[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. III THE ELECTRIC MOMENTS OF CERTAIN ORGANIC MOLECULES IN CARBON TETRACHLORIDE SOLUTION

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In the preceding paper of this series,[1] as well as in a number of other articles,[2,3,4] it has been shown that the concept of molar polarization introduced by Debye[5] has made possible a treatment of dielectric constant and density data for certain binary liquid mixtures such that the electric moments of the solute molecules can be calculated provided they are dissolved in a medium which has no electric moment itself. It was stated[1] that liquids such as carbon tetrachloride, carbon bisulfide, pentane, hexane and benzene should act as suitable solvents of this type. The purpose of this paper is to present the results of calculations of the electric moments of certain organic molecules from measurements of the dielectric constants and the densities of their solutions in carbon tetrachloride. The mathematical expressions necessary for this calculation were presented in the previous paper and will not be repeated here.

Method

Two distinct methods were used for the determination of the dielectric constants of the binary mixtures. The first, an electrical resonance method, was described in some detail in the first paper of this series.[6] The second was one of the so-called bridge methods. It was necessary to use this second method for certain of the binary mixtures since a resonance method of the type referred to above fails for liquids which have any appreciable electrical conductance.

Since the bridge as set up contains several novel features it will be briefly described. It is shown diagrammatically in Fig. 1. The instantaneous potential of an alternating current for any given instant is determined by the "phase angle" obtained in a vectorial consideration of the inductance and capacitance. The phase angle of the current at the point "a" must equal the phase angle of the current at "b" in order that the points "a" and "b" be at equal potential at all times and that no current be detectable in "G." Since the phase angle is dependent on the resistance, inductance and capacitance in the arms, then in this sort of bridge a balance of resistance and inductance is required along with a balance of capacitance.

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[1] Williams and Krchma, THIS JOURNAL, **49**, 1676 (1927).

[2] Lange, *Z. Physik*, **33**, 169 (1925).

[3] Debye, "Handbuch der Radiologie" (Marx), **6**, 625 (1925).

[4] Smyth, THIS JOURNAL, **49**, 1030 (1927).

[5] Debye, *Phys. Z.*, **13**, 97 (1912); *Verhandl. deut. phys. Ges.*, **15**, 777 (1913).

[6] Williams and Krchma, THIS JOURNAL, **48**, 1888 (1926).

A bridge of this kind lends itself to the measurement of the capacitance of a "leaky" condenser (that is, one having a conducting or current-absorbing dielectric) since it involves a simultaneous balance of resistance, capacitance and inductance. A "leaky" condenser may be treated as a capacitance with a large resistance in parallel or a small resistance in series.[7] In either case a condition of balance may be obtained by simultaneous adjustment of capacitance and resistance in the proper arms of the bridge. Therefore, determinations of the capacitance may be made as if the resistance were not there. The determination of the dielectric constant may then be accomplished in the usual manner.

The source of alternating current is "D," which in this case is simply a Hartley circuit. A honeycomb coil, "E," is placed in inductive relation to the inductance "F" of the Hartley circuit. A two stage amplifier, "G," made by the General Radio Co., Cambridge, Mass., serves to detect the signals. "R_1" and "R_2" are non-inductive resistance (Curtis) coils of 1000 ohms each. In arm "3" is placed a variable air capacitance "C_1" of 2000 MMF, shunted by a resistance "R_3," variable by steps between 10 and 10,000 ohms. In the fourth arm of the bridge is placed the standard variable condenser, "C_2," in parallel with the dielectric cell, "C_x," and a continuously variable, non-inductive, liquid resistance "R_4." A large unknown resistance, "R_x," is set up by the "leaky" condenser "C_x." The dielectric cell and the standard condenser are the same as employed in the resonance circuit and have been described previously.[6] Condensers "C_1," "C_2" and "C_x" are so arranged that the stator plates are attached to the ground "d," thus effecting a shielding the same as in the resonance circuit.

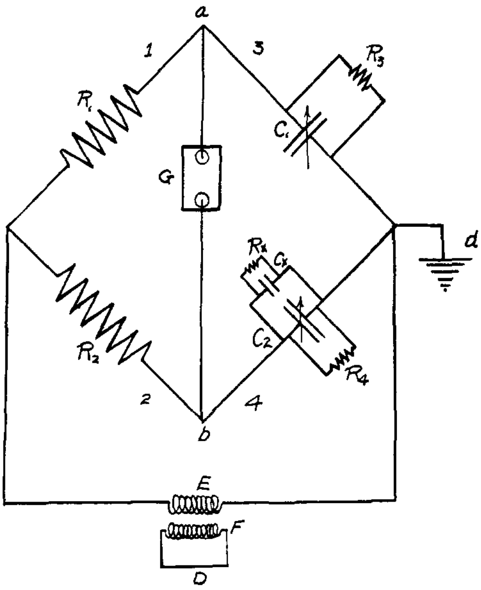

Fig. 1.

R_x—resistance of liquid in condenser C_x; R_1,R_2—1000-ohm Curtis coils; R_3—variable resistance of 10,000-ohms; R_4—variable non-inductive liquid resistance; C_1—variable air condenser of 2000 MMF; C_2—standard variable condenser of 1500 MMF; C_x—dielectric cell; R_x—resistance of liquid in dielectric cell; d—ground.

The principle of detection is briefly as follows. Oscillations of a very high frequency are set up in "D." Oscillations of a frequency approaching that of "D" are set up in "G." When the current flows between "a" and "b," audible beats are set up between the two frequencies, which cease when the bridge is balanced. By proper adjustment of the capacitances and inductances of the two circuits, "D" and "G," it is possible to obtain a loud ringing tone in the telephones which yields a sharp,

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[7] Terry, "Advanced Laboratory Practice in Electricity and Magnetism," McGraw-Hill Book Co., New York, 1922, p. 191.

narrow, distinct minimum entirely free from confusion by harmonics. A minimum of width corresponding to 1.5 MMF may be obtained.

Of course this arrangement, employing a very high frequency, is very susceptible to small irregularities in the inductance or capacitance of the bridge arms. By the ordinary methods of balance such an arrangement would be incapable of producing accurate results, since a bridge of this kind is certain to have its balance ratio affected by change of frequency,[8] and a change of inductance or capacitance in the bridge as is required by the ordinary methods of balance would necessarily alter the frequency greatly. This is true since it is difficult to obtain capacitanceless, inductanceless resistances and leads, and under the usual conditions a so-called "frequency" bridge is almost unavoidable. It is the difficultly controlled stray capacitances and inductances that exist in all ordinary apparatus that cause the trouble. In the apparatus as set up this difficult feature of the very high frequency bridge is avoided by employment of the variable dielectric cell and the continuously variable non-inductive resistance "R_4." The measurement is carried out as follows. The bridge is first brought to balance, having "R_3," "C_1," "C_2," "C_x" and "R_4" all attached as in Fig. 1. The plates of "C_x" are set at a position "A" exactly as in the case of the resonance circuits. The bridge being in balance for this point, "C_x" is adjusted to a point we may again call "B," whereupon "R_x" also changes. The condition of balance is then quite simply restored by adjustment of the standard variable condenser "C_2" and the non-inductive liquid resistance "R_4." Knowing from the resonance method what the capacitance change produced by the change of "C_x" from "A" to "B" in air is, the dielectric constant of a liquid is obtained simply by dividing the change in "C_2" necessary to restore bridge balance when "C_x" contains that liquid, by this value in air.

The advantage of this method of balance is at once apparent. The arms "1," "2" and "3" are held non-variable for a measurement. Hence for the condition of balance at "B" the relations between the capacitances, resistances and inductances must equal those at "A." Thus we obtain a measurement without change of arm ratios and the fact that we may have a "frequency" bridge presents no difficulties. This method even eliminates the necessity of using Curtis coils at "R_1" and "R_2" or of having "R_3" non-inductive.

The fact that the bridge method described above gives reliable results for the dielectric constants of the mixtures is indicated by a comparison with the results obtained by the electrical resonance method. In a large number of cases it was possible to measure the dielectric constants of the pure liquids and their solutions by both resonance and bridge methods, and in every case a very good agreement was found.

[8] Ref. 7, p. 186.

The densities of the pure liquids and of the solutions were determined at the same temperature at which their dielectric constants were measured, namely, 25°. An Ostwald-Sprengel pycnometer was used for the purpose. A Pulfrich refractometer was used to measure their refractive indices, also at 25°.

Purification of Materials

Carbon Tetrachloride.—The carbon tetrachloride used was the highest grade material which could be obtained from the Eastman Kodak Company. Since no trace of sulfides was found, it was simply dried and fractionated; b. p. (760 mm.) 76.45–76.52°.

Methyl Acetate.—This material was obtained from the Eastman Kodak Company. It was shaken with a concentrated potassium carbonate solution and washed with water. A rough drying was effected with anhydrous potassium carbonate; then it was completely dehydrated with phosphorus pentoxide. It was fractionated in the usual manner; b. p. (760 mm.) 57.0–57.2°.

Ethyl Acetate.—The ethyl acetate, also obtained from the Eastman Kodak Company, was subjected to a treatment similar to that of the methyl acetate; b. p. (760 mm.) 76.7–76.9°.

Acetone.—The acetone used was an Eastman Kodak Company product. It was crystallized out with sodium iodide and distilled directly from this compound. It was then thoroughly dried (six months) over boric anhydride and fractionated; b. p. (760 mm.) 56.00–56.05°.

Ethyl Alcohol.—A 99% alcohol was purified by the method described by Noyes.[9]

***iso*-Amyl Alcohol.**—This was a Kahlbaum product. After standing over anhydrous copper sulfate for a number of months, it was digested over unslaked lime and fractionated; b. p. (760 mm.) 131.2–131.7°.

The benzene, toluene, chloroform and ethyl ether were purified in the manner described in the preceding papers of this series and their physical constants were essentially the same as those previously reported.

With the exception of the solvent, carbon tetrachloride, all liquids were fractionated immediately before use.

Experimental Results

The experimental work is summarized in Table I. The columns of this table give, from left to right, the mole fraction of the carbon tetrachloride which was used as the solvent, $\mathrm{M.F.}_{\mathrm{CCl_4}}$; the refractive index of the solution, n_{D}^{25}; the density of the solution, d_4^{25}; the observed dielectric constant at 25°, ϵ; the molar polarization of the solution, $P_{1,2} = \frac{\epsilon - 1}{\epsilon + 2}\frac{f_1m_1 + f_2m_2}{d} = f_1P_1 + f_2P_2$; and the molar polarization of the second component, $P_2 = \frac{P_{1,2} - f_1P_1}{f_2}$.

The dielectric constant data for solutions of benzene, toluene, chloroform and ethyl ether in carbon tetrachloride were obtained using the electrical resonance method and are accurate to within one-tenth of one per cent. The dielectric constant data for the other binary mixtures were obtained using the bridge method described above. Wherever possible these

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[9] Noyes, This Journal, **45**, 857 (1923).

values were checked using the more accurate resonance method. This was always possible in the case of the solutions containing the highest mole fractions of the solvent. It may be pointed out here that these are the

TABLE I

DIELECTRIC CONSTANT AND DENSITY DATA

M.F.$_{CCl_4}$	n_D^{25}	d_4^{25}	ϵ	$P_{1,2}$	P_2
1. Carbon Tetrachloride-Benzene[a]					
1.00	1.45724	1.5835	2.230	28.24	26.73
0.75	1.46747	1.4159	2.240	27.85	26.73
.50	1.47766	1.2433	2.253	27.46	26.73
.25	1.48770	1.0624	2.267	27.09	26.73
.10	1.49738	0.9498	2.274	26.83	26.73
.0	1.49780	.8731	2.282	26.73	26.73
2. Carbon Tetrachloride-Toluene					
1.00	1.45724	1.5835	2.230	28.23	33.66
0.90	.....	1.5053	2.246	28.78	33.66
.75	1.46798	1.3880	2.271	29.62	33.66
.50	1.47605	1.2048	2.310	31.02	33.66
.0	1.49392	0.8593	2.378	33.66	33.66
3. Carbon Tetrachloride-Chloroform					
1.00	1.45724	1.5835	2.230	28.23	49.8
0.75	1.45433	1.5602	2.682	33.43	49.0
.50	1.45062	1.5350	3.215	37.80	47.4
.25	1.44720	1.5082	3.901	41.70	46.2
.0	1.44394	1.4978	4.770	44.93	44.9
4. Carbon Tetrachloride-Ethyl Ether					
1.00	1.45724	1.5835	2.230	28.23	56.0
0.75	1.43127	1.3583	2.722	35.75	58.2
.50	1.40448	1.1375	3.210	42.48	56.7
.35	1.38843	....	3.491	46.09	55.7
.25	1.37782	0.9197	3.700	48.39	55.1
.0	1.34993	.7079	4.265	54.54	54.5
5. Carbon Tetrachloride-Methyl Acetate					
1.00	1.45724	1.5835	2.230	28.23	78.0
0.90	1.44976	1.5256	2.610	33.32	79.0
.75	1.43458	1.4400	3.192	39.20	72.1
.50	1.41133	1.2840	4.225	45.96	63.7
.362	1.39795	....	4.880	48.63	60.4
.25	1.38593	1.1134	5.400	50.13	57.4
.0	1.35938	0.9272	6.680	52.26	52.3
6. Carbon Tetrachloride-Ethyl Acetate					
1.00	1.45724	1.5835	2.230	28.23	87.0
0.75	1.43519	1.4101	3.220	41.42	81.0
.50	1.41312	1.2530	4.201	50.47	72.7
.25	1.39134	1.0657	5.11	56.64	66.1
.0	1.36948	0.8946	6.03	61.65	61.6

TABLE I (*Concluded*)

7. Carbon Tetrachloride-Acetone

M.F.$_{CCl_4}$	n_D^{25}	d_4^{25}	ϵ	$P_{1,2}$	P_2
1.00	1.45724	1.5835	2.230	28.23	170.0
0.90	1.45036	1.5215	3.28	40.93	155.1
.75	1.43780	1.4260	4.98	51.98	123.2
.70	1.43378	1.3906	5.67	54.72	116.5
.60	1.42494	1.3202	6.17[b]	66.06	122.8
.0	1.35695	0.7855	21.3	64.38	64.4
8. Carbon Tetrachloride-Ethyl Alcohol					
1.00	1.45724	1.5835	2.230	28.23	73.5
0.90	1.45106	1.5325	2.560	31.91	64.9
.75	1.44082	1.4491	3.74	41.88	82.8
.60	1.42926	1.3540	5.45	48.83	79.7
.50	1.42042	1.2833	7.05	51.72	75.2
.0	1.35894	0.7862	25.2	52.13	52.1
9. Carbon Tetrachloride-*iso*-Amyl Alcohol					
1.00	1.45724	1.5835	2.230	28.23	86.0
0.90	1.45106	1.4965	2.502	32.81	74.0
.75	1.44273	1.3700	3.127	41.54	81.4
.60	1.43468	1.2453	4.61[b]	55.89	97.4
.0	1.40568	0.8083	14.55	89.24	89.2

[a] Data previously reported.

[b] Values do not fall on smooth curve.

most important points of the whole curve, since it is the electric moment of a single solute molecule completely surrounded by the electrically inert solvent molecules that is desired. The value of the molar polarization of the second component is obtained by taking a tangent to the $P_{1,2}$-mole fraction curve at the point where the mole fraction of the reference liquid is unity and prolonging it to cut the axis where the mole fraction of the solute is unity. The dielectric constant data obtained for these binary mixtures are accurate to within three-tenths of one per cent.

Discussion of Results

The results obtained from the dielectric constant and density data using carbon tetrachloride as a non-polar solvent for certain organic molecules are in all respects similar to those obtained from the binary liquid mixtures considered in the preceding paper[1] in which benzene was used as the solvent. As before, the assumption is made that the polarization due to the non-polar solvent, carbon tetrachloride, is always directly proportional to its mole fraction in solution. The results obtained for the various binary mixtures reported in this article seem to indicate the correctness of this assumption.

It is convenient to divide the systems studied into two groups. For a detailed discussion of this method of grouping of the systems the reader is referred to the article in which the benzene systems are reported.[1]

GROUP 1.—Those in which the molar polarization of the second component, P_2, is constant throughout the whole range of concentration.

1. Carbon Tetrachloride-Benzene
2. Carbon Tetrachloride-Toluene

GROUP 2.—Those in which P_2 is not a constant.

3. Carbon Tetrachloride-Chloroform
4. Carbon Tetrachloride-Ethyl Ether
5. Carbon Tetrachloride-Methyl Acetate
6. Carbon Tetrachloride-Ethyl Acetate
7. Carbon Tetrachloride-Acetone
8. Carbon Tetrachloride-Ethyl Alcohol
9. Carbon Tetrachloride-*iso*-Amyl Alcohol

Calculation of the Electric Moments of the Molecules

The electric moments of the solute molecules have been calculated from the values of their molar polarizations, P_2. This molar polarization contains two terms, a polarization due to an orientation effect, P_2', and a polarization due to a deformation effect, P_2''. Since the polarization due to the deformation of the molecule may be approximated by the familiar Lorenz-Lorentz formula,[1,2,3,10] the polarization due to the orientation effect may be calculated. This term contains the electric moment of the molecule, μ, in the following manner, $P_2' = \frac{4\pi}{3} N \frac{\mu^2}{3kT}$, where the symbols have their usual significance.[1]

The electric moments of the several solute molecules, calculated from dielectric constant and density of their solutions in carbon tetrachloride, are given in Table II.

TABLE II

ELECTRIC MOMENTS OF SOLUTE MOLECULES AT 25°

Molecule	P_2'', cc.	P_2' cc.	$\mu \times 10^{18}$
Benzene	25.8	0.9	0.06
Toluene	30.3	3.4	.40
Chloroform	21.3	28.5	1.15
Ethyl ether	23.0	33.0	1.24
Methyl acetate	18.0	60.0	1.67
Ethyl acetate	22.2	64.8	1.74
Acetone	16.0	154.0	2.70
Ethyl alcohol	16.0	57.5	1.63
iso-Amyl alcohol	13.0	73.0	1.85

Discussion of Table of Electric Moments

The value of the electric moment of benzene is of considerable interest. Smyth,[11] using various physical constants, calculated its moment to be

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

[11] Smyth, THIS JOURNAL, **46**, 2151 (1924).

0.2×10^{-18}, a value so small as to be indistinguishable from zero by the method of calculation employed and recognized by Smyth as indicating that the molecule of benzene had little, if any, moment. Sänger[12] concluded from a careful consideration of the accurate measurements of the dielectric constant of liquid benzene by Graffunder[13] that the moment of the benzene molecule must be practically zero. The value presented above for benzene in the liquid state indicates that if benzene has any moment at all it must be of an exceedingly small magnitude and must, therefore, be considered as experimental verification of the calculations and conclusions of Smyth and Sänger.

The toluene molecule is found to have a moment $\mu = 0.40 \times 10^{-18}$. This value is, without doubt, more reliable than the value (0.52×10^{-18}) reported in the previous paper.[1] It was stated in that article that the latter value was somewhat larger than might have been predicted, and the reasons were given.

Chloroform and ethyl ether are found to have moments which are almost identical in value with those calculated from the dielectric constant and density data of their solutions in benzene, which, in turn, were shown to be in excellent agreement with values found by other investigators.[1,2,14]

The values obtained for the methyl acetate and ethyl acetate molecules are not widely different in magnitude. There can be no doubt from the results of the experimental work that the moment of the ethyl acetate molecule, in carbon tetrachloride solution at least, is the larger of the two. This tends to confirm the statement of Smyth[11] that organic molecules having longer carbon chains will have higher electric moments. His statements are again confirmed by the calculations reported above for the ethyl alcohol and *iso*-amyl alcohol molecules. Their moments are of the expected order of magnitude. Miss Lange[2] determined the moments of a number of the three, four and five carbon alcohols in benzene solution, finding values between 1.53 and 1.83×10^{-18}. *Iso*-amyl alcohol was assigned the value 1.76×10^{-18}. The value for the moment of ethyl alcohol was not reported by this investigator. Her values show this tendency to increase as the length of the carbon chain is increased.

Acetone gives the largest moment of any molecule reported in this paper. It is a fact that the measurements of the dielectric constants for the system carbon tetrachloride-acetone were the most difficult of any of the systems herein reported, yet satisfactory check determinations were obtained for the concentrations studied. The greatest uncertainty lies in the extrapolation of the tangent to the $P_{1,2}$-mole fraction carbon tetrachloride curve to obtain the molar polarization, P_2, of a single acetone molecule completely

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[12] Sänger, *Physik. Z.*, **27**, 165 (1926).

[13] Graffunder, *Ann. Physik.*, **70**, 225 (1923).

[14] Sänger, *Physik. Z.*, **27**, 556 (1926).

surrounded by carbon tetrachloride molecules. A slight movement of the position of the tangent makes considerable difference in the P_2 value obtained. Extreme care has been taken to obtain an accurate tangent, and it is believed that the value reported for the moment of the acetone molecule is significant. It is in excellent agreement with the value, $\mu = 2.61 \times 10^{-18}$, reported by Loeb[15] in his recent book.

Summary

1. Dielectric constant and density data at 25° for eight binary liquid mixtures have been determined at various concentrations. The systems studied were solutions of toluene, chloroform, ethyl ether, methyl acetate, ethyl acetate, acetone, ethyl alcohol and *iso*-amyl alcohol dissolved in carbon tetrachloride.

2. The various systems have been grouped according to whether or not the molar polarization of the solute in solution changes with concentration.

3. The electric moments of each of the solute molecules in carbon tetrachloride solution have been calculated using the Langevin-Debye modification of the Clausius-Mossotti Law. These results have been critically discussed. Wherever possible they have been compared with the results obtained by other investigators.

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THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. IV BENZENE AS A SOLVENT FOR CERTAIN SOLID SUBSTANCES

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The previous papers of this series[1,2,3] have dealt with the dielectric constants of binary liquid mixtures of particular types. The systems to be discussed in this article consist of a solvent, benzene, and certain solid solutes, substances which, with one exception, have been described in the literature as being relatively non-polar in character. The solubility relations of these systems as well as of a number of other similar systems have been the subject of considerable study, the chief results of which are given by Hildebrand.[4] This author points out that they are governed by certain regularities, particularly as regards their relative internal pressures; and yet numerous exceptions to these generalizations

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[15] Loeb, "Kinetic Theory of Gases," McGraw-Hill Book Co., New York, **1927**, p. 408.

[1] Williams and Krchma, This Journal, **48**, 1888 (1926).

[2] Williams and Krchma, *ibid.*, **49**, 1676 (1927).

[3] Krchma and Williams, *ibid.*, **49**, 2408 (1927).

[4] Hildebrand, "Solubility," Chemical Catalog Co., New York, **1924**, Chapter 14.