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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[Contribution from the Laboratory of Physical Chemistry, University of Wisconsin]

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.

are known and have been the subject of much speculation. The terms "polar" and "non-polar" are continually used in such discussions, terms which can be but qualitative in nature. The present authors believe that if sufficient dielectric constant data were available for solutions of the type referred to above, the polarities of the molecules involved might be quantitatively expressed and certain explanations given to account for irregular solubility relations, for certain it is that the dielectric constant gives the most direct evidence that is available concerning polarity. The accumulation of these data will, of course, require a number of years and the results on the benzene systems to be given in this paper can only be considered as a beginning. The work is being continued in this Laboratory.

For the present it is of sufficient interest to calculate the electric moments of the various solute molecules in the electrically inert solvent, benzene. These moments are to be calculated from dielectric constant and density data, using the Langevin[5]-Debye[6] concept of molar polarizability. The equations actually used have been presented in the second paper of this series.[2] In all cases the symbols used in that paper have been retained.

Method

The method used for the determination of the dielectric constant of the benzene and of its solutions was the electrical resonance method described in the first paper of the series,[1] using the same frequency, 10^6 cycles per second. The measurements were made at 25°.

Density determinations on the solutions were made. In all cases a fifty cc. pycnometer of the Ostwald-Sprengel type was used.

Purification of Materials

Benzene.—The benzene, obtained from the Eastman Kodak Company, was treated in the usual manner to remove thiophene, after which it gave no test for this substance. It was purified by fractional crystallizations and distillations until the liquid gave practically the same physical constants as are given by Richards and Shipley.[7] The fraction used boiled between 80.15 and 80.22°, corrected to 760 mm. pressure, and had a density, d_{25}^{25}, 0.8748.

Benzoic Acid (C_6H_5COOH).—This material, obtained from the Mallinckrodt Chemical Company, was recrystallized from toluene and sublimed. The final product was in the form of pure, white crystals having a melting point of 121.8°.

Phenol (C_6H_5OH).—This substance, obtained from Merck and Company under the label "U. S. P.—C. P.—Loose Crystals" was melted and fractionally distilled. The fraction used boiled between 179.5 and 180.0°.

Iodine (I_2).—The iodine, a Mallinckrodt product, was simply resublimed and used without further treatment.

Antimony Iodide (SbI_3).—This material was obtained through the kindness of

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[5] Langevin, *Ann. chim. phys.*, **5** [8], 70 (1905).

[6] Debye, *Physik. Z.*, **13**, 97 (1912); "Handbuch der Radiologie" (Marx), **6**, 597 (1925).

[7] Richards and Shipley, THIS JOURNAL, **41**, 2022 (1919).

Mr. R. W. Gooding of this University. It had been subjected to a very careful purification by repeated recrystallizations from carbon tetrachloride.

Stannic Iodide (SnI_4).—The stannic iodide was a Kahlbaum product which had been carefully preserved in a pure condition. It was presented by Professor J. H. Walton of this department.

Silver Perchlorate ($AgClO_4$).—This salt was prepared by the G. Frederick Smith Manufacturing Company of Urbana, Illinois. Dr. Smith[8] did not give details of the method used except to say that it was dehydrated in vacuo at 135° for thirty hours and at ordinary pressure for sixty hours at the same temperature. It gave no test for perchloric acid.

Experimental Results

The experimental data are presented in Table I. The columns of this table give, from left to right: the per cent. by weight of benzene which was used as solvent, %, C_6H_6; the mole fraction of benzene, M. F., C_6H_6; the density of the solution, d_{25}^{25}; the observed dielectric constant of the solution, ϵ; the molar polarization of the solution, $P_{1,2} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{f_1m_1 + f_2m_2}{d} = f_1P_1 + f_2P_2$; and the molar polarization of the second component, $P_2 = \frac{P_{1,2} - f_1P_1}{f_2}$.

TABLE I

DIELECTRIC CONSTANT AND DENSITY DATA AT 25°

1. Benzene-Benzoic Acid

%, C_6H_6	M.F., C_6H_6	d_{25}^{25}	ϵ	$P_{1,2}$	P_2
100.00	1.000	0.8748	2.280	26.68	43.5
99.25	.995	.8763	2.287	26.77	43.5
98.50	.990	.8780	2.290	26.86	43.5
97.78	.986	.8796	2.294	27.01	43.5
97.06	.981	.8812	2.309	27.20	43.5
96.35	.976	.8828	2.314	27.32	43.5
95.65	.972	.8842	2.322	27.41	43.5
94.28	.963	.8874	2.332	27.57	43.5
92.96	.954	.8904	2.340	27.74	43.5
92.00	.947	.8923	2.371	28.23	43.5

2. Benzene-Phenol

%, C_6H_6	M.F., C_6H_6	d_{25}^{25}	ϵ	$P_{1,2}$	P_2
100.00	1.000	0.8748	2.280	26.68	89.0
96.12	.968	.8813	2.403	28.44	89.0
91.67	.930	.8887	2.567	30.54	89.0
87.90	.897	.8929	2.765	32.76	89.0
84.61	.869	.9015	2.913	34.64	89.0
77.73	.808	.9153	3.300	38.48	89.0
73.34	.768	.9243	3.602	41.01	89.0
61.12	.655	.9461	4.664	48.47	89.0

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[8] The authors wish to take this opportunity to thank Dr. Smith for his extreme generosity in furnishing this material for the work.

TABLE I (*Concluded*)

3. Benzene-Iodine

%, C_6H_6	M.F., C_6H_6	d^{25}_{25}	ϵ	$P_{1,2}$	P_2
100.00	1.000	0.8748	2.280	26.68	60.2
99.10	.998	.8817	2.285	26.75	60.2
98.20	.994	.8861	2.295	26.90	60.2
96.77	.990	.8984	2.310	27.05	60.2
96.49	.989	.9000	2.316	27.09	60.2
93.75	.979	.9211	2.335	27.31	60.2

4. Benzene-Antimony Tri-iodide

%, C_6H_6	M.F., C_6H_6	d^{25}_{25}	ϵ	$P_{1,2}$	P_2
100.00	1.0000	0.8748	2.282	26.68	..
99.86	.9998	.8758	2.285	26.74	..
99.83	.9997	.8763	2.287	26.77	..
99.67	.9995	.8773	2.291	26.88	..
99.50	.9992	.8788	2.300	26.95	..

5. Benzene-Stannic Iodide

%, C_6H_6	M.F., C_6H_6	d^{25}_{25}	ϵ	$P_{1,2}$	P_2
100.00	1.0000	0.8748	2.280	26.68	26.7
99.83	.9998	.8754	2.282	26.68	26.7
99.67	.9996	.8770	2.284	26.69	26.7
99.17	.9990	.8801	2.288	26.68	26.7
99.01	.9988	.8813	2.290	26.68	26.7
98.68	.9983	.8838	2.291	26.65	26.7
97.84	.9973	.8888	2.297	26.59	26.7

6. Benzene-Silver Perchlorate

%, C_6H_6	M.F., C_6H_6	d^{25}_{25}	ϵ	$P_{1,2}$	P_2
100.00	1.0000	0.8748	2.280	26.68	477.0
99.66	.9987	.8770	2.336	27.44	477.0
99.27	.9973	.8790	2.384	28.12	477.0
98.58	.9946	.8832	2.454	29.13	477.0
97.64	.9909	.8940	2.597	30.85	477.0

It will be observed that these data differ from those of the previous articles[2,3] in that it was not possible to determine the densities and dielectric constants of the solutions over a wide range of concentration. In the case of the binary liquid mixtures the two components were mutually soluble in all proportions. In the case of the solid substances used as solutes in Table I it was possible to make the measurements over but a small range of concentration, due to their limited solubility. However, with one exception (antimony tri-iodide) it was possible to dissolve enough of the solute in benzene so that when the molar polarization of the solution, $P_{1,2}$, was plotted against mole fraction of the solvent, a curve was obtained from which a significant value for the molar polarization of the second component or the solute, P_2, resulted. It was found for each of the five solutes reported that its molar polarization in solution was exactly proportional to its mole fraction in solution over the range of its solubility. Thus, taking the tangent to the $P_{1,2}$ curve at the point where the mole fraction of the solvent is unity and prolonging it to cut the axis where the mole fraction of the other component would be unity consisted simply of a mathematical extrapolation.

Calculation of the Electric Moments of the Molecules

The electric moments of the various solute molecules have been calculated from their molar polarizations after the manner described in the second article of this series,[2] using the equation $P_2 = P'_2 + P''_2$, where P'_2 = polarization due to orientation of molecule $= \frac{4\pi}{3} N \frac{\mu^2}{3\,kT}$; and P''_2 = polarization due to deformation of molecule $= \frac{n_0^2 - 1}{n_0^2 + 2} \cdot \frac{M}{d}$.

The term P''_2 has been approximated in each case using data obtained either from the Landolt-Börnstein "Tabellen" or from Volume I of the "International Critical Tables." If these values are in error by 5 cc., an improbable value, the electric moments as reported are not changed by a correction of this magnitude since they have been reported to two significant figures only.

The electric moments of solute molecules, computed as indicated above, are presented in Table II.

TABLE II

ELECTRIC MOMENTS OF SOLUTE MOLECULES AT 25°

Molecule	P_2	P''_2	P'_2	$\mu \times 10^{18}$
C_6H_5COOH	43.5	24.6	19	1.0
C_6H_5OH	89.0	27.7	61	1.7
I_2	60.2	20	40	1.4
SnI_4	26.7	30	...	0.0
$AgClO_4$	477.0	16	461	4.7

Discussion of Table of Electric Moments

C_6H_5COOH.—It has been shown by Nernst[9] from distribution experiments that benzoic acid in benzene solution undergoes a polymerization which may be represented by means of the equation $2C_6H_5COOH \longrightarrow (C_6H_5COOH)_2$. It is difficult at present to state exactly what the effect of this association is upon the value of the electric moment reported in the above table. Values for the electric moments of water and ammonia in liquid or associated condition, and in vapor or non-associated condition, reported by Smyth[10] indicate that the effect of association is to lower the electric moment.

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[9] Nernst, *Z. physik. Chem.*, **8**, 110 (1891).

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

C_6H_5OH.—The value of the moment of this molecule was reported in a preceding paper of this series.[2] It is in excellent agreement with the value calculated by Smyth[11] from the experimental data of Philip and Haynes,[12] and will not be discussed further here.

I_2.—The magnitude of the moment found for the iodine molecule was higher than might have been expected, since that molecule has been considered as a symmetrical one. A symmetrical molecule should, of course, give no moment, a fact which has actually been shown experimentally for gases like hydrogen and nitrogen.[13] However, Lewis[14] has explained that a symmetrical molecule like iodine may become polarized in one direction or another. This polarization means that the molecule will have an electric moment. Lewis shows that this polarization extends to a slight ionization in the case of iodine, and that bromine, chlorine, fluorine and hydrogen, in the order named, show a diminishing tendency toward this ionization. Table III, presented below, shows that this is also the order of decreasing electric moments or, what is equivalent, the order of decreasing polarity.

TABLE III

COMPARISON OF MOMENTS OF HALIDE MOLECULES AND HYDROGEN

Molecule..............	Iodine	Bromine	Chlorine	Fluorine	Hydrogen
$\mu \times 10^{18}$...............	1.4	0.58[15]	0.13[16]	....	0.0[13]

In making the calculation for the electric moment of the iodine molecule the chemical changes taking place upon its solution have not been considered. These chemical changes have been discussed at length by Hildebrand.[17] The present authors are of the opinion that these changes in the dilute iodine solutions did not materially affect the accuracy of the calculation, the result of which is reported above. In the method used for the calculation of the moment it is necessary to assume that the polarization due to the solvent, in this case benzene, is always directly proportional to its mole fraction in solution. This assumption, as has already been indicated,[2] may lead to somewhat erroneous conclusions since it does not take into account what has been termed the chemistry of solution. However, the solution of iodine in benzene has been found to be ideal with respect to its molar polarization in solution over the range

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

[12] Philip and Haynes, *J. Chem. Soc.*, **87**, 998 (1905).

[13] Von Braunmühl, *Physik. Z.*, Forthcoming Publication.

[14] Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Company, New York, **1923**, p. 83.

[15] Schaefer and Schlundt, *J. Phys. Chem.*, **13**, 669 (1909).

[16] Eversheim, *Ann. Physik*, [4] **13**, 492 (1904). The values of the moments of chlorine and bromine were calculated by Smyth from these data.

[17] Hildebrand, ref. 4, pp. 148–151.

of concentration studied, since when this molar polarization is plotted against the mole fraction of the solvent a straight line results. This fact seems to eliminate the possibility of chemical interference.

SnI_4.—That the stannic iodide molecule would show a zero moment might have been predicted from atomic structure considerations. It has always been considered as a "non-polar" substance by Hildebrand[4] in his solubility studies. The value for its moment reported in this paper is of interest in connection with the study of its solubility relations which have recently been reported by that author with one of his collaborators.[18]

$AgClO_4$.—The solubility relations of this interesting substance in benzene have been studied by Hill.[19] This author states that a molecular complex, $AgClO_4.C_6H_6$, is formed when $AgClO_4$ is added to benzene. The value found for the moment of this molecule is very large; nevertheless it is believed to be significant. As in the case of the iodine the molar polarization-mole fraction curve is a straight line over the range of concentration studied, again indicating the elimination of possible chemical interference.

Summary

1. Dielectric constant and density data have been obtained for benzene solutions of benzoic acid, phenol, iodine, stannic iodide, antimony triiodide and silver perchlorate.

2. By means of the Debye modification of the Clausius-Mossotti Law these data have been used to calculate the electric moments of the various solute molecules.

3. The results of these calculations have been discussed with particular reference to the conceptions of atomic structure and to solubility relationships.

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[18] Dorfman and Hildebrand, THIS JOURNAL, **49**, 729 (1927).

[19] Hill, *ibid.*, **44**, 1163 (1922). This article gives references to previous papers.