

Studies on the Dielectric Losses due to Polar Molecules. I. Determination of the Loss Angles of Liquids.

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As was reported in an earlier paper⁽¹⁾ by S. Mizushima and the present writer, we carried out an experiment concerning the absorption of electric waves by several polar compounds in dilute solutions of non-polar solvents. We discussed the relaxation phenomena of the molecules of these substances rotating under the alternating electric field. The apparatus used was constructed mainly for the purpose of determination of the dielectric constants and loss angles of solid samples and semi-solid ones, for which laws of dilute solution must be applied with precaution. It was deemed desirable to measure the dielectric constants and loss angles of liquid solutions. The object of the present work is to investigate, with the aid of the knowledge of molecular structure and intramolecular forces, the dielectric loss, which is one of the most important problems of electrical engineering apart from its theoretical interest in physical chemistry. The present paper describes the apparatus recently constructed to satisfy these requirements.

For the measurement of loss angles, the so-called reactance variation method⁽²⁾ was applied. The circuits are shown diagrammatically in Figure 1. Circuit I was an oscillator, the frequency of which could be varied

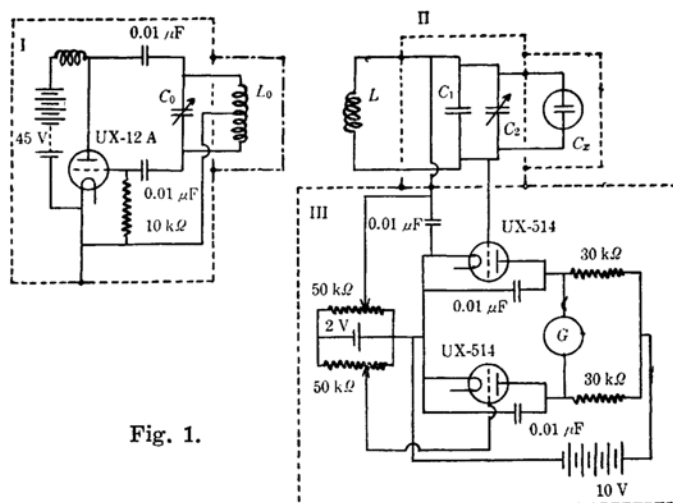


Fig. 1.

(1) Mizushima and Kubo, *J. Chem. Soc. Japan*, **62**(1941), 502.

(2) Hartshorn and Ward, *J. Inst. Elec. Eng.*, **79**(1936), 597. The 18th Subcommittee of the Foundation for the Promotion of Scientific and Industrial Research of Japan, *J. Inst. Elec. Eng. Japan*, **59**(1939), 519.

continuously over a wide range by means of a variable condenser C_0 and a coil L_0 interchangeable by others of different capacities and inductances respectively. This was necessary for the present purpose. Polar molecules such as those having a molecular form represented by an ellipsoid and a dipole moment the direction of which is coincident with none of the three main axes of the ellipsoid⁽³⁾ are expected to have two or more times of relaxation for the rotation of molecules under the alternating electric field. The same is true for molecules with an axis or axes of free rotation of polar groups⁽⁴⁾. The dispersion curve of molecular polarization exhibits corresponding inflection points. But, owing to the complicated functional relationship between dielectric constant, loss angle, and molecular polarization, the dispersions of dielectric constant and loss angle do not exhibit markedly wavy curves⁽⁵⁾, and will escape our detection if we examine only data for several different wave-lengths chosen discontinuously. The resonator II, designed by the Institute of Physical and Chemical Research for the determination of the dielectric losses of solid samples, was used after improvements necessary for measurements on liquids were performed. A parallel plate condenser C_1 consisted of two metal disks 5 cm. in diameter, the distance between the plates being adjustable with the accuracy of 2×10^{-4} cm. in the range 0–1.5 cm. It could, when necessary, hold a solid sample in the form of a disk. For measurement on liquid it was used merely to vary the capacity of the resonator circuit and adjust the frequency of the oscillation. C_2 was a micrometer condenser of cylindrical type for bringing the circuit to resonance. The change in capacity was linear to the displacement of the inner cylinder, one scale division 10^{-3} cm. corresponding to the capacity change of $2.447 \times 10^{-3} \mu\text{F}$. C_x was a liquid condenser containing the sample under investigation. III was a valve voltmeter. The grid potential was regulated (–1.35 volts) in such a way that the galvanometer deflection was strictly proportional to the square of the input voltage. These circuits were completely shielded separately by enclosure in wooden boxes covered with copper plates, except two coils L_0 and L , which were coupled together electromagnetically, electrostatic interaction being prevented by shielding with a specially designed copper grating.

The experimental procedure was as follows. For a given wave-length of the electric oscillation, the condenser C_1 of the resonator circuit was adjusted so that the resonance curve of the form given in Figure 2 could be followed by changing C_2 for the test condenser filled with liquid as well as for the empty condenser. Calculations showed that if the conditions such as (1) that the coupling between the oscillator and the resonator was electromagnetic, (2) that the impressed electromotive force from the oscillator acted on the resonator only through the coil L , and (3) that the resistances, the inductances, and the capacities of the leads

(3) Perrin, *J. Physique*, (7) 5(1934), 497. Budó, Fischer, and Miyamoto, *Physik. Z.*, 40(1939), 337.

(4) Budó, *Physik. Z.*, 39(1938), 706; 40(1939), 603. Fischer and Frank, *Physik. Z.*, 40(1939), 345.

(5) Fischer, *Physik. Z.*, 40(1939), 645.

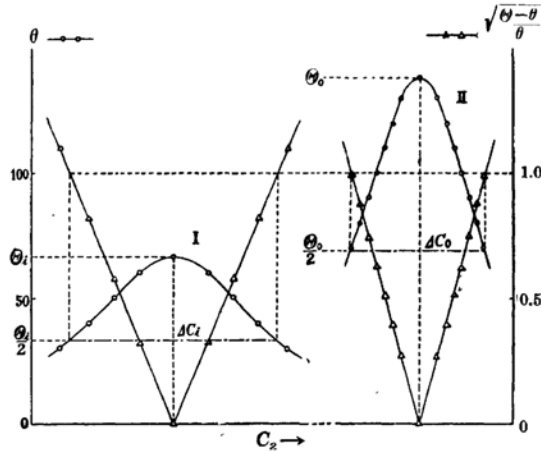


Fig. 2. I: sample, II: air.

connecting the condensers C_1 , C_2 , and C_x could be neglected, the resonance curves should be given by the following equation.

$$\theta \propto V^2 = \frac{E^2}{Z^2} \left[\left(G + \frac{R}{Z^2} \right)^2 + \omega^2 \left(C - \frac{L}{Z^2} \right)^2 \right]^{-1},$$

where θ denotes the galvanometer deflection of the valve voltmeter, V the potential difference between the plates of the condenser in the resonator circuit, E impressed electromotive force acting on the coil L , $Z^2 = R^2 + \omega^2 L^2$, R the resistance of the coil L , ω 2π times the frequency of the electric oscillation, L the inductance of the coil L , G the equivalent parallel conductance of the condensers C_1 , C_2 , and C_x , and C the equivalent parallel capacity, i.e. $C = C_1 + C_2 + C_x$. θ - C curve should therefore be symmetric with a maximum θ at a centre and moreover

$$\sqrt{\frac{\theta - \theta}{\theta}} \propto \omega \left| C - \frac{L}{Z^2} \right| \left(G + \frac{R}{Z^2} \right)^{-1},$$

i.e. $\sqrt{(\theta - \theta)/\theta}$ should be a linear function of C or C_2 , and the inclination of the straight line representing $\sqrt{(\theta - \theta)/\theta}$ - C relation should, for a given frequency of the oscillation, be inversely proportional to $G + R/Z^2$, i.e. to the equivalent parallel conductance of the condensers C_1 , C_2 , and C_x and the coil L . The results of the experiment as shown in Figure 2 conformed to this relation, which showed that the apparatus operated in a proper manner. Knowing this, it was no longer necessary to trace the whole resonance curve, and the determination of the maximum galvanometer deflection θ and the breadth of the resonance curve ΔC corresponding to half the maximum deflection $\theta/2$ was sufficient to give the loss angle δ . It was given by any of the following three formulas,

$$\tan \delta = \frac{\Delta C_i - \Delta C_0}{2C_s} = \frac{\Delta C_0}{2C_s} \left(\sqrt{\frac{\theta_i}{\theta_0}} - 1 \right) = \frac{\Delta C_i}{2C_s} \left(1 - \sqrt{\frac{\theta_i}{\theta_0}} \right),$$

where suffixes i and 0 refer to the sample and air respectively and C_s denotes the electrostatic capacity of the sample. In a preliminary experiment carried out for a specimen of methyl methacrylate resin (at a temperature of 14.0°C. and for a wave-length of 104.6 m.) the three formulas gave the values 191.3, 191.4, and 191.3×10^{-4} respectively for the loss tangent in perfect mutual agreement. This proved the reliability of the present apparatus. The dielectric constant could be calculated from the scale readings corresponding to the resonance points. It was often necessary to use different cells having cell constants appropriate for dielectric constant and loss angle respectively for a single solution.

In the case of solid, the capacity of the condenser C_1 was determined for each sample, and even if coils of different inductances were used the wave-length could be changed merely discontinuously. In the case of liquid continuous variation was possible for the capacity of the condenser C_1 so that data could be obtained for any desired frequency of the oscillation. On the other hand, as the proportion occupied by the sample in the total capacity was comparatively small, determination of a very small loss angle was disadvantageous and could only be compensated by the use of cells of large capacities. The electrostatic capacity C_s of the sample could be calculated for a solid specimen from its thickness and the dimensions of the electrodes. For liquid it was determined by calibration with a standard liquid, which made the absolute calibration of the micrometer condenser C_2 unnecessary.

As to the accuracy of the determination of loss angle, no general account could be made. The higher accuracy could be obtained for a liquids of small dielectric losses by the use of a cell of large cell constant. The accuracy of loss tangent was naturally higher for liquids of large ϵ' than those of smaller ones, where

$$\epsilon^* = \epsilon' - i\epsilon'' = \epsilon'(1 - i \tan \delta),$$

ϵ^* denoting complex dielectric constant. In the best condition the accuracy of $\tan \delta$ of a solid sample was as high as 0.1×10^{-4} . For liquids the accuracy was lower in general. It was able to limit the error of ϵ'' always smaller than 0.002, which for dilute solutions in ordinary non-polar solvents corresponded nearly to $\tan \delta$ of 10×10^{-4} .

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