

## Dielectric Relaxation in Glycerine

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In liquid benzene there is an indication of a shoulder in the region of  $34000\text{ cm}^{-1}$ , which may be related to the low intensity bands discussed by Shull,<sup>3</sup> and Roothaan and Mulliken.<sup>4</sup>

\* The author acknowledges the suggestions and the study of the data made by Dr. Marcus E. Hobbs of this laboratory and Dr. Emma P. Carr, Professor Emeritus, Chemistry Department, Mount Holyoke College, South Hadley, Massachusetts.

<sup>1</sup> A. L. Sklar, *J. Chem. Phys.* **5**, 669 (1937).

<sup>2</sup> G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* **67**, 994 (1945).

<sup>3</sup> H. Shull, *J. Chem. Phys.* **17**, 295 (1949).

<sup>4</sup> C. C. J. Roothaan and R. S. Mulliken, *J. Chem. Phys.* **16**, 118 (1948).

## Dielectric Relaxation in Glycerine

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August 28, 1950

DATA of Morgan<sup>1</sup> and Mizushima<sup>2</sup> for dielectric polarization in glycerine are fitted only qualitatively by dispersion equations of the Debye type, but are not sufficiently extensive for a better function to be uniquely determined. We have made such measurements at temperatures from  $0^\circ\text{C}$  to  $-75^\circ\text{C}$ , by a bridge method over the range 50 cycles/sec. to 5 Mc/sec. and by a transient method at longer times. A typical plot of the complex dielectric constant  $\epsilon^* = \epsilon' - i\epsilon''$  at  $-50^\circ\text{C}$  is shown in Fig. 1. At high frequencies the locus is similar to the arc function found to describe many relaxation processes,<sup>3</sup> but at low frequencies it approaches a semicircle as predicted by simple dispersion theory.

The data can be fitted, except for the small high frequency "bump," by the expression

$$\epsilon^* - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty) / (1 + i\omega\tau_0)^{1-\alpha}, \quad (1)$$

where  $\epsilon_0$  and  $\epsilon_\infty$  are the limiting low and high frequency values,  $\omega$  is radian frequency, and  $\tau_0$  a characteristic relaxation time. The curve in Fig. 1 is computed from Eq. (1) with  $\alpha = 0.397$ ,  $\epsilon_0 = 64.11$ ,  $\epsilon_\infty = 4.18$ , and the value of  $\tau_0$  to fit the data is found to be  $1.26 \times 10^{-4}$  sec. The necessary values of  $\alpha$  vary only slightly with temperature, while  $\epsilon_0$  increases gradually and  $\tau_0$  exponentially with reciprocal temperature. The slight high frequency increment in  $\epsilon^*$  appears at all temperatures in a frequency range of the order 500 times that for the time  $\tau_0$ .

The distribution function  $F(\tau/\tau_0)$  for relaxation times  $\tau$  in the interval  $d \ln(\tau/\tau_0)$  is of interest, and is defined by the relation

$$\epsilon^* - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty) \int_{-\infty}^{\infty} \frac{F(\tau/\tau_0) d \ln(\tau/\tau_0)}{1 + i\omega\tau}.$$

Inversion of this equation by use of Fourier transforms gives for the  $\epsilon^*$  of Eq. (1) the result

$$F(\tau/\tau_0) = (\sin \alpha \pi / \pi) [\tau / (\tau_0 - \tau)]^{1-\alpha}, \quad \tau < \tau_0, \\ = 0, \quad \tau > \tau_0. \quad (2)$$

From this expression one finds that a broad distribution including significant contributions for  $\tau$  as small as  $\tau_0/100$  is necessary with  $\alpha = 0.4$ .

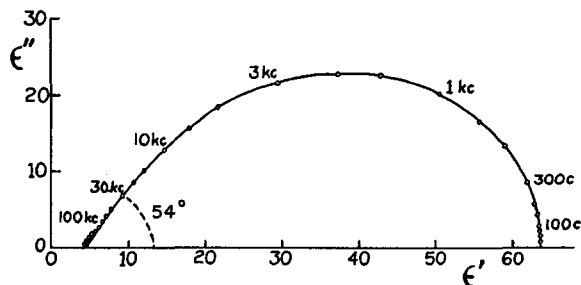


FIG. 1. Complex dielectric constant locus of glycerine at  $-50^\circ\text{C}$ . Numbers beside points are frequencies of measurement.

Yager<sup>4</sup> has suggested that the earlier data could be explained by overlapping relaxation processes, possibly corresponding to orientations of molecules and of associated groups. This hypothesis becomes unattractive in the light of Eq. (2). In the first place, the largest value of  $\tau$ , namely  $\tau_0$ , is of the order of magnitude but smaller than the value predicted by the Debye relation<sup>5</sup>  $\tau_0 = 3\eta V/kT$  for reasonable values of viscosity  $\eta$  and molecular volume  $V$ . Second, the spectrum of  $\tau$  extends continuously in the direction of shorter rather than longer times.

The limitations of the Debye model of a molecular sphere reorienting in a viscous fluid are well known, and an argument involving its quantitative use to object to the concept of association in a simple sense necessarily loses some force as a result. The more important consideration is the fact that the necessary distribution of relaxation times behaves in a fashion quite contrary to what one would expect as a result of such association. We conclude that a more detailed analysis of the interaction of polar groups is necessary to account for the relaxation process satisfactorily. The observed complex locus of  $\epsilon^*$  for glycerine is striking in being intermediate between the semicircle of simple theory and the arc locus found in many cases, and in this behavior being quantitatively described over most of the frequency range by such a simple expression.

This study is part of a program made possible by a Frederick Gardner Cottrell grant from the Research Corporation.

<sup>1</sup> S. O. Morgan, *Trans. Electrochem. Soc.* **65**, 109 (1934).

<sup>2</sup> S. Mizushima, *Bull. Chem. Soc. Japan* **1**, 47 (1926).

<sup>3</sup> K. S. Cole and R. H. Cole, *J. Chem. Phys.* **9**, 341 (1941).

<sup>4</sup> W. A. Yager, *Physics* **7**, 434 (1936).

<sup>5</sup> The correction factor for the Lorentz field in Debye's original treatment is omitted as being probably inappropriate and in any case increasing the discrepancy.

## Rotational Isomerism in Perfluoro Paraffins

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August 23, 1950

RECENT interest in the properties of fluorocarbons<sup>1</sup> has shown that these are generally similar to those of the corresponding hydrocarbons. One would thus expect that rotational isomerism, which has been exhaustively studied in the paraffin series<sup>2-7</sup> will make a significant contribution to the stereochemistry of the analogous completely fluorinated substances.

We have investigated the infra-red absorption spectra of perfluoro *n*-pentane, *n*-hexane, and *n*-heptane in the region 9 to  $13\mu$ . The spectra were obtained in the vapor, liquid, and crystalline solid phases. In addition quantitative intensity measurements were made on appropriately chosen pairs of lines belonging to different isomers as a function of temperature in the liquid phase. The detailed results and experimental techniques will be presented later.

As for the paraffin hydrocarbons a striking simplification occurs abruptly at the freezing point. This permits the separation of the bands belonging to the most stable isomer from the rest of the spectrum. The results of the quantitative intensity measurements are summarized in Table I. The results are very similar to those obtained for the corresponding hydrocarbons.<sup>8</sup> In the absence of additional information we assume that the extended, zig-zag form again represents the most stable configuration and is the only one present in the solid.

Recent evidence<sup>9-10</sup> suggests that there exist strong repulsive forces between fluorines on adjacent carbon atoms and thus one would perhaps expect higher values for the energy differences between the rotational isomers than those observed by us. While the "straight" forms of these molecules are non-polar, the "bent" forms will possess permanent electric dipoles. Consideration of the electrostatic forces shows<sup>11</sup> that this would tend to stabilize the "bent" forms in the liquid phase as compared with the vapor.

TABLE I. The energy difference between rotational isomers in liquid perfluoro *n*-paraffins.

Compound	Line pair(s), cm <sup>-1</sup>	Temperature range, °K	Energy difference cal. mole <sup>-1</sup> , $-\Delta H$
<i>n</i> -C <sub>8</sub> F <sub>18</sub>	834-881	150-220	460±100
	990-1022	150-220	350±150
<i>n</i> -C <sub>6</sub> F <sub>14</sub>	795-818	195-280	600±150
	818-833	195-280	580±150
<i>n</i> -C <sub>7</sub> F <sub>16</sub>	1030-1058	220-330	600±100

However, the similarity of the vapor and liquid spectra at comparable temperatures shows that the different rotational isomers are present in nearly the same relative concentration in the two phases. We believe therefore that the energy differences in the vapor phase will not be significantly higher than those obtained in this investigation.

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<sup>1</sup> Report on Conference on Fluorides and Fluorocarbons, ONR, Washington, D. C. (1949).

<sup>2</sup> K. W. F. Kohrausch and F. Köppl, *Zeits. f. physik. Chemie* **B26**, 209 (1934).

<sup>3</sup> Szasz, Sheppard, and Rank, *J. Chem. Phys.* **16**, 704 (1948).

<sup>4</sup> Rank, Sheppard, and Szasz, *J. Chem. Phys.* **17**, 83 (1949).

<sup>5</sup> N. Sheppard and G. J. Szasz, *J. Chem. Phys.* **17**, 86 (1949).

<sup>6</sup> D. W. E. Axford and D. H. Rank, *J. Chem. Phys.* **17**, 430 (1949).

<sup>7</sup> D. W. E. Axford and D. H. Rank, *J. Chem. Phys.* **18**, 51 (1950).

<sup>8</sup> H. P. Lemaire and R. L. Livingston, *J. Chem. Phys.* **18**, 569 (1950).

<sup>9</sup> F. A. M. Buck and R. L. Livingston, *J. Chem. Phys.* **18**, 570 (1950).

<sup>10</sup> W. F. Edgell and D. G. Weiblen, *J. Chem. Phys.* **18**, 571 (1950).

<sup>11</sup> Morino, Mizushima, Kuratani, and Katayama, *J. Chem. Phys.* **18**, 754 (1950).

## The Variation of Rate of Desorption with Extent of Surface Coverage

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August 14, 1950

RECENTLY Rideal and Trapnell<sup>1</sup> reported results on adsorption heats which lead to the conclusion that whereas dilute films of hydrogen on tungsten evaporate very slowly, more concentrated films evaporate much more rapidly. This effect is due to the repulsive forces acting between adsorbed molecules, and has an important bearing on the mechanism of the parathydrogen conversion and many other reactions. In connection with a study of the catalyzed ammonia-deuterium exchange reaction, using the technique of microwave spectroscopy to determine NH<sub>3</sub> concentrations, we have recently demonstrated directly that rates of desorption are markedly increased as the surface becomes more fully covered.

The work has been done with a singly promoted iron catalyst (No. 631) kindly supplied by Dr. P. H. Emmett. We have found that the rate of evaporation of deuterated ammonia from the surface is increased markedly as the pressure of NH<sub>3</sub> in the gas phase is increased. For example, with 40 g of catalyst at 122°C and a pressure of 1  $\mu$  the rate of desorption of deuterated ammonia is  $5 \times 10^{-9}$  mole sec.<sup>-1</sup>. With a NH<sub>3</sub> pressure of 20 cm on the other hand, the rate of desorption is  $1.4 \times 10^{-6}$  mole sec.<sup>-1</sup>; in a 2-liter vessel deuterated ammonia corresponding to a pressure of 1 cm is in fact desorbed in less than 10 min. In view of the effect it is not sufficient, before starting a new experiment, merely to pump out the reaction vessel: the catalyst must be washed several times with the gas mixture to be employed in the experiment.

The effect was first noticed by us on the walls of the 1-cm copper wave guide used. Since the adsorption on an untreated

wave guide was sufficient to interfere with the analysis, it was coated with a layer of Glyptal which was then baked; the coating thickness was 0.0003 in. If NH<sub>3</sub> is introduced into such a wave guide and the system then pumped down to  $10^{-4}$  mm, the desorption can be followed both by observation of the increase of pressure and of the pressure broadening of the 3-3 line of the ammonia inversion spectrum. Under these conditions the initial pressure rise is about 5  $\mu$  per minute. On adding a mixture of NH<sub>3</sub> and deuterated ammonias the rate of desorption of NH<sub>3</sub> can be followed by measuring the total pressure and the peak absorption of the 3-3 line, this peak being approximately proportional to the mole fraction of NH<sub>3</sub>. In this way we have found, for example, that a pressure of 0.4 mm increases the rate of desorption of NH<sub>3</sub> by a factor of at least 100. The desorption of deuterated ammonia is found to be similarly increased. In order to analyze mixtures of the ammonias we have therefore found it necessary to wash several times with the mixture to be analyzed.

These results, like those of Rideal and Trapnell, cannot be explained on the basis of variability of the catalyst surface, but only in terms of repulsive forces. Since the rates of catalyzed reactions are sometimes controlled by desorption rates it follows that surfaces may be rendered more active catalytically by the adsorption of reactant or other molecules.

Further details of this work will be included in a later paper on the kinetics of the ammonia-deuterium exchange.

<sup>1</sup> E. K. Rideal and B. M. W. Trapnell, *Faraday Soc. Discussion on Heterogeneous Catalysis*, Liverpool (April, 1950).

## The Magnetic Susceptibility of Europium and Samarium Amalgam

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August 16, 1950

THE difficulties encountered in preparing the rare-earth metals have seriously hampered the investigation of the physical and chemical properties of these substances.<sup>1</sup> By far the most extensive piece of work is that of Klemm and Bommer.<sup>2</sup> These investigators prepared the metals by reducing the anhydrous trichlorides with the stoichiometric amount of potassium. We are reporting the results of some preliminary studies of the magnetochemical properties of the rare-earth amalgams. While the literature contains many references to the magnetochemical properties of amalgams,<sup>3</sup> particularly those of the alkali metals, it appears that this approach to the study of the rare-earth metals has been overlooked. Samarium and europium were chosen as the first objects of study because of the considerable theoretical importance attaching to their position near the middle of the lanthanide series.

The origin and purity of the europium used in this research has been discussed in a previous publication.<sup>4</sup> The samarium was obtained from Research Chemicals, Inc.,<sup>5</sup> and was reported by them to be better than 99 percent Sm<sub>2</sub>O<sub>3</sub>. Purification of the mercury was effected by the usual acid washing and a single distillation. The magnetic susceptibilities of the samarium and mercury were determined in order to establish their purity as regards paramagnetic or ferromagnetic substances. A solution of SmCl<sub>3</sub> in dilute HCl was used for the samarium measurement; and the result obtained was  $\chi_{sm} = 6.75 \pm 0.07 \times 10^{-6}$  c.g.s./g at 27.5°C, in good agreement with Sugden and Tailby's recent determination.<sup>6</sup> The specific susceptibility of mercury was found to be  $-0.166 \pm 0.001 \times 10^{-6}$  c.g.s./g, agreeing well with the best values from the literature.<sup>7,8</sup>

The amalgams were prepared by reducing the rare-earth acetates in solution with sodium amalgam.<sup>9</sup> After washing with water to remove any unreacted sodium the amalgams were introduced into the sample tubes under dry nitrogen. The susceptibilities were