Dielectric Relaxation Process of Rigid Molecules[1]

Sir:

We wish to report the results of recent work in our laboratory which may have a considerable bearing on our present understanding of the dielectric absorption due to molecular reorientation. We studied the dielectric absorption of several small rigid polar molecules, namely, the halogen-substituted benzenes and naphthalenes, in supercooled decalin at audio- and radiofrequencies. All these rigid molecules show a very broad distribution of relaxation times. The Cole–Cole plots for a solution of chlorobenzene in decalin at several temperatures, which also represent the general behavior found in our study, are shown in Figure 1. We find that the distribution of relaxation times (distribution parameter, α) increases with decreasing temperature or increasing solvent viscosity. The enthalpy of activation for dielectric relaxation is closely similar in all these molecules, and the differences in their relaxation times seem mainly due to the entropy factors.

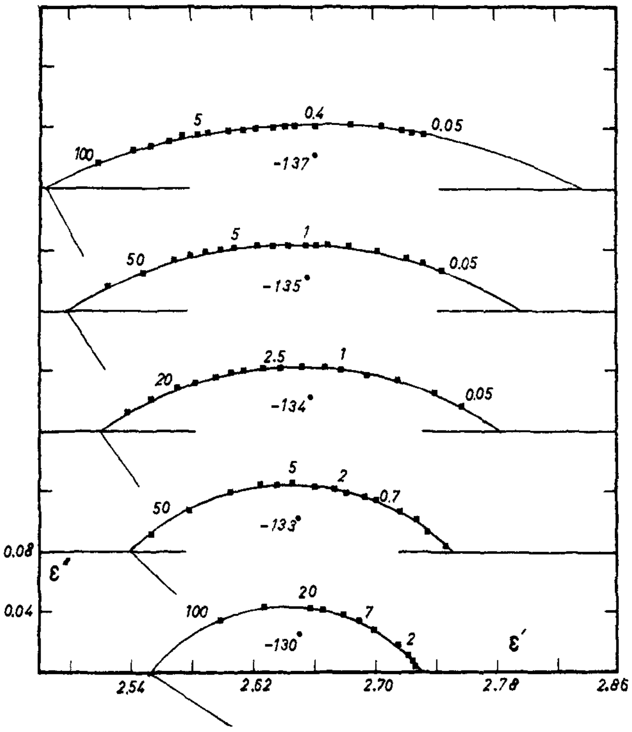

Figure 1. Cole–Cole plots for 7.8 mole % solution of chlorobenzene in decalin at several temperatures. Curves have been shifted upward as shown by the ordinate. Figures near the data points are the frequencies in kHz. Figures below the arcs are the the rounded-off temperatures in °C.

At ambient temperature these molecules in benzene and *n*-heptane show a single relaxation time ($\alpha = 0$) at the microwave frequencies. However, it has often been observed that, in viscous solvents, such as Nujol, they show a small distribution of relaxation times.[2] This small distribution has often been suggested to originate from a fluctuation in the environment of a reorienting dipole. We believe that the very broad distribution found at low temperatures in our study cannot, however, be due to a fluctuation of environment.

We propose the following picture of dielectric relaxation in solutions of rigid molecules in nonpolar solvents. This picture includes the effect of viscoelastic relaxation of the solvent on the reorientation of a dipole. Liquids show viscoelastic relaxation in the same frequency range in which dielectric absorption due to molecular processes is found,[3] the viscoelastic relaxation time being $\tau_{\text{ve}} = \eta/G_\infty$, where η is the steady-flow viscosity, and G_∞ is the high-frequency shear modulus, $\approx 1 \times 10^{10}$ dynes/cm^2. On application of a periodic electric field, as in dielectric measurements, a rotating molecule displaces the solvent and thus causes local alternating shear stress in the solvent. A dipole thus transforms a periodic field to a periodic mechanical stress on the solvent. As a result of viscoelastic relaxation, the dynamic viscosity of the solvent in the immediate vicinity of the reorienting dipole is lowered. The over-all effect is that the dipole reorients in a medium whose dynamic viscosity is frequency dependent, decreasing with increasing frequency. The dipole thus reorients with a time that decreases with increasing frequency. This would give rise to a distribution of relaxation times in the dielectric absorption spectrum. The breadth of distribution would then be directly related to the steady-flow viscosity of the solvent. In benzene and *n*-heptane solutions, whose steady-flow viscosity is already very low, there will be a very small or zero distribution but, in viscous solvents, one should find a broad distribution. An additional advantage of this picture is that it explains the often-found lack of agreement with the Debye theory when the dependence of relaxation time on the macroscopic viscosity is examined.[2] In fact, the classical Debye model seems to be valid; what need to be considered are the additional processes which occur at the microscopic level on application of a periodic field.

It follows from this picture that no dielectric absorption due to molecular reorientation in solutions should occur with a single relaxation time, although, in solvents of very low viscosity, the distribution is very small and, within experimental error, is indistinguishable from zero. This represents a crucial experiment: if a molecular reorientation process in viscous liquids, or in polymers, shows a single dielectric relaxation time, the theory is refutable.

Details of the experimental results with a discussion of dielectric relaxation will be reported at a later date.

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[2] C. P. Smyth, "Molecular Relaxation Processes," Chemical Society Publication No. 20, Academic Press, New York, N. Y., 1966.

[3] A. J. Barlow and J. Lamb, *Discussions Faraday Soc.*, 43, 223 (1967).

Free-Radical Molecular Complexes

Sir:

We have discovered that aliphatic nitroxide free radicals form monomeric molecular complexes with strong Lewis acids. These complexes contain a nitroxide