# DIELECTRIC CONSTANTS OF CERTAIN ORGANIC LIQUIDS AT MEDIUM FREQUENCY

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#### Abstract

At a frequency of 85.8 kilocycles the dielectric constant was determined at one temperature for each of the following: benzene, 2.279 at 22.9°C; cinnamic aldehyde, 16.918 at 24.2°C; ethyl ether, 4.197 at 26.9°C; methyl cyclohexane, 2.071 at 24.8°C; methyl o-nitrobenzoate, 27.756 at 26.9°C; nitrobenzene, 34.369 at 26.1°C; oxalyl chloride, 3.470 at 21.2°C; n-propyl ether, 3.394 at 25.7°C; iso-propyl ether, 4.449 at 25.9°C; and propylene chloride, 8.925 at 26.1°C. At this same frequency the temperature coefficients of the dielectric constants for ortho-, meta-, and para-xylenes were determined over a temperature range of about 30°C. The data on the three xylenes were tested with the Debye theory.

# INTRODUCTION AND THEORY

THE dielectric constant of an organic liquid has been considered to be allied with the other physical properties of the compound such as solvent power and molecular constitution. By methods to be explained later the dielectric constant is used to obtain the electric moment of the molecule and thus account for the symmetry or dissymmetry of its structure.

By a nulled heterodyne method the dielectric constant was determined at a frequency of 85.8 kilocycles and at one temperature for each of the following: benzene, cinnamic aldehyde, ethyl ether, methyl cyclohexane, methyl o-nitrobenzoate, nitrobenzene, oxalyl chloride, n-propyl ether, iso-propyl ether and propylene chloride.

In determining the dielectric constants of some of these compounds it was necessary to fill the test condenser only partially with the liquid under test so that the limit of the capacity of the apparatus was not exceeded. For these cases the following equations were developed with metric units used throughout:

$$h_1 = M'L/V\rho \tag{1}$$

where M' represents the mass of liquid required to fill the test condenser to height  $h_1$  which was just sufficient to null the beat note,  $\rho$  the density of the liquid, V the total volume of the test condenser and L its length.

$$h_2 = L - h_1 \tag{2}$$

where  $h_2$  is the height of the air dielectric in the test condenser.

$$C_4 = \frac{(R_1 + C) - (R_2 + Ch_2/L)}{h_1}$$
(3)

where  $R_1$  is the reading of the precision condenser with only air in the test condenser, C the corrected capacity of the test condenser with air as the dielectric,  $R_2$  the reading of the precision condenser with  $h_1$  cm of liquid in the test condenser and  $C_4$  the capacity in mmf for each cm of liquid dielectric in the test condenser.

$$\epsilon = LC_4/C \tag{4}$$

where  $\epsilon$  is the dielectric constant of the liquid under test.

When the test condenser was partially filled with a liquid the air space above the liquid contained some vapor due to evaporation. The dielectric constant of the mixture of air and vapor could not vary much from unity because the dielectric constant of most pure vapors at atmospheric presure and room temperature exceed unity less than 0.5 percent A few pure vapors from liquids with high dielectric constants have dielectric constants which exceed unity by 2.5 percent. Certainly in this work no serious error is introduced by considering the dielectric constant of the mixture of air and vapor equal to unity since only a small amount of liquid could evaporate while pouring sufficient liquid into the test condenser to null the beat note.

At a frequency of 85.8 kilocycles the temperature coefficients of the dielectric constants for ortho-, meta-, and para-xylenes were determined over a temperature range of about 30°C.

For organic liquids whose dielectric constants are only slightly affected by temperature a satisfactory relation is expressed by the simple linear formula

$$\epsilon_t = K_0 - \beta t \tag{5}$$

where  $\epsilon_i$  is the dielectric constant at temperature *t*,  $K_0$  the dielectric constant at 0°C and  $\beta$  is the temperature coefficient.

However, nitrobenzene, alcohol, etc., which have comparatively large dielectric constants are considerably influenced by a change in temperature and hence the linear law does not obtain. For these cases Abegg<sup>1</sup> proposed the following formula

$$\log_{10} \epsilon_t = \log_{10} \epsilon_0 - \alpha t \tag{6}$$

where  $\epsilon_0$  is the dielectric constant at 0°C and  $\alpha$  is the temperature coefficient. Lattey and Gatty<sup>2</sup> have found this equation concordant with their experimental results over a wide temperature range.

In this work the data on o-xylene, m-xylene and p-xylene are tested with the Debye<sup>3</sup> theory. In general Debye's theory has applied only to gases as shown by Zahn<sup>4</sup> and to very dilute solutions of polar compounds in non-polar solvents as found by Stranathan.<sup>5</sup>

<sup>2</sup> Lattey and Gatty, Phil. Mag. 7, 985 (1929).

<sup>8</sup> Debye, "Polar Molecules" (Chemical Catalogue Co., New York).

<sup>&</sup>lt;sup>1</sup> Abegg, Wied. Ann. **60**, 54 (1897).

<sup>&</sup>lt;sup>4</sup> Zahn, Phys. Rev. 24, 400 (1924).

<sup>&</sup>lt;sup>5</sup> Stranathan, Phys. Rev. 31, 653 (1928).

Polar molecules in the gaseous phase or in dilute solution with a nonpolar solvent are sufficiently separated to render negligible the mutual interaction due to the overlapping of the electrostatic fields of the molecules.

The well-known Clausius-Mosotti relation leads to the expression

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi n}{3} \alpha \tag{7}$$

where the dielectric constant  $\epsilon$  is expressed in terms of  $\alpha$  the molecular polarizability and *n* the number of molecules per cubic centimeter. If both members of equation (7) are multiplied by the quotient of the molecular weight M and the density  $\rho$ , we obtain

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = \frac{4\pi M n}{3\rho} \alpha. \tag{8}$$

The right hand member of equation (8) is called P, the molar polarization. Since  $nM/\rho$  equals Avogadro's number N (6.06×10<sup>23</sup>) equation (8) can be expressed thus

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = 2.54 \times 10^{24} \alpha.$$
(9)

From Maxwell's hypothesis the dielectric constant  $\epsilon$  is identified with the square of the index of refraction r.

Substituting  $r^2$  for  $\epsilon$  in equation (8) we have the familiar Lorentz-Lorenz relation

$$P_0 = \frac{r^2 - 1}{r^2 + 2} \frac{M}{\rho} = \frac{4\pi N}{3} \alpha$$
(10)

where  $P_0$  is called the molar refraction. The molar polarization can be construed as the molar refraction for zero frequency.

Debye<sup>6</sup> expresses the polarizability in the general formula

$$\alpha = \alpha_0 + \mu^2 / 3kT \tag{11}$$

where  $\alpha_0$  accounts for the distortion effect and  $\mu^2/3kT$  takes care of the orientation effect.

Substituting equation (11) in (9) we get

$$P = 2.54 \times 10^{24} \alpha_0 + 2.54 \times 10^{24} \mu^2 / 3kT$$
(12)

where k represents the Boltzmann constant, T the absolute temperature and  $\mu$  the electric moment of the molecule.

Considering  $\alpha_0$  as an invariable molecular constant we can write equation (12) thus

$$P = A + B/T \tag{13}$$

where A and B are constants for a given dielectric.

<sup>6</sup> Debye, "Polar Molecules," p. 36.

Comparing equations (12) and (13) we see that

$$A = 2.54 \times 10^{24} \alpha_0 \tag{14}$$

$$B = 0.618 \times 10^{40} \mu^2 \tag{15}$$

$$\mu = 1.27 \times 10^{-20} B^{1/2} \text{ e.s.u.}$$
(16)

If P is plotted against 1/T equation (13) gives a straight line with intercept A and slope B. If the experimental polarization-temperature curve of a substance obeys the linear relationship the slope B may prove to be either positive, zero or negative. If the slope is positive the molecule has an electric moment and it is therefore a polar molecule. If the curve has zero slope the electric moment is zero and the molecule is non-polar. By this method several substances have been definitely classified as polar and non-polar.<sup>7</sup>

If the slope comes out negative the electric moment is the square root of a negative number and is therefore imaginary. This is frequently the case when this simple theory is applied to pure liquid compounds.

Debye<sup>8</sup> quotes an example of the data on liquid ethyl alcohol resulting in an imaginary electric moment. The inadequacy of the theory in the case of pure polar liquids is generally attributed to association and the effect of temperature on the manner and degree of mutual interaction between the molecules.

#### Source of Liquids

A technical grade of methyl cyclohexane was procured from the Eastman Kodak Company, Rochester, N. Y.

A highly purified sample of each of the following was purchased from the Eastman Kodak Company: benzene, cinnamic aldehyde, ethyl ether, methyl o-nitrobenzoate, nitrobenzene, oxalyl chloride, n-propyl ether, iso-propyl ether, propylene chloride, o-xylene, m-xylene and p-xylene.

### Description of Apparatus

The heterodyne arrangement adopted for this work was composed of two high frequency oscillators (Hartley type) and a detector with two stages of audiofrequency amplification. The beat note between the oscillators was picked up by the floating grid of the detector and after amplification was received by the headphones which is similar to the method described by Stranathan<sup>9</sup> and Zahn.<sup>10</sup>

One of the high frequency oscillators was held at the constant frequency of 85.8 kilocycles (3500 meters) by a quartz crystal properly mounted in the grid circuit. This crystal had been carefully calibrated by Dr. Tadashi Fujimoto in this laboratory in 1927. The frequency of the other oscillator was readily altered by variable condensers.

<sup>&</sup>lt;sup>7</sup> Debye, "Polar Molecules," pp. 40, 50.

<sup>&</sup>lt;sup>8</sup> Marx, Handbuch der Radiologie 6, 614 (1925).

<sup>&</sup>lt;sup>9</sup> Stranathan, Phys. Rev. 31, 653 (1928).

<sup>&</sup>lt;sup>10</sup> Zahn, Phys. Rev. 24, 400 (1924).

At first a 1000-cycle tuning fork coupled electrically to the grid circuit of the second amplifier was used for some preliminary determinations. However, due to harmonics produced by the tuning fork it was difficult to null completely the beat note between the heterodyne of the high frequency oscillators and the tuning fork note. The tuning fork was discarded for subsequent determinations.

The apparatus (Fig. 1) consisted of: one UX-200A tube for the detector, four UX-201A tubes for the oscillators and amplifiers, three Hammarlund variable air condensers, suitable inductance coils, two standard audio frequency transformers and a General Radio Precisión Condenser, type 222, with maximum range 1500 mmf.



Fig. 1. Diagram of apparatus.

The entire apparatus was shielded with iron sheet and controlled by small wooden pulleys mounted outside the shield. The shield was well grounded thus eliminating the effect of the body capacity of the operator. The three electrical circuits were supplied by independent batteries to eliminate possible synchronizing effects.

In Fig. 1,  $T \cdot C$  represents the test condenser,  $P \cdot C$  the variable precision condenser,  $C_2$  a variable air condenser of 0.0005 mmf,  $C_3$  a variable air condenser of 0.00014 mmf with vernier attachment and Q a quartz crystal. The conventional symbols of the diagram make the rest of it self-explanatory.

Several test condensers were constructed and tried. The most satisfactory one, designated as condenser No. 2, was made of two coaxial brass cylinders (Fig. 2) cemented with sodium silicate to a ground glass base. The inside of the larger brass cylinder and the outside of the smaller one were gold-

plated to preclude metallic contamination of the organic liquids. The sodium silicate made a rigid bond between the brass cylinders and glass base thus making the condenser fragile to handle. The condenser was insulated with felt three-fourths of an inch thick to retard heat radiation.

#### Procedure

With S (a mercury switch) in the proper position and test condenser  $T \cdot C$  disconnected, the precision condenser  $P \cdot C$  was adjusted so that the fre-



Fig. 2. Diagram of test condenser No. 2

quency of the variable oscillator equalled exactly that of the constant oscillator and under this condition the beat note was completely nulled. The sensitivity of the method was satisfactory because a beat note was heard if the capacity of the variable oscillator circuit was varied 0.2 mmf on either side of the mean nulled position of the precision condenser. The mean nulled position could be determined to within 0.1 mmf.

In making a run S was thrown to position 2, condensers  $C_2$  and  $C_3$  were adjusted so that the beat note was nulled, then S was thrown to position 1 and with  $T \cdot C$  disconnected,  $P \cdot C$  was adjusted to the nulled position and read. Then  $T \cdot C$  was connected in parallel with  $P \cdot C$  and  $P \cdot C$  was again ad-

justed to the nulled position and read. Then *S* was thrown back to position 2 to see if any shift in frequency had occurred. The shift, if any, was always very small.

The difference between the two readings of  $P \cdot C$  gave the apparent capacity of  $T \cdot C$ . The apparent capacity of  $T \cdot C$  should be corrected for lead capacity, inductance of leads, leakage and stray capacity if the frequency used and the method employed warrant it.

By using two General Radio precision condensers the capacity of dummy leads was measured by a substitution method.

To determine if any appreciable capacity correction due to the inductance of the leads should be taken into account let us consider the following expression

$$L_a = \frac{L(1 - \omega^2 L C_0) - C_0 R^2}{\omega^2 C_0^2 R^2 + (1 - \omega^2 L C_0)^2}$$
(17)

where  $L_a$  is the apparent inductance of the leads, L the calculated inductance of the leads,  $C_0$  the calculated capacity of the leads, R the resistance of the leads and  $\omega$  equals  $2\pi$  times the frequency.

We see from equation (17) that terms  $C_0R^2$  and  $\omega^2 C_0^2R^2$  are negligible except when approaching the frequency for which  $\omega = 1/(LC_0)^{1/2}$ . When just approaching this frequency we have  $L_a$  becoming strongly negative. For higher frequencies it remains negative but as the frequency is still increased it approaches zero. This negative value of the inductance indicates that the leads are behaving as a small condenser.

At the frequency of 85.8 kilocycles used in this work and with the short leads employed the terms  $\omega^2 L C_0$ ,  $C_0 R^2$  and  $\omega^2 C_0^2 R^2$  in equation (17) become negligible. Therefore  $L_a = L$  which itself proved to be a negligible positive value. Certainly for frequencies for which the value of the inductance is appreciably negative proper compensation for the capacity should be made.

The nulled heterodyne method can be used satisfactorily to determine the dielectric constants only for liquids with very small conductivity or so-called leakage. Otherwise the leakage sufficiently shortcircuits the condenser so that no beat note is obtainable. This was the writer's experience with acetone and aniline. By bridge methods, however, the power factor of imperfect liquid dielectrics can be measured and the dielectric constant determined.

It is believed that careful grounding and shielding practically eliminated the effect of stray capacities.

The correction of the capacity of the test condenser for difference in density of charge at the ends was considered inappreciable for the slender test condensers used in this work. Attempts to eliminate this end effect by the use of guard rings is described in the Bulletin of the Bureau of Standards, 3,433.

The formula for calculating the capacity of a condenser made of two coaxial cylinders is

$$C = 0.2416L/\log_{10} r_1/r_2 \tag{18}$$

where L is the length of the cylinders,  $r_1$  the radius of the outer cylinder,  $r_2$ 

the radius of the inner cylinder and C the capacity in mmf. All dimensions are expressed in centimeters.

For the test condenser No. 2, L = 25.44 cm,  $r_1 = 2.89$  cm and  $r_2 = 2.54$  cm. By calculation, the capacity of this test condenser equals 109.6 mmf.

After taking into account the capacity of the leads the capacity of test condenser No. 2 as measured with the precision condenser was found to be 106.9 mmf. Thus the calculated value is about 2.5 percent greater than the measured value.

The calculated value may be in error, (a) due to the cylinders not being exactly coaxial, (b) due to the diameters varying slightly throughout the length of the cylinders and (c) due to small errors in measurement.

The liquid whose dielectric constant was desired was placed in the test condenser and its capacity determined by the compensation necessary on the precision condenser to null the beat note.

For the liquids with high dielectric constants it was necessary to set the precision condenser near its maximum range and partially fill the test condenser until the note was nulled. The mass of the organic liquid required was determined with a balance. The height of the liquid in the test condenser was determined by taking into account the mass and density of the liquid as well as the physical dimensions of the test condenser as already described.

After a run a small glass tube properly bent was inserted to the bottom of the test condenser and the liquid pumped out. The condenser was then filled with ethyl ether which was a solvent for all the liquids used in this work. After a few minutes the ether was pumped out and the condenser was blasted with compressed air and fanned electrically until the ether residue was evaporated. This process was repeated before a new run was made.

Sample calculation of the dielectric constant for oxalyl chloride at  $21.2^{\circ}C$ Substituting in Eq. (1)

$$h_1 = \frac{(181.69)(25.44)}{(154.68)(1.488)} = 20.08 \text{ cm}.$$

Substituting in Eq. (2)

$$h_2 = 25.44 - 20.08 = 5.36$$
 cm.

Substituting in Eq. (3)

$$C_4 = \frac{(265.4 + 106.9) - (57.0 + 22.52)}{20.08} = 14.5\varepsilon.$$

Substituting in Eq. (4)

$$\epsilon = \frac{(25.44)(14.58)}{106.9} = 3.470.$$

Sample calculations of P,  $P_0$  and  $\mu$  for o-xylene. From Eq. (9)

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = \frac{(1.558)}{(4.558)} \frac{(106.08)}{(.879)} = 41.3 \ \epsilon$$

From Eq. (10)  $P_0 = \frac{r^2 - 1}{r^2 + 2} \frac{M}{\rho} = \frac{(1.265)}{(4.265)} \frac{(106.08)}{(.879)} = 35.8 \text{ cc.}$ 

From Eq. (16)

 $\mu = 1.27 \times 10^{-20} [(P - P_0)T]^{1/2} = 1.27 \times 10^{-20} [(5.5)(293)]^{1/2}$ = 0.51 × 10<sup>-18</sup> e.s.u. RESULTS

In Tables I and II are listed the values of the dielectric constants as found in this work. Figs. 3, 4 and 5 show graphically the values of the dielectric constants at different temperatures for othro-, meta-, and para-xylenes respectively.

TABLE I. Dielectric constants.

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Organic liquid	ρ	M'	V	$h_1$	$h_2$
Cinnamic aldehyde Ethyl ether Methyl o-nitrobenzoate Nitrobenzene Oxalyl chloride n-Propyl ether iso-Propyl ether Propylene chloride	$1.049 \\ .714 \\ 1.284 \\ 1.207 \\ 1.488 \\ .747 \\ .735 \\ 1.166$	$\begin{array}{r} 9.95 \\ 67.00 \\ 8.30 \\ 10.85 \\ 181.69 \\ 90.40 \\ 63.21 \\ 44.88 \end{array}$	9.4993.846.468.99122.10123.8686.0037.41	$\begin{array}{c} 1.56 \\ 15.43 \\ 1.06 \\ 1.48 \\ 20.08 \\ 20.37 \\ 14.14 \\ 6.15 \end{array}$	$\begin{array}{c} 23.88 \\ 10.01 \\ 24.38 \\ 23.96 \\ 5.36 \\ 5.07 \\ 11.30 \\ 19.29 \end{array}$
Organic liquid	t	$R_1$	$R_2$	<i>C</i> <sub>4</sub>	é
Cinnamic aldehyde Ethyl ether Methyl o-nitrobenzoate Nitrobenzene Oxalyl chloride n-Propyl ether iso-Propyl ether Propylene chloride	24.2 26.9 26.9 26.1 21.2 25.7 25.9 26.1	$\begin{array}{c} 267.8\\ 264.3\\ 264.3\\ 264.3\\ 265.4\\ 261.9\\ 261.9\\ 261.9\\ 261.9\end{array}$	$\begin{array}{c} 163.5\\57.0\\144.8\\57.0\\57.0\\57.0\\57.0\\57.0\\57.0\\57.0\\57.0$	$71.09 \\ 17.63 \\ 116.63 \\ 144.42 \\ 14.58 \\ 14.26 \\ 18.69 \\ 37.50$	$\begin{array}{c} 16.918\\ 4.197\\ 27.756\\ 34.369\\ 3.470\\ 3.394\\ 4.449\\ 8.925 \end{array}$
Air	4.20	1.000			

represents density ρ

M' grams of liquid in test condenser to null beat note

Vcc of liquid in test condenser to null beat note

 $h_1$  height of liquid in test condenser to null beat note (cms)

 $h_2$  height of air in test condenser (cms)

t temperature of liquid in degrees centigrade

 $R_1$  reading of precision condenser with only air in T.C (mmf)  $R_2$  reading of P.C with  $h_1$  cms of liquid and  $h_2$  cms of air in T.C

 $C_4$  capacity per centimeter of liquid in test condenser

dielectric constant of liquid at 85.8 kilocycles per sec. TABLE II. Dielectric constants.

Organic liquids	t	$R_1$	$R_2$	C5	e
Benzene Methyl cyclohexane o-Xylene m-Xylene p-Xylene	$ \begin{array}{r} 22.9\\ 24.8\\ 24.2\\ 24.1\\ 24.3 \end{array} $	264.3261.9248.0248.0248.0248.0	$ \begin{array}{r} 127.6 \\ 147.5 \\ 81.9 \\ 101.5 \\ 112.4 \end{array} $	$\begin{array}{r} 243.7\\ 221.4\\ 273.0\\ 253.4\\ 242.5\end{array}$	$\begin{array}{r} 2.279 \\ 2.071 \\ 2.553 \\ 2.371 \\ 2.269 \end{array}$

t represents the temperature in degrees centigrade  $R_1$  reading of precision condenser with air in T.C. (mmf)  $R_2$  reading of P.C. with liquid in T.C. (mmf)  $C_5$  capacity of T.C. filled with liquid (mmf)

 $\epsilon$  dielectric constant of liquid at 85.8 kilocycles per sec.



Fig. 3. Dielectric constant-temperature curve for o-xylene.



Fig. 4. Dielectric constant-temperature curve for m-xylene.

Table III gives the temperature coefficients of the dielectric constants of the three xylenes for the linear formula and for the formula proposed by Abegg.<sup>11</sup>

Table	III.	Temperature	coefficients.
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Liquid	$K_0$	β	€0	$lpha  imes 10^3$		
o-Xylene m-Xylene p-Xylene	$2.590 \\ 2.414 \\ 2.283$	0.0016 .0018 .0006	$\begin{array}{c} 2.5902 \\ 2.4141 \\ 2.2833 \end{array}$	0.270 .318 .117		

Linear formula,  $\epsilon_t = K_0 - \beta t$ Abegg's formula,  $\log_{10} \epsilon_t = \log_{10} \epsilon_0 - \alpha t$ 





The density data for the three xylenes were obtained with a Westphal balance. These data are tabulated in Table IV.

	o-Xylene	m-Xylene	p-Xylene
Т	ρ	ρ	ρ
288 293 298 303 308 313 318	0.883 .879 .875 .871 .867 .863 .859	$\begin{array}{c} 0.869 \\ .864 \\ .860 \\ .856 \\ .852 \\ .847 \\ .843 \end{array}$	0.865 .861 .857 .852 .847 .843 .838

TABLE IV. Density data.

 $\rho$  represents density and T absolute temperature.

The values of the polarization P for the three xylenes were calculated for several temperatures from the dielectric constant and density data. These values are plotted in Figs. 6, 7 and 8.

The values of the polarization  $P_0$  for the three xylenes were calculated by substituting optical data in Eq. (10). From the values of P and  $P_0$  the elec-

<sup>11</sup> Abegg, Wied. Ann. **60**, 54 (1897).



Fig. 6. Polarization-temperature curve for o-xylene.



Fig. 7. Polarization-temperature curve for m-xylene.



Fig. 8. Polarization-temperature curve for p-xylene.

tric moment  $\mu$  was calculated for the molecules of each of the three xylenes.  $P_0$  corresponds to the intercept A in Eq. (13). The values of P,  $P_0$  and  $\mu$  are given in Table V.

TABLE	V.	Electric	moments	of	molecules.
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Liquid	r	Р	$P_0$	$(P - P_0)$	$\mu \times 10^{18}$ e.s.u.
o-Xylene	$1.505 \\ 1.496 \\ 1.498$	41.3	35.8	5.5	0.51
m-Xylene		38.6	35.8	2.8	.36
p-Xylene		36.7	36.1	.6	.17

Symbol r represents the index of refraction

 $\vec{P}_0$  the polarization calculated from refractive data

 $\mu$  the electric moment of the molecule P the polarization at 20°C as determined in this work

Results recorded by Williams and Krchma (14)					
Liquid	Р	$P_0$	$(P-P_0)$	$\mu \times 10^{18}$ e.s.u.	
o-Xylene p-Xylene	40.8 36.7	35.0 35.5	5.8 1.2	0.52 .06	

#### DISCUSSION OF RESULTS

For a check on the method and technique employed in this work the dielectric constants were determined for ethyl ether, nitrobenzene, benzene, oxylene, m-xylene and p-xylene and were compared with the findings of several other experimenters. The results were in good agreement considering the different methods used, the experimental error and the inevitable variation in the purity of the organic liquids.

Table III shows that over the temperature range covered that either the linear formula or Abegg's formula is applicable. For large temperature ranges, however, Abegg's formula or the one proposed by Adams<sup>12</sup> are valid. The apparatus at hand did not permit working an extensive temperature range.

The polarization-temperature curves in Figs. 6, 7 and 8 for o-xylene, mxylene and p-xylene respectively each show a negative slope. Thus the experimental data leads to an imaginary electric moment for the molecules of each xylene. These results illustrate the inadequacy of the simple Debye theory when applied to pure organic liquids where the mutual interaction of the molecules is a dominant factor.

Debye<sup>13</sup> shows that molecules of organic liquids such as toluene  $C_6H_5$ (CH<sub>3</sub>) with monosubstituents are all dissymmetrical or polar as indicated by the magnitude of the electric moment. For molecules of compounds such as xylene  $C_6H_4(CH_3)_2$  and dinitrobenzene  $C_6H_4(NO_2)_2$  with two equal substituents the electric moment should be greatest in the ortho position, less in the meta and zero in the para position. The findings in this work on xylene as tabulated in Table V are in accord with this view. For molecules of compounds such as nitrotoluene  $C_6H_4(CH_3)(NO_2)$  with two unequal substituents the electric moment is greatest in the para position.

<sup>&</sup>lt;sup>12</sup> Adams, J. Am. Chem. Soc. 48, 621 (1926).

<sup>&</sup>lt;sup>13</sup> Debye, "Polar Molecules," p. 50.

Consulting Table V it is seen that the value of  $\mu$  for o-xylene accords well with the value found by Williams and Krchma<sup>14</sup> for o-xylene in dilute solution with a non-polar solvent. Also the electric moments for p-xylene are in fair agreement and they are so near zero that p-xylene is considered nonpolar.

# Conclusions

The writer can find no record of the previous determination of the dielectric constants of cinnamic aldehyde, methyl cyclohexane, methyl o-nitrobenzoate, oxalyl chloride, n-propyl ether, iso-propyl ether and propylene chloride.

It seems reasonable to believe that the values of the dielectric constants are relatively as accurate as the purity of the organic liquids.

The temperature coefficients of the dielectric constants for ortho-, meta-, and para-xylenes have been determined over a temperature range of about 30°C.

The experimental findings which led to negative electric moments further stress the inadequacy of the simple Debye theory when applied to pure organic liquids.

It is indeed a pleasure to give acknowledgment to Dr. F. C. Blake for his constant encouragement and valuable suggestions throughout these experiments.

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14 Williams and Krchma, J. Am. Chem. Soc. 49, 1676 (1927).