Studies on the Dielectric Losses due to Polar Molecules. II. Loss Angles of Some Pure Liquids.

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For the investigation of the nature of dielectric loss from the standpoint of molecular theory it is most desirable to study the behaviour of a molecule in free state. For gaseous molecule, however, the studies on the energy absorption due to the rotation of molecules are very scanty owing to the experimental difficulties inevitable for the range of wave-length concerned. Among these studies must be mentioned the theoretical work by Debye and Sack⁽¹⁾ on hydrogen chloride and the experimental investigation by Cleeton and Williams⁽²⁾ on ammonia for the wave-length of 1.25 cm. Though experimental investigations on pure polar liquids are somewhat easier, the theoretical interpretations are exceedingly difficult, as the strong mutual action between polar molecules invalidates the Mosotti's formula concerning the internal field. To avoid these difficulties, polar molecules in dilute solutions will be used in the present investigation. Before doing this it is necessary to know the dielectric losses of pure polar liquids to be used as solvents. Measurements were carried out upon three liquids, namely non-polar benzene, feebly polar toluene, and strongly polar water, the last of which, though unsuitable solvent for the present purpose, may be of interest for the sake of comparison. The apparatus and the experimental procedure employed were already reported in the previous paper⁽³⁾.

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(1) Debye and Sack, "Handbuch der Radiologie," Bd., 6/2, 142, Leipzig (1934).

(2) Cleeton and Williams; *Phys. Rev.*, **45**(1934), 234.

(3) Kubo, this Bulletin, **18**(1943), 190.

Preparation of Materials.

Benzene: Guaranteed reagents free from thiophene were dehydrated over sodium and subjected twice to fractional distillations, b.p. 80.1°C.

Toluene: The material marked as "extra-pure" was dehydrated over sodium and subjected twice to fractional distillations, b.p. 111.1°C.

Water: Ordinary distilled water and the so-called conductivity water were used.

For benzene (at the temperature of 24.0°C. and the wave-length of 107.8 m.) the galvanometer deflection at the resonance point ($\Theta_i=158.0$ mm.) and the breadth of the resonance curve for half the maximum galvanometer deflection ($\Delta C_i=2.196$ mm.) coincided respectively with those for air ($\Theta_0=158.1$ mm., $\Delta C_0=2.204$ mm.) within the experimental errors, therefore the dielectric loss was undetectable in the present investigation. According to the Debye's theory(4), only permanent dipoles contribute to the dielectric absorption, the dielectric loss due to induced moments, i.e., the effect of orientation of molecules due to the anisotropy of polarizability is too small to be observed under the ordinary experimental conditions. In fact, in the calorimetrical method(5), recently employed by many investigators, it is usual to ascribe the heat evolved under the alternating electric field of high frequencies entirely to glass and lead wires of the cell when it is filled with benzene or other non-polar solvents. Martin(4)(6), measuring calorimetrically the evolved heat of several non-polar liquids, showed that the heat evolution could be wholly attributed to the vessel containing the liquid, considering the differences in density, specific heat, thermal expansion coefficient and dielectric constant of these non-polar liquids. He carried out measurements also on *p*-dichlorobenzene in 5 mole percent solution in benzene and found that the loss of the sample was zero, supporting the Debye's view mentioned above. At any rate, however, the calorimetrical method is a kind of relative measurements which compares the solutions with pure solvents, and by this method it is difficult to determine absolutely the dielectric losses of non-polar solvents. Wulff and Schwindt(7), on the other hand, employing the Rohde's method, noticed that benzene and other non-polar hydrocarbons showed dielectric losses of the order of $\tan\delta=1\times10^{-4}$. According to their results the loss was independent of the temperature and the frequency in the range of wave-length 200–1600 m. They thought that the results could never be explained by the Debye's theory as the loss due to induced moments should depend on the temperature, the frequency, and the field strength and moreover should not be so great. As they report, they do not think that the problem has come to a conclusion by their experimental results. Elle(8) using the optical method also found for benzene and cyclohexane a slight absorption at a wave-length of 4 cm. (refractive index $n=1.48$, extinction coefficient $k=0.015$ for benzene*). He did not give a clear explanation for its cause but paid his attension to the possible influence of infra-red absorption

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(4) Debye, *Physik. Z.*, **35** (1934), 101; *Trans. Faraday Soc.*, **30** (1934), 679.

(5) Fischer and Frank, *Physik. Z.*, **40** (1939), 345; *Fischer, ibid.*, **40** (1939), 645.

(6) Martin, *Physik. Z.*, **37** (1936), 665.

(7) Wulff and Schwindt, *Z. physik. Chem.*, B, **39** (1938), 290.

(8) Elle, *Ann. Physik*, (5) 30 (1937), 354.

* This corresponds to $\tan\delta=\varepsilon''/\varepsilon'=2nk(n^2-k^2)=2.0\times10^{-2}$.

band as he employed very short wave-length. The results of the present measurements with the accuracy of $1\text{–}10\times10^{-4}$ for loss tangent supports the view of Debye and Fischer. For the decisive conclusion it will be necessary to increase the experimental accuracy of the absolute method such as employed in the present work. The reactance variation method employed has advantages over the Rohde's resistance substitution method used by Wulff and Schwindt, because the former does not necessitate to employ as a standard the resistance, which lacks reliability especially in high frequency circuits. It was confirmed that for the present purpose benzene is an ideal solvent without any detectable dielectric loss.

For toluene (at the temperature of 22.0°C. and the wave-length of 107.8 m.) the galvanometer deflection $\Theta_i=194.0$ mm. and the breadth of the resonance curve $\Delta C_i=2.146$ mm. revealed the existence of a slight absorption comparing with the case of air for which Θ_0 and ΔC_0 were 194.5 mm. and 2.139 mm. respectively, but the loss, if any, was of the order of the experimental errors. Toluene as a free molecule has surely a finite dipole moment of $\mu=0.37$ D(9), but as a pure liquid it resembles in many respects to non-polar substances and belongs to the group of normal unassociated liquids. As pointed out by Hassel and Uhl(10) and Mizushima, Morino, and Higasi(11) it can be used as a solvent for the determination of dipole moments just as well as other non-polar solvents. Wulff and Schwindt(12), measuring the loss of toluene at 23°C. for the wave-length of 263 m., found that the dielectric loss of toluene was of the same order of magnitude such as benzene and other non-polar substances, while Debye(13), using the calorimetrical method, observed very slight but detectable dilatation in alternating electric field, and Henrion(14) by the same method confirmed that toluene suffered greater heating than benzene. Though as has been stated above the calorimetrical method involves uncertainty as an absolute measurement of dielectric loss, it has high sensitivity as a relative one. Estimating from the rising velocity of the dilatometer used by Debye, it seems that the loss angle of toluene is of the order of magnitude 10^{-5}. Therefore if we discuss it within the accuracy of $\tan\delta=10^{-4}$, the present limit of the accuracy of absolute measurements (sufficient for the present investigation), toluene can be used as a solvent free from dielectric loss just like non-polar substances.

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(9) McAlpine and Smyth, *J. Am. Chem. Soc.*, **55** (1933), 453.

(10) Hassel and Uhl, *Z. physik. Chem.*, *B.*, **8** (1930), 187.

(11) Mizushima, Morino, and Higasi, *Sci. Pap. Inst. Phys. Chem. Research*, **25** (1934), 159.

(12) Wulff and Schwindt, *loc. cit.*

(13) Debye, *loc. cit.*

(14) Henrion, *Rev. univ. Mines* 8/VIII (Nov. 1937); *Bull. Roy. Soc. Sci. Liège*, (1938), 229. Henrion and van der Grinten, *Bull. Roy. Soc. Sci. Liège*, (1935), 181. Quoted by Horst Müller, *Erg. d. exakt. Naturwiss.*, XVII (1938), 207.

Table 1. Dielectric Loss of Water.

$t = 24.0°$C., $\lambda = 107.8$ m., $\varepsilon' = 78.5$.

	$\tan\delta$	ε''	Λ (ohm^{-1} cm.$^{-1}$)
Distilled water	251.3×10^{-4}	1.971	3.05×10^{-6}
Conductivity water	87.9	0.690	1.07

If we adopt the value 78.5(15) for the dielectric constant ε' of water at 24.0°C. we can calculate ε'' from the measured value of $\tan\delta$, which in terms of equivalent conductivity Λ in ohm^{-1} cm.$^{-1}$ can be converted as

$$\Lambda = \frac{\varepsilon''}{60\lambda}, \quad \text{(16)}$$

where λ denotes the wave-length employed. The results are shown in Table 1. For water measurements covering the whole range of anomalous dispersion of electric waves have not yet been carried out. Dielectric constants for wave-lengths of several decimeters found by Seeberger(17) (λ=12.6–24 cm.) and by v. Ardenne, Groos, and Otterbein(18) (λ=13.45–56.7 cm.) coincide nearly with the value in electrostatic field, while Rubens(19) and Cartwright(20) found low values in the infra-red region (23–313 μ and 52–152 μ respectively). As to the dispersion expected between these two extremities, Bäz's(21) measurements by the optical method in the wave-length range 2.8–9.35 cm. have only revealed a part of the dispersion curve, i.e., the deviation from the static value. Elle's(22) measurements at 4 cm. are in agreement with it. Bäz studied distilled water, redistilled water, and that from water-supply and did not find, contrary to the present investigation, any difference coverning the degree of purity, showing that in the wave-length range employed by him conductivity due to ions is negligible as compared with the loss due to dipoles. His values can well be represented by Debye's formula with a single time of relaxation* and obtained for the Wien's characteristic wave-length λ_s** (Sprungwellenlänge) the value of 1.85 cm.*** at 19°C. Giving for ε_0 and ε_∞ at 19°C. the values 81.0 and 1.8 respectively, we can calculate theoretically ε' and ε'' from λ_s in the whole range of wave-length by the following equations(25).

$$\varepsilon' = \frac{\varepsilon_0 + x^2\varepsilon_\infty}{1+x^2}, \quad \varepsilon'' = \frac{x(\varepsilon_0 - \varepsilon_\infty)}{1+x^2}, \quad x = \frac{\varepsilon_0+2}{\varepsilon_\infty+2}\omega\tau, \quad \lambda_s = \frac{\varepsilon_0+2}{\varepsilon_\infty+2}2\pi c\tau,$$

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(15) Kockel, *Ann. Physik*, (4) 77 (1925), 417; Lattey, Gatty and Davies, *Phil. Mag.*, **12** (1931), 1019; Linton and Maass, *J. Am. Chem. Soc.*, **53** (1931), 957; *ibid.*, **54** (1932)), 1863.

(16) Debye, "Polare Molekeln", Leipzig (1929), 114.

(17) Seeberger, *Ann. Physik*, (5) 16 (1933), 77.

(18) v. Ardenne, Groos, and Otterbein, *Physik. Z.*, **37** (1936), 533.

(19) Rubens, *Verh. dtsch. physik. Ges.*, **17** (1915), 315.

(20) Cartwright, *J. Chem. Phys.*, **5** (1937), 776; Hettner, *Physik. Z.*, **38** (1937), 771.

(21) Esau and Bäz, *Physik. Z.*, **38** (1937), 774; Bäz, *ibid.*, **40** (1939), 394.

* Tear(23) measuring the optical constants of water for short electric waves (4–27 mm.) suggests the presence of two or three absorption bands instead of only one.

** Wave-length for which the dielectric constant ε' assumes the arithmetical mean of the static and optical values, and ε'' has its maximum.

*** Elle found for λ_s the value of 1.13±0.08 cm. at 18°C., and Schmelzer(24) 1.2–1.7 cm. at 20°C.

(22) Elle, *loc. cit.*

(23) Tear, *Phys. Rev.*, **21** (1923), 611.

(24) Schmelzer, *Ann. Physik*, (5) 28 (1937), 35.

(25) Debye, "Polare Molekeln", Leipzig (1929), 108.

where ε_0 denotes the dielectric constant for the static field, ε_∞ that for high frequencies (frequencies high enough compared with the frequency corresponding to λ_s, but very low as compared with the frequency of the vibrations of molecules in the infra-red region), ω 2π times the frequency of the oscillation, τ the time of relaxation of the orientation of molecules in external electric field, and c the light velocity. For the wave-length 107.8 m. employed in the present work*, calculation gives for ε'' 1.36×10^{-2}, which converted into the conductivity scale yields 2.10×10^{-8} ohm^{-1} cm.$^{-1}$, showing that the loss due to dipoles is about 1/100 of the measured conductivity, i.e., the latter originates almost entirely from the migration of ions. To compare this with the conductivity measured by the ordinary Kohlrausch bridge, we must consider Debye-Falkenhagen Effect. As the concentration of ions decreases the time of relaxation of ionic atmosphere increases, consequently the dispersion of conductivity is transfered to longer wave-length range and it is not seldom that the dispersion can be observed in the wave-length range as long as 100 m. According to the Debye's theory of strong electrolytes, the time of relaxation of ionic atmosphere is given by the following equation⁽²⁶⁾.

$$\Theta = \frac{|z_1|\,|z_2|}{|z_2|\,l_1+|z_1|\,l_2}\,\frac{Ne^2}{9\times10^{11}kTq}\,\frac{1}{K^2}\,,$$

where z_1 and z_2 denote the valencies of the positive and the negative ions respectively, l_1 and l_2 ion equivalent conductivities for infinite dilution in ohm^{-1} cm.^{2}, N Avogadro's number, e electronic charge, k the Boltzmann constant, and T the absolute temperature. The parameter q is given by the equation

$$q = \frac{|z_1|\,|z_2|}{|z_1|+|z_2|}\,\frac{l_1+l_2}{|z_2|\,l_1+|z_1|\,l_2}\,.$$

The square of the thickness of ionic atmosphere $1/K^2$ is given by

$$\frac{1}{K^2} = \frac{10^3 D_0 kT}{4\pi Ne^2\gamma(\nu_1 z_1^2+\nu_2 z_2^2)}\,,$$

in which D_0 is the dielectric constant of the solvent, γ the concentration of electrolyte in mol./l., and ν_1 and ν_2 the number of the positive and the negative ions respectively which one chemical molecule can give. If we consider for simplicity water as a solution of electrolyte of the concentration $\gamma=7.8\times10^{-8}$ mol./l. (the hydrogen ion concentration at 18°C.), using

$$\begin{aligned}
&|z_1| = |z_2| = 1\,, \qquad \nu_1 = \nu_2 = 1\,,\\
&l_1 = 314.5\,\text{ohm}^{-1}\,\text{cm.}^2\,, \qquad l_2 = 174\,\text{ohm}^{-1}\,\text{cm.}^2\,,\\
&D_0 = 81.3\,,
\end{aligned}$$

In referring to the value of Bäz, a slight difference in temperature from the present work was disregarded, as it does not influence the conclusion to be drawn. If this be considered the theoretical value of the dipole loss will still become smaller, because, as the temperature rises the maximum of dipole loss $\varepsilon''_{\max}=(\varepsilon_0-\varepsilon_\infty)/2$ decreases and moreover the dispersion displaces to shorter wave-length, so that in the wave-length range in question dipole loss will decrease.

(26) Debye and Falkenhagen, *Physik. Z.*, **29** (1928), 401; Falkenhagen, "Elektrolyte", 107, Leipzig (1932).

we have $\Theta=1.89\times10^{-4}$ sec., with the corresponding wave-length and the frequency of 5.67×10^{4} m. and 5.29×10^{3} sec.$^{-1}$ respectively. Taking into account that the ordinary distilled water and the conductivity water have specific conductivity about 100 times as great as that of the purest water prepared by Kohlrausch, and multiplying γ by 100*, we have shorter time of relaxation Θ corresponding to the wave-length of 6×10^{2} m. At any rate the dispersion of conductivity due to the relaxation of ionic atmosphere lies between the wave-length 107.8 m. employed in the present investigation and the wave-length of about 3×10^{5} m. corresponding to the audio-frequency of about 1000 cycles frequently employed in an ordinary Kohlrausch bridge. So that conductivity determined by the bridge should be smaller than that for ca. 100 m. by an amount due to the relaxation force, which referring to molecular conductivity is given by(27)

$$\Lambda_{10}=\frac{e^{3}}{6(D_{0}T)^{3/2}}\sqrt{\frac{4\pi N}{10^{3}k^{3}}}\,\frac{2q}{1+\sqrt{q}}\,|z_{1}|\,|z_{2}|\,\Lambda_{\infty}\sqrt{(\nu_{1}z_{1}^{2}+\nu_{2}z_{2}^{2})\gamma}\ ,$$

where Λ_{∞} denotes molecular conductivity for infinite dilution. Using the values given above for water 18°C. we have

$$\Lambda_{10}=6.25\times10^{-5}\Lambda_{\infty}\ ,$$

and even if we multiply γ by 100 for conductivity water Λ_{10} is only of the order of magnitude $6\times10^{-4}\Lambda_{\infty}$, showing that the frequency change of molecular conductivity is negligibly small compared with molecular conductivity for water having ions in small concentrations. As the specific conductivity $\mathscr{K}$ is given by

$$\mathscr{K}=\Lambda_{\infty}\frac{\gamma}{1000}\ ,$$

the frequency change of specific conductivity is also negligible compared with the specific conductivity, i.e., conductivity measured by the present apparatus should coincide theoretically with that of Kohlrausch bridge, so that for the accurate determination of electric conductivity a new method is proposed suited especially for low conductivity.

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The calculation serves only for the rough estimation of the order of magnitude of the time of relaxation Θ, as the conductivities of ordinary distilled water and conductivity water are due to impurities such as carbon dioxide.

(27) Falkenhagen, *loc. cit.*, 192, 205.