When c_1 is not very different from c_2, it is permissible to form a temperature-reducing parameter for the mixture as

$$\theta_{\mathrm{L}} = [\theta_{\mathrm{L}}(1)\cdot\theta_{\mathrm{L}}(2)]^{1/2}$$

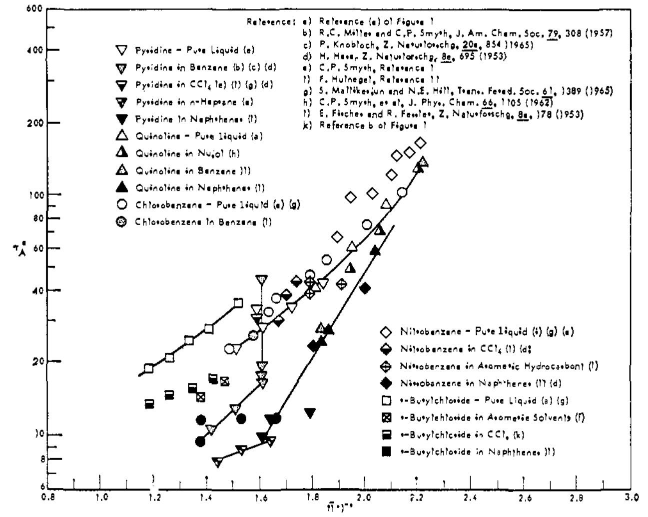

Figure 6. Generalized dipole relaxation time of rigid polar molecules in various solvents (note the lower level of the solution in naphthenic solvents).

because then $(c_1c_2)^{1/2}$ does not differ much from $(c_1 + c_2)/2$; $\theta_{\mathrm{L}} \equiv E^\circ/5cR$.

Ideally a plot of the reduced relaxation time of the solute should be a function of $\bar{T}$ only, independent of the solvent. The most severe test of this approach, the correlation of data points obtained in a nonviscous solvent with those in a very viscous solvent on a single curve, has been very well met by the examples shown in Figure 5. The close fit of the solution and pure liquid data for *n*-tetradecyl bromide to a single curve is particularly gratifying.

The sharp reduction of the relaxation time curve of the methylchloroform solutions below that for the pure liquid, on the other hand, is in rather good agreement with expectation from the "bumpiness" parameter discussed earlier, because of the smoothness of the solvent molecules compared with those of the solute. A similar drop below the pure liquid relaxation curve is observed with solutions of *t*-butyl chloride, probably for the same reason.

The dearth of extended runs of precision relaxation time *vs.* temperature on solutions of rigid polar molecules makes it difficult to obtain good evidence for agreement. An indication of the general applicability of the correlation is again obtained from the proximity of the data for quinoline in the viscous Nujol to those of the pure liquid (Figure 6). The scatter of the other solution data on the same figure may be due to the fact that almost every solution point is just a single datum, often involving a different author for each point.

An Unsolved Puzzle

The viscosity-reduced dipole relaxation time τ/η of solutions of polar molecules in cyclohexane has often been observed as rather lower than in other solvents. Recently Hufnagel and his students[11] demonstrated that this peculiarity of excessively short (τ/η) relaxation times is common to all naphthenes and is the more pronounced the smaller the molecule. One might have ascribed this effect to the somewhat higher viscosity of naphthenes than of other solvents of the same molal volume. The

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(11) F. Hufnagel, *et al.*, *Z. Naturforsch.*, **18a**, 769 (1963); **20a**, 630 (1965).

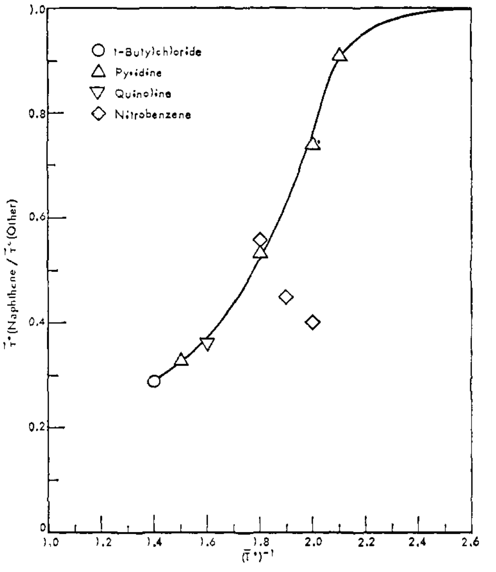

Figure 7. Ratio of dipole relaxation time of rigid polar molecules in naphthene solvents to that in other nonpolar solvents as a function of reduced temperature.

present correlation, which makes no explicit reference to viscosity, might have been expected to suppress this "naphthene effect". Even cursory inspection of Figure 6 reveals, however, that solutions in naphthenes exhibit depressed reduced relaxation times in the present correlation as well.

Expressing the naphthene effect as τ^*(naphthene)/τ^*(pure liquid), one finds that the effect is primarily a function of the reduced temperature, regardless of the compound involved. A plot of τ^*_{A}(naphthene)/τ^*_{A}(pure liquid) *vs.* T^* in Figure 7 shows that the effect decreases with decreasing reduced temperatue and seems to vanish at $\bar{T}^* = 0.45$. This relation is, of course, a reflection of the molecule size effect noted by Hufnagel. A much larger range in absolute temperature needs to be covered in experiments in order to obtain better insight into the possible origins of this effect.

Other Work

The importance of the moment of inertia for dipole relaxation had been noted earlier by Powles[12] and by Hill.[13] However, neither of these authors used his observations as a basis for a systematic correlation of dipole relaxation data.

Conclusions

The present treatment of the dipole relaxation was motivated by the need for methods to predict the rotation and diffusion rates for small molecules and molecule segments in polymeric liquids, where macroscopic viscosity is obviously meaningless as a correlating parameter. The success of the new correlation in handling Nujol solvent augurs well for its applicability in the intended field.

A useful by-product of the work is the definition of a generalized reference system, deviations from which are more easily detected than has been possible before. Already some of these deviations suggested the introduction of a new "roughness" parameter into the consideration of the transport properties of liquids.

A great deal of further work will be necessary to define the barriers to the external rotation of molecules in liquids more accurately. The present assumption that these barriers are proportional to the energy of vaporization is too crude to be satisfactory in the long run. Only after that problem has been solved can one consider the correlation as a safe method to estimate dipole relaxation rates from molecular structure data.

Acknowledgment. The writer is indebted to Dr. J. H. Schachtschneider for many of the moment of inertia data used in this work, especially those of the primary alkanes in their various conformations, and to Dr. T. F. Schatzki for a valuable discussion.

[12] J. G. Powles, *Trans. Faraday Soc.*, **44**, 802 (1944).

[13] N. E. Hill, *Proc. Phys. Soc.* (London), **B67**, 149 (1954).

Isotope Effects in Optical Rotation[1]

Norah V. Cohan[2] and Hendrik F. Hameka[3]

Contribution from the Laboratory for Research on the Structure of Matter,
University of Pennsylvania, Philadelphia 4, Pennsylvania. Received June 25, 1965

Abstract: A general theory is derived for the optical rotatory power of molecules which exhibit this property only on account of isotopic substitution. The optical rotatory power is evaluated from the interaction between the nuclei and the radiation field only, and it is concluded that this is a good approximation for infrared light. Detailed calculations are performed for the molecules CHDBrCl, $\mathrm{CCl^{35}Cl^{37}BrF}$, and CHDTBr. Various summation rules are derived for the vibrational rotatory strengths.

Recently an attempt was made[4] to assess the relative magnitudes of electronic and vibrational contributions to molecular optical rotatory power (OR). It was found that the vibrational contributions are usually small and that they may be neglected with respect to the

[1] This work was supported in its early stages by the National Science Foundation and later by the Advanced Research Projects Agency.

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[3] Alfred P. Sloan Foundation Fellow.

[4] H. F. Hameka, *J. Chem. Phys.*, **41**, 3612 (1964).