The Dielectric Constant and Absorption of Several Organic Fluids at 1.82 m

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For the further test of Debye's theory of anomalous dispersion, dielectric constants and absorptions were measured at $\lambda = 1.82$ m for the following fluids: ethyl alcohol, n-propyl alcohol, isopropyl alcohol, isobutyl alcohol, n-butyl alcohol, amyl alcohol, chlorobenzene, quinoline and nitrobenzene. The resonance method for undamped waves was used. The results are generally in good agreement with Debye's theory as well as with the results of Mizushima and others for fluids whose polarizations for infinite dilu-

tion do not differ greatly from those at normal concentration, as for the alcohols and chlorobenzol. For fluids like quinoline and nitrobenzene, the agreement is far from satisfactory. For these, however, when Malsch modification of Debye's theory is taken into account, a somewhat improved check is found, that for the dielectric constant being satisfactory, but that for the absorption of energy, while improved, being still far from satisfactory.

INTRODUCTION

DEBYE'S dipole theory of anomalous dispersion in the region of short electric waves has been lately confirmed by several authors. However, certain discrepancies have been found as in the case of glycerine by Bock [1] and Mizushima.[2] These have been attributed to three possible causes. (1) Debye's equations neglect the possible effects of associations of molecules. (2) The Debye equations are based on Mossotti's hypothesis for the internal field. (3) The calculation of the relaxation time is based on the assumption of a spherical molecule and therefore, on the validity of Stokes' formula. The third assumption does not seem, however, to cause very great discrepancies between theory and experimental data since Johnston and Williams[3] obtained for nitrobenzene, a highly associated fluid, a value of the right order for the molecular radius calculated from the relaxation time obtained by extrapolation to infinite dilution.

The purpose of this paper is the collection of further data on dielectric constants for wave-lengths of the order of a few meters, especially for associated fluids for the sake of a further test of Debye's dipole theory.

[1] R. Bock, Zeits. f. Physik 31, 534 (1925).

[2] San-Chiro Mizushima, Bull. Chem. Soc. Japan 1, 47, 83, 115, 143, 163 (1926); Phys. Zeits. 28, 418 (1927).

[3] J. H. L. Johnston and John Warren Williams, Phys. Rev. 34, 1483 (1929).

EXPERIMENTAL METHOD

A simple resonance method was used. Two UX 852 Radiotron tubes, as in Fig. 1, generated short electric waves. The resonance circuit consisted of a small loop, a variable condenser C_v, and, connected in parallel with the latter, a Pyrex glass vessel C_x with short platinum or tungsten lead-in wires, containing the liquid under investigation. The aperiodic circuit consisted of a loop of wire, a Weston thermocouple and a galvanometer. To eliminate any systematic error, preliminary measurements were made: (1) with two different condensers, one a variable
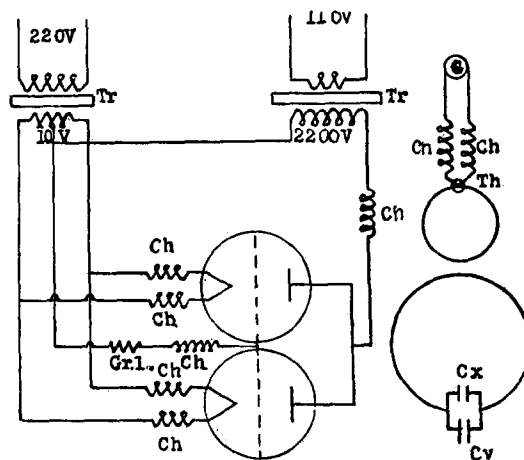

FIG. 1. Wiring diagram. Tr, transformer; Ch, choke coils; Gr, grid leak; Th, thermocouple; C_x, Pyrex vessel; C_v, variable condenser.

glass condenser, the other a variable cylindrical air condenser. Both had linear characteristics and the two sets of measurements gave the same results within the limits of experimental error, which amounted to a few percent. (2) The measurements were made under different coupling conditions. (3) Vessels of different capacity were used, their capacities being as 1 : 1.4 : 2. In this way, it was possible to measure the dielectric constants of the investigated fluids through a wide range, and also to eliminate systematic errors by repeating single sets of measurements with different vessels.

Calibration curves showing condenser setting for each vessel, as a function of the dielectric constant, were obtained with the aid of benzene-acetone and acetone-water solutions of known dielectric constants. These curves were approximately linear. A curve showing absorption of energy by the liquid in the cell C_x of Fig. 1 was determined by a method similar to Mizushima's in which KI solutions in acetone of known concentration and conductivity were used. The deflections α of the galvanometer at the point of resonance were noted for each vessel containing a fluid of a given conductivity at a given temperature. The ratios of these deflections to the deflections at resonance point without the fluid in the vessel $k = \alpha/\alpha_0$ were the ordinates of the absorption curves, whose abscissae were the corresponding conductivities in $ohm^{-1} \, cm^{-1}$. To correct for the apparent increase in capacity due to the conductivities of the fluids, correction curves for each vessel were drawn in a way similar to Mizushima's. At the wave-length used in this investigation, acetone had not yet shown any effect of anomalous absorption at room temperature. Distilled water, however, showed a marked anomalous absorption.* A corresponding

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* Although this seems to be surprising, many measurements made in different coupling conditions and with acetone-water solutions of different concentrations showed always this absorption effect. A marked heating of distilled water was also observed at this frequency, if the vessel were put between two plates in a resonating circuit.

That this absorption was not a normal absorption effect but an anomalous one must be concluded from the galvanometer deflection data at different temperatures. These deflections showed an increase with temperature elevation which expressed in equivalent conductivity ranged from about 11.4×10^{-5} to $6.5 \times 10^{-5} \, ohm^{-1} \, cm^{-1}$ for a temperature interval of about 15–30°C.

smaller effect was also observed in the water-acetone solutions used for the calibration of the vessels, therefore, the calibration curve of the vessels with greater capacity had to be corrected for the small apparent increase in capacity due to this effect.

A wave-length of $\lambda = 1.82$ m was chosen. By this choice, difficulties involved in using a thermostat with a resonating circuit for short electric waves were avoided, and data at a wave-length other than those already reported (Mizushima used $\lambda = 3.08$, 9.5, and 50 m) were obtained. Further, it was expected that the anomalous dispersion and absorption effects would be marked enough at this wave-length for the substances under investigation, without using extremely low temperatures. The wave-length was measured in a parallel wire Lecher system. The fluids were cooled and then allowed to warm up slowly. In the meantime, the temperature of the fluid $t°$, the condenser setting S, and the galvanometer deflection α were noted. The same observations were made during the cooling of the heated fluids. Before and after each set of measurements, and without fluid in the cell, the condenser setting S_0 and the galvanometer deflection α_0 were carefully determined. Although the condenser allowed a sharp determination of the resonance point, the effects of the anomalous absorption in the investigated fluids flattened the resonance curve appreciably and caused errors ranging from one to three percent. This accuracy, however, was thought to be sufficient for the purpose of this investigation, since it was of the same order of Mizushima's. The resonance curve did not have any irregularities.

RESULTS

Alcohols

All alcohols used in this investigation were C.P. products of the Eastman Kodak Research Laboratories, with the exception of ethyl alcohol which was purified and distilled from a technical product.

Ethyl alcohol

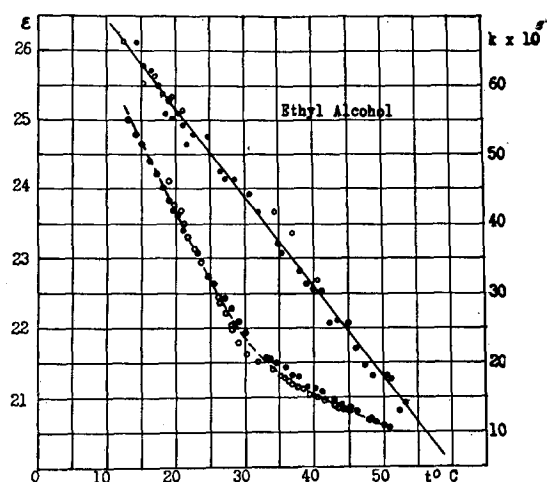Fig. 2 shows the dielectric constant and absorption curves for an interval of 0–50°C.

FIG. 2. Variation with temperature of dielectric constant ε (———) and absorption k (- - - -) for ethyl alcohol at λ = 1.82 m.

These data may be compared in Table I with the values computed from Debye's equations:[4]

$$\epsilon'_{calc.} = \epsilon_0 + \frac{\epsilon_1 - \epsilon_0}{1 + [(\epsilon_1+2)/(\epsilon_0+2)]^2 \omega^2 t^2} \quad (1)$$

$$\epsilon''_{calc.} = (\epsilon_1 - \epsilon_0) \frac{[(\epsilon_1+2)/(\epsilon_0+2)]\omega t}{1 + [(\epsilon_1+2)/(\epsilon_0+2)]^2 \omega^2 t^2} \quad (2)$$

$$t = 4\pi\eta a^3 / KT \quad (3)$$

where:

T = absolute temperature; η = viscosity;

$t°$ = temperature in °C; K = Boltzmann constant;

t = relaxation time; $\omega = 2\pi \times$ frequency;

a = molecular radius;

ϵ_0 = dielectric constant at high frequency = square of the refractive index for the D lines;

ϵ_1 = dielectric constant for zero frequency;

$\epsilon'_{obs.}$ = real part of the complex dielectric constant interpolated from Fig. 2 at λ = 1.82 m;

$\epsilon'_{calc.}$ = calculated value for the real part of the dielectric constant for λ = 1.82 m from Eq. (1);

$\epsilon''_{obs.}$ = imaginary part of the complex dielectric constant = $4\pi\sigma/\omega$ where σ is the electrical conductivity corresponding, as shown by a calibration curve, to the observed ratio k of Fig. 2;

$\epsilon''_{calc.}$ = imaginary part of the generalized dielectric constant calculated from Eq. (2).

[4] P. Debye, *Polar Molecules*, p. 97, 1929, Chem. Cat. Co., New York.

TABLE I. *Ethyl alcohol.**

$a = 1.8 \times 10^{-8}$ cm; λ = 1.82 m.

$t°C$	η (poise)	ϵ_0	ϵ_1	$\epsilon'_{obs.}$	$\epsilon'_{calc.}$	$\epsilon''_{obs.}$	$\epsilon''_{calc.}$
50	0.00701	1.8	21.2	21.3	21.11	1.20	1.47
40	0.00831	1.82	22.7	22.6	22.52	1.69	1.97
30	0.00992	1.83	24.25	23.9	23.93	2.57	2.74
20	0.0119	1.85	25.8	25.15	25.15	4.48	3.80
10	0.0145	1.86	27.0	26.45	25.86	6.88	5.24
0	0.0177	1.88	28.4	27.72	26.28	9.10	7.10

* Debye's Eqs. (1) and (2) were used in obtaining $\epsilon'_{calc.}$ and $\epsilon''_{calc.}$ in Tables I through IV.

The computations were made under the assumption of a molecular radius $a = 1.8 \times 10^{-8}$ cm. The values for ϵ_0 and ϵ_1 at 30°, 40°, and 50°C were extrapolated from Mizushima's data. The experimental values of $\epsilon'_{obs.}$ and k at 0°C were also extrapolated from the curves in Fig. 2. The same extrapolation procedure was used in all the following tables. From Table I, we can see that the theoretical values check well the experimental ones as was found by Mizushima for other wave-lengths. However, considerable discrepancies are noted when the computations are carried out under the assumption of $a = 2.0 \times 10^{-8}$ cm as calculated from critical point data,[5] the van der Waals constant b being taken as $16/3\pi Na^3$.

n-Propyl alcohol

The absorption curve shows a maximum at around 5°C. The dielectric constant starts to decrease in the region of 20°C (Fig. 3). For an assumed molecular radius $a = 2.2 \times 10^{-8}$ cm as calculated from critical data, a comparison of experimental and theoretical values is shown in

TABLE II. *n-Propyl alcohol.*

$a = 2.2 \times 10^{-8}$ cm; λ = 1.82 m.

$t°C$	η (poise)	ϵ_0	ϵ_1	$\epsilon'_{obs.}$	$\epsilon'_{calc.}$	$\epsilon''_{obs.}$	$\epsilon''_{calc.}$
50	0.011305	1.87	18.35	16.2	17.77	1.80	2.96
40	0.01405	1.89	19.65	16.85	18.57	2.95	4.26
30	0.0178	1.90	20.9	17.42	18.82	4.48	5.67
20	0.0226	1.92	22.2	17.4	18.35	7.54	7.92
10	0.0292	1.94	23.5	15.35	16.73	10.1	9.97
0	0.0388	1.95	24.8	12.6	13.73	10.6	11.42

[5] Landolt and Bornstein, Tables, 5th Edition. VI.

Table II. The check is not as good as for ethyl alcohol. The general characters of the theoretical and experimental curves, however, are the same.
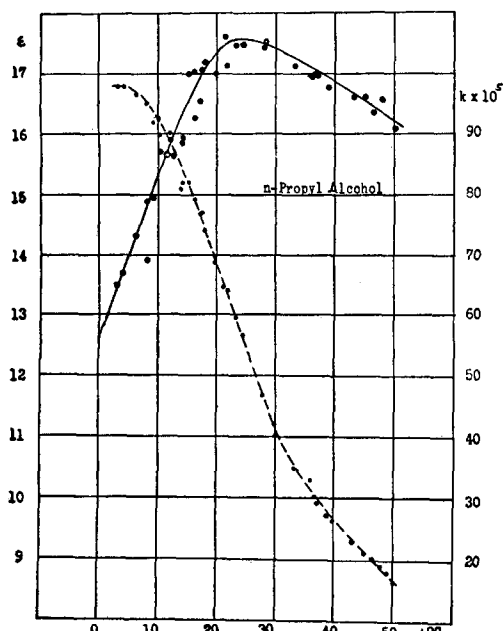

FIG. 3. Variation with temperature of dielectric constant ϵ (——) and absorption k (- - - -) for n-propyl alcohol at $\lambda = 1.82$ m.
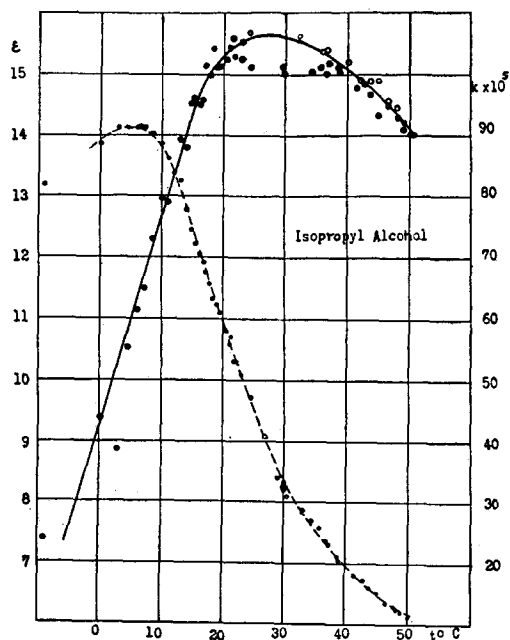

FIG. 4. Variation with temperature of dielectric constant ϵ (——) and absorption k (- - - -) for isopropyl alcohol at $\lambda = 1.82$ m.

Isopropyl alcohol

We do not have sufficient data for ϵ_0 and ϵ_1 at different temperatures to compare the theoretical and the experimental values; however, since the viscosity of isopropyl alcohol is but little different from that for n-propyl alcohol, we expect, according to Debye's theory, the maximum of absorption and the decrease of the dielectric constant to be in the same region as for n-propyl alcohol. Fig. 4 shows this to be the case.

Isobutyl alcohol

In Fig. 5 we find a maximum for the absorption at about 15°C and a decrease of the dielectric constant at about 30°C. Calculating the molec-

TABLE III. *Isobutyl alcohol.*

$a = 2.3 \times 10^{-8}$ cm; $\lambda = 1.82$ m.

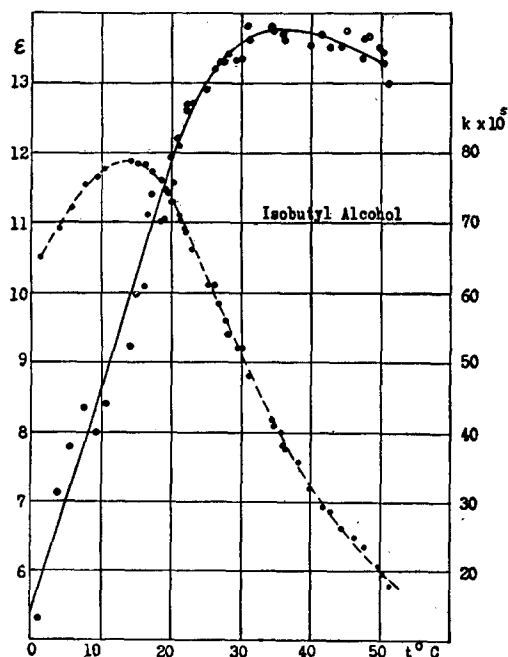| t°C	η (poise)	ϵ_0	ϵ_1	$\epsilon'_{obs.}$	$\epsilon'_{calc.}$	$\epsilon''_{obs.}$	$\epsilon''_{calc.}$
50	0.0161	1.88	17.4	13.25	16.19	2.14	4.12
40	0.0212	1.90	18.25	13.7	15.92	3.54	5.71
30	0.0287	1.93	19.15	13.6	14.74	5.56	7.51
20	0.0391	1.95	20.0	11.9	12.33	8.00	8.92
10	0.0555	1.97	21.0	8.6	8.92	8.45	9.20
0	0.0804	1.99	21.8	5.4	5.88	6.82	7.88

FIG. 5. Variation with temperature of dielectric constant ϵ (——) and absorption k (- - - -) for isobutyl alcohol at $\lambda = 1.82$ m.

ular radius from critical data, we obtain $a = 2.3 \times 10^{-8}$ cm. With this value, Table III was computed and the experimental values compared with the theoretical ones. In general the check is good except for the higher temperatures.

n-Butyl alcohol

Here again we do not have sufficient data for ϵ_0 and ϵ_1 at different temperatures in order to compare theoretical and experimental values as for isobutyl alcohol; however, since the viscosity of n-butyl alcohol is less than that of isobutyl alcohol, we expect a shift of both the absorption and the dielectric constant curves towards lower temperatures. This is the case, as may be seen from a comparison of Figs. 5 and 6.
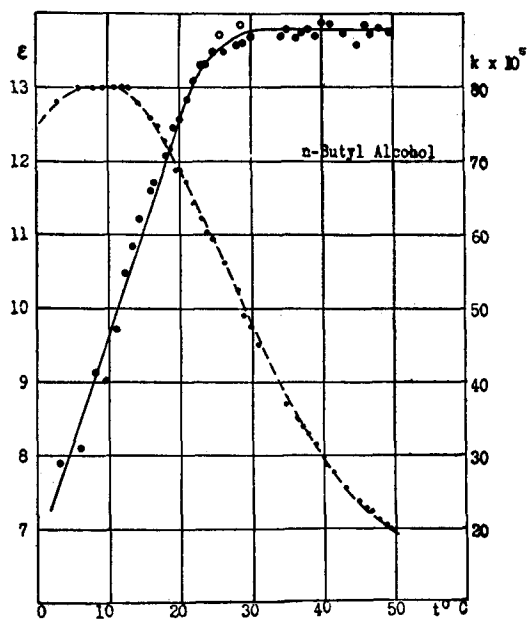

FIG. 6. Variation with temperature of dielectric constant ϵ (———) and absorption k (- - - -) for n-butyl alcohol at $\lambda = 1.82$ m.

Amyl alcohol

Here η is greater than that of the above-mentioned alcohols; therefore, a shift towards higher temperatures for the maximum of absorption and for the bend in the dielectric constant curve must be expected. Fig. 7 shows this to be the case. The maximum absorption occurs
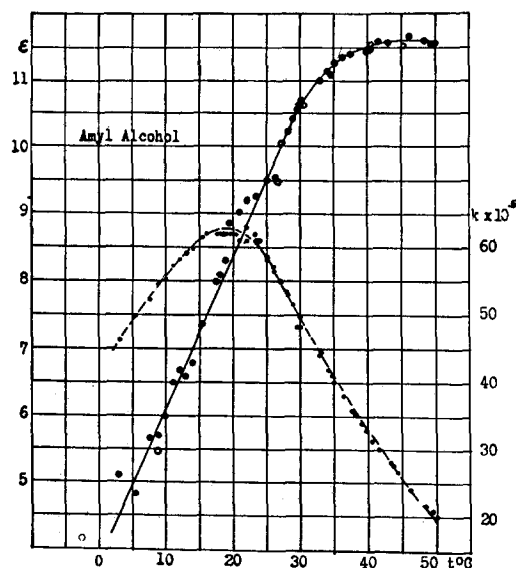

FIG. 7. Variation with temperature of dielectric constant ϵ (———) and absorption k (- - - -) for amyl alcohol at $\lambda = 1.82$ m.

at about 20°C and the bend in the dielectric constant curve starts at about 40°C. We are not in possession of sufficient critical data in order to compute the molecular radius. It is expected, however, to be much greater than that of the above-mentioned alcohols. Assuming $a = 2.5 \times 10^{-8}$ cm, Table IV was computed. The check is, in general, good.

TABLE IV. *Amyl alcohol.*

$a = 2.5 \times 10^{-8}$ cm; $\lambda = 1.82$ m.

$t°C$	η (poise)	ϵ_0	ϵ_1	$\epsilon'_{obs.}$	$\epsilon'_{calc.}$	$\epsilon''_{obs.}$	$\epsilon''_{calc.}$
50	0.01864	1.91	13.85	11.6	12.58	2.13	3.69
40	0.02434	1.94	14.6	11.55	12.16	3.60	4.95
30	0.03235	1.96	15.3	10.7	11.00	5.46	6.24
20	0.0437	1.98	16.0	8.4	9.02	6.84	7.00
10	0.0610	2.00	16.8	6.1	6.56	6.11	6.84
0	0.0876	2.02	17.5	3.9	4.58	4.58	5.73

Chlorobenzene

A C.P. product from the Eastman Kodak Research Laboratories was used. For chlorobenzene the molecular radius computed from critical data is $a = 2.4 \times 10^{-8}$ cm. From Eq. (1) we compute for 18°C and for $\lambda = 1.82$ m $\epsilon'_{calc.} = 5.7$. On the other hand, the experimental

value is $\epsilon'_{obs.} = 5.61$. The discrepancy is still not great. No anomalous absorption was observed at this temperature.

Quinoline

A C.P. product from the Eastman Kodak Research Laboratories was used. For quinoline sufficient critical data are not known for the computation of the molecular radius. We have here to compute it from the experimental dielectric constant in a manner similar to that used by Mizushima for glycerine and to consider whether or not this value is reasonable. Putting in Eq. (1) the observed experimental value of the dielectric constant for quinoline at 18°C, $\lambda = 1.82$ m; namely, $\epsilon'_{obs.} = 8.74$, we obtain as the molecular radius $a = 2.3 \times 10^{-8}$ cm. This value seems to be small, since the benzene molecule has a radius of about 2.3×10^{-8} cm and quinoline has a benzene and a pyridine ring. We can see, therefore, that for such a degree of association as is in quinoline, the simple Debye equations do not check the experimental data. Quinoline shows a small anomalous absorption corresponding to a conductivity of about 4×10^{-5} ohm^{-1} cm^{-1} at about 10°C.

Nitrobenzene

Nitrobenzene was investigated in two different samples. Sample 1 was a C.P. Baker Company product, sample 2 was obtained by double distillation of Baker's technical nitrobenzene. The experimental values for both samples checked well within the limits of the experimental error which was about 1 percent. Fig. 8 shows the curves for dielectric constants and absorptions at different temperatures. Table V, based on a
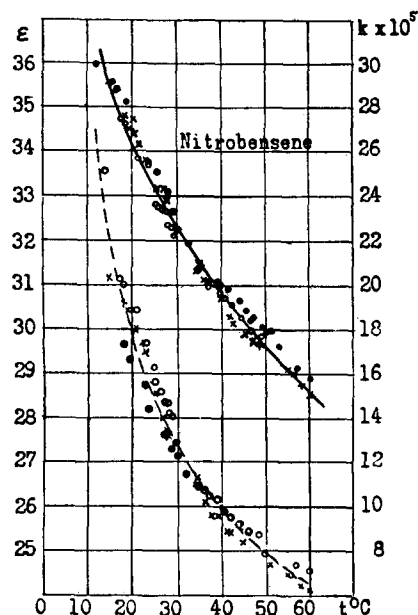

Fig. 8. Variation with temperature of dielectric constant ϵ (——) and absorption k (-----) for nitrobenzene at $\lambda = 1.82$ m.

value of $a = 2.4 \times 10^{-8}$ cm for the molecular radius of nitrobenzene according to Johnston and Williams,[3] shows great discrepancies between experimental and theoretical values. For this highly associated fluid, Eqs. (1), (2) and (3) are not sufficient. Taking the experimental values for the dielectric constant of nitrobenzene, we can compute again the molecular radius from Eq. (1). This is found to be $a = 1.53 \times 10^{-8}$ cm at 20°C. The value computed this way is too small, in agreement with what was found above for quinoline and by Mizushima for glycerine.

TABLE V. *Nitrobenzene.**

$a = 2.4 \times 10^{-8}$ cm; $\lambda = 1.82$ m.

t°C	η (poise)	ϵ_0	ϵ_1	$\epsilon'_{obs.}$	$\epsilon'_{calc.}$	$\epsilon''_{obs.}$	$\epsilon''_{calc.}$
60	0.0109	2.36	28.61	28.58	26.46	0.71	7.2
50	0.0125	2.37	30.03	29.6	26.67	0.82	8.3
40	0.0144	2.38	31.56	30.8	26.37	1.07	11.1
30	0.0168	2.39	33.35	32.3	25.50	1.40	13.5
20	0.0201	2.41	35.46	34.2	23.27	1.96	15.95

* Debye's Eqs. (1) and (2) were used in obtaining $\epsilon'_{calc.}$ and $\epsilon''_{calc.}$. (See Table VI.)

DISCUSSION OF RESULTS

The foregoing shows that as long as the molar polarizations at normal concentration and at infinite dilution are not very different as in the case of alcohols and chlorobenzene, Eqs. (1), (2) and (3) yield, at least qualitatively, values for the real and the imaginary parts of dielectric constants in agreement with experiment. This conclusion checks not only with the results of Mizushima, but also with the more

recent* results of Goldhammer,[6] Malsch,[7] and Girard and Abadie[8] who investigated alcohols and alcohol solutions. The latter, however, were tested at different wave-lengths from those used in the present investigation. For fluids where molar polarization at infinite dilution P_∞ differs very much from that at normal concentration P_n as in the case of quinoline, where this ratio $P_\infty/P_n \lesseqgtr 1.7$ (Rolinski[9]), and nitrobenzene, where $P_\infty/P_n \lesseqgtr 3.6$, and possibly glycerine, Eqs. (1) and (2) need a correction. At first, it seemed that such a correction for associations could be easily made in accord with Debye's theory of association,[10] where the molecules are assumed to produce associated molecular groups, having a smaller or a larger electric moment. This theory was developed by Wolfke[11] and the theoretical molar polarization curves as a function of the concentration for different alcohols agreed well with the experimental ones. For chlorobenzene, quinoline, and nitrobenzene the computation of the degree of association was in good accordance with the experimental data. If we want to apply, however, this theory to measurements at a high frequency, we must introduce in the equations for the molar polarization, P, a frequency factor $1/(1+i\omega t)$ Debye[4] (p. 90).

The equation will then be:

$$P_{(\omega)} = \frac{\epsilon-1}{\epsilon+2}\frac{M}{\rho} = \frac{4\pi}{3}N\alpha_0$$
$$+ \frac{4\pi}{3}N_0\frac{\mu^2}{3KT}\left(\frac{1}{1+i\omega t}\right) \quad (4)$$

where:

$P_{(\omega)}$ = molar polarization at a given frequency;
M = molecular weight;
ρ = density;
N = total number of molecules per mole;
N_0 = number of unassociated molecules;
α_0 = molecular polarizability taking account of the distortion effect;
μ = electric moment;
$\omega = 2\pi \times$ frequency.

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* The present investigation was made in 1931. Since that time, several papers appeared dealing with a similar subject.

[6] Goldhammer, Phys. Zeits. 33, 361 (1932).

[7] Malsch, Ann. d. Physik 12, 865 (1932); Phys. Zeits. 33, 19 (1932).

[8] Girard and Abadie, Comptes Rendus 195, 119, 217 (1932).

Deducing the expression for ϵ we can find, however, that this substitution does not change the final expressions (1) and (2), as found by Debye. The above theory of association cannot, therefore, explain the discrepancies encountered at a higher frequency.

Malsch[12] recently proposed a correction of the Debye equations, based on the introduction of an additional internal force, as already used by Lorentz.[13] This internal force is due to the interaction of the molecules and, therefore, can be considered the result of association. Such an assumption brings the problem back to a correction of the Clausius Mossotti relation, which can be then deduced from:

$$F = E + (4\pi/3)(1+\nu)P$$

where

F = total force acting on a molecule per unit charge;
E = field strength;
P = polarization = electric moment per unit volume;
ν = factor for the introduction of an additional force.

We have then according to Malsch:[12]

$$\left(\frac{\epsilon-1}{\epsilon+2}\frac{M}{\rho}T\right)_{obs.} = \frac{(4\pi/3)N\alpha T}{1-\nu(\rho/M)(4\pi/3)N\alpha}$$

where $\alpha = \alpha_0 + \mu^2/3KT$. Having the experimental values for the molar polarization at normal concentration and at infinite dilution, we can find ν as a function of the temperature. The correction factor in Debye's Eqs. (1) and (2) would then be:

$$z = \frac{\epsilon_1 + 2 + (\epsilon-1)\nu}{\epsilon_0 + 2 + (\epsilon_0-1)\nu}$$

instead of $(\epsilon_1+2)/(\epsilon_0+2)$. Finally the Debye equations will have the form:

$$\epsilon' = \epsilon_0 + (\epsilon_1-\epsilon_0)/[1+(z\omega t)^2] \quad (5)$$

$$\epsilon'' = \epsilon_1 - \epsilon_0 z\omega t/[1+(z\omega t)^2]. \quad (6)$$

If we now apply this new equation to nitro-

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[9] Rolinski, Phys. Zeits. 29, 658 (1928).

[10] Debye, Handbuch d. Radiologie, Vol. 6.

[11] Wolfke, Phys. Zeits. 29, 713 (1928); Comptes Rendus de la Soc. Pol. de Phys.

[12] Malsch, Phys. Zeits. 33, 383 (1932).

[13] Lorentz, Wied. Ann. 9, 641 (1880).

TABLE VI. *Nitrobenzene.*

$a = 2.4 \times 10^{-8}$ cm; $\lambda = 1.82$ m.

$t°C$	ϵ'obs.	ϵ'calc.	ϵ''obs.	ϵ''calc.
60	28.58	28.26	0.71	2.9
50	29.60	29.47	0.82	3.96
40	30.8	30.58	1.07	5.0
30	32.3	31.99	1.40	6.3
20	34.2	33.11	1.96	8.4

* Debye-Malsch Eqs. (5) and (6) were used in computing ϵ'calc. and ϵ''calc.. (See Table V.)

benzene, we see from Table VI that the agreement between experimental and theoretical values is much better for the dielectric constant. For the absorption, the discrepancy is still very great, although it is better than that in Table V. In Tables V and VI, the molecular radius was assumed to be 2.4×10^{-8} cm which is a rather small value, since x-ray studies indicate that it should be about 3.0×10^{-8} cm $- 4.0 \times 10^{-8}$ cm in which case the correction used above would still be insufficient. If this correction were applied to the alcohols, then all values would be overcorrected unless we would assume higher radii. For instance, for ethyl alcohol, with a radius of 2.0×10^{-8} cm and the correction of Malsch, we again find a good agreement between theoretical and experimental data. n-Propyl alcohol, however, would seem to be overcorrected unless a higher radius were taken. The corrections for isobutyl alcohol, amyl alcohol, and chlorobenzene are negligible. Applying the correction to quinoline, we find a much bigger radius, that of 2.6×10^{-8} cm instead of 2.3×10^{-8} cm as found without correction. The bigger radius certainly seems more reasonable. From the above, however, we can see that without a knowledge of the exact molecular radius, no quantitative comparison as to the validity of the introduced corrections can be made, since even a small change in the radius will change considerably the computed results. As it was pointed out by Oncley and Williams,[14] the radii can be several times larger, at low temperatures, than kinetic theory values because of association effects. This would bring the association phenomena back to the Debye association

theory[10] mentioned above. However, only comparatively small parts of the alcohol molecules would have a double moment, as can be seen from the comparison of polarization at infinite dilution and of that at normal concentration. Therefore the correction of the average relaxation time would be small. In a triple molecule with a zero resultant moment there would be no influence on the relaxation time.

Since there are, at present, insufficient data available for molecular radii at different temperatures for associated fluids, we have to use the kinetic theory values as a first approximation, or preferably x-ray data, so far as they are known.

Another way of explaining the discrepancy between the theoretical and experimental data would be that of Oncley and Williams.[14] On the basis of many experiments with solutions of various polar substances in mineral oils of varying viscosities, they found that there was no dispersion even at 1.727×10^7 cycles. These results are consistent with the experiments of Goldhammer[6] and Weigle and Lüthi.[15]

Oncley and Williams give a probable explanation of the results by the failure of Stokes' law. The reason for such a result may be either because the application of a law in a form of Stokes' law is not justified, or because the use of macroscopic viscosity is not permissible. The experiments of Oncley and Williams on floricin and rosin solutions seem to indicate that Stokes' law is true in its general form. Therefore, we must assume that for the calculation of the relaxation time of an associated fluid, we have to use a corrected macroscopic viscosity.

Such a correction has been used by Goldhammer,[6] who found a much better agreement between experimental and theoretical data for a solution of n-butyl alcohol in paraffin oil at $\lambda = 0.72$ m if the viscosity were decreased 15 percent.

The same procedure applied to nitrobenzene would, in our case, give a higher value for the molecular radius of nitrobenzene than 2.4×10^{-8} cm which is rather small.

[14] Oncley and Williams, Phys. Rev. **43**, 341 (1933).

[15] Weigle and Lüthi, Comptes Rendus **49**, 130 (1932).