reciprocal of the mean molality of the thallous and chloride ions and the last the activity coefficient of the thallous chloride in the mixture.

These results have been reviewed in the previous paper. The specific gravity of the saturated solution was found to be 1.0034 and its density 1.0004. Bray and Winninghoff[2] give 0.9994 as the density of the saturated solution, which corresponds to a solubility of 0.01615 mole per 1000 g. of water. Butler and Hiscocks[3] found the same solubility, 0.01607 mole per liter, as that found by Bray and Winninghoff, but found the density to be 1.0004, from which the solubility is 0.01612 mole per 1000 g., in agreement with our value.

Summary

The solubility of thallous chloride in water and aqueous magnesium sulfate and lanthanum nitrate solutions and the density of the saturated aqueous solution at 25° have been determined.

Berkeley, California

[Contribution from the Departments of Chemistry and Physics of Princeton University]

THE DIELECTRIC POLARIZATION OF LIQUIDS. I. THE DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS OF THE CHLOROBENZENES IN BENZENE AND IN HEXANE[1]

By C. P. Smyth, S. O. Morgan[2] and J. C. Boyce

Received December 30, 1927 Published June 5, 1928

Some years ago it was recognized that the calculation of the electric moments of molecules from dielectric constants might provide valuable aid in solving the complex problems of molecular structure. An approximate method of calculation was devised and applied to data on pure substances already existing in the literature to obtain the moments of a large number of molecules.[3]

It was evident, however, that many molecules which were surrounded by strong fields of force did not lend themselves to this calculation. The experimental work, which was then being initiated in the Palmer Physical

---

[2] Bray and Winninghoff, This Journal, **33**, 1663 (1911).

[3] Butler and Hiscocks, *J. Chem. Soc.*, **129**, 2554 (1926).

[1] Papers based upon the data of the present contribution were presented before the Physical and Inorganic Division and before the Organic Division of the American Chemical Society in Philadelphia, September, 1926. The results of the measurements upon the substituted benzene compounds have been applied in a study of the structure of the benzene ring, Smyth and Morgan, This Journal, **49**, 1030 (1927).

[2] DuPont Fellow in Chemistry, 1926–27.

[3] (a) Smyth, *Phil. Mag.*, **45**, 849 (1923); (b) **47**, 530 (1924); (c) This Journal, **46**, 2151 (1924); (d) **47**, 1894 (1925).

Laboratory, was, therefore, directed to the measurement of the dielectric constants and densities of liquid mixtures in which a molecule with a strong field of force could be surrounded by molecules with weak fields. It is our aim to use these data not only for the calculation of electric moments and the study of molecular structure, but also for the investigation of the effect of the force fields of the molecules upon one another in causing molecular association and deviations from ideal behavior.

Theoretical

As the nature of the electric moment and its relation to molecular structure has been discussed in the papers already referred to, only the equations immediately necessary will be given here. The molar polarization P of a substance in which the molecules are free to assume a perfectly random orientation may be represented by the Debye equation,[4] written in the following form

$$P = \frac{\epsilon - 1}{\epsilon + 2}\frac{M}{d} = \frac{4\pi}{3}N\gamma + \frac{4\pi N}{9k}\frac{\mu^2}{T} \tag{1}$$

in which ϵ = the dielectric constant; M = the molecular weight; d = the density; N = the number of molecules in a gram molecule = 6.061×10^{23}; γ = the molecular polarizability; k = the molecular gas constant = 1.372×10^{-16}; μ = electric moment of a single molecule; and T = the absolute temperature. $(4\pi/3)N\gamma$ is the polarization due to shifts of charges in the molecule induced by the external field. It is commonly calculated as the molar refraction for light of infinite wave length, $MR_\infty = [1-\lambda_0^2/\lambda^2]\ [(n^2-1)M]/[(n^2+2)d]$, where n is the index of refraction for light of wave length λ, and λ_0 is the wave length corresponding to a characteristic vibration frequency in the ultraviolet region. The quantity thus calculated by extrapolation from the visible region takes account only of the electronic shifts induced, and is, therefore, designated as P_E, but atoms and groups of atoms or radicals may shift under the influence of an external field in such a way as to contribute somewhat to the polarization.[5] We may, therefore, write $(4\pi/3)N\gamma = P_E + P_A$, where P_A, the difference between P_E and the total polarization induced in the molecules may be termed the atomic and radical contribution to the polarization. Setting $(4\pi N/9k)$ (μ^2/T), the contribution of the moments of the molecules oriented by the external field, $= P_M$, we have $P = P_E + P_A + P_M$.

When the molecules are rigidly bound in the solid state and, therefore, unable to orient themselves in an applied field, $P_M = 0$. By determining the polarization P in the solid state, calculating P_E from optical data, and

---

[4] Debye, *Physik. Z.*, **13**, 97 (1912); "Handbuch der Radiologie (Marx)," Akademische Verlagsgesellschaft M. B. H., Leipzig, **1925**, VI, p. 619.

[5] Ebert, *Z. physik. Chem.*, **113**, 1 (1924); **114**, 430 (1925).

setting $P_M = 0$, Errera[6] has obtained values of P_A for a number of substances. When the molecules in a liquid affect one another to such an extent that they are not oriented at random in the absence of an external field, the expression for P_M may no longer be expected to hold. If the molecules are oriented in such a way that the axes of their electric doublets tend to point in the same direction, P_M is increased, while if these doublets tend to oppose one another, it is decreased. This arrangement of the doublets relative to one another may be anything from a very slight orientation of the molecules to an association in the form of molecular complexes.

The molar polarization of a mixture of two substances, 1 and 2, is given by the expression[4]

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \frac{c_1M_1 + c_2M_2}{d} = c_1P_1 + c_2P_2 \tag{2}$$

in which c_1 and c_2, M_1 and M_2, and P_1 and P_2 are, respectively, the mole fractions, molecular weights and polarizations of the individual components. As $c_1 = 1-c_2$, it is evident that P_{12} is a linear function of c_2 when P_1 and P_2 are constant. If P_1 is constant but P_2 varies with concentration the latter may be calculated by writing the equation in the form

$$P_2 = \frac{P_{12} - P_1}{c_2} + P_1 \tag{3}$$

In the study of binary mixtures, one may choose a liquid 1, such as benzene or hexane, the molecules of which have no moment and may be described as non-polar, and, for liquid 2, a substance[3c] the molecules of which have large moments and will be referred to as polar. In such mixtures, P_1 may be assumed to be approximately constant, since its value is equal to $P_E + P_A$, which are dependent upon intramolecular behavior and vary little with concentration. The variation of P_2 with concentration may then be taken as an indication of the character and extent of the molecular orientation or association of substance 2.

The equation of Debye was criticized by exponents of the older quantum theory, but applications of the newer quantum mechanics to simple polyatomic molecules have given equations from which results practically identical with those of the Debye equation may be obtained and Van Vleck[7] has recently given a general proof of the equation on the basis of the new mechanics. Experimental investigations have shown[8] that, in a simplified form, the equation represents admirably the temperature variation of the dielectric constants of a number of dipole gases but, presum-

---

[6] Errera, *Physik. Z.*, **27**, 764 (1926).

[7] Van Vleck, *Phys. Rev.*, **29**, 727 (1927); **30**, 31 (1927).

[8] (a) Jona, *Physik. Z.*, **20**, 14 (1919); (b) Zahn, *Phys. Rev.*, **24**, 400 (1924); (c) Smyth and Zahn, THIS JOURNAL, **47**, 2501 (1925); (d) Sänger, *Physik. Z.*, **27**, 556 (1926); **28**, 455 (1927).

ably, because of lack of complete freedom of the molecules, it has not been found generally satisfactory when applied to a pure dipole liquid.

Apparatus and Procedure

The measurements of dielectric constant were made with a capacity bridge, which was used in preference to newer methods involving coupled oscillating circuits because of the frequent failure of the latter to distinguish between capacity and conductance, which failure may introduce a serious error into apparently precise results. It is probable, however, that a newer circuit of established accuracy may be used in later measurements.

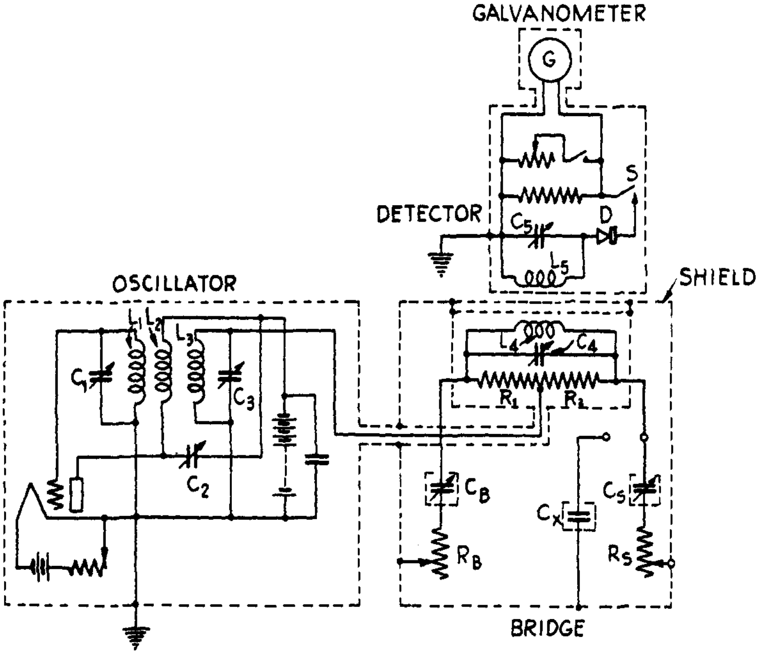

Fig. 1.—Capacity bridge.

As the apparatus possessed certain novel features, a diagram is given in Fig. 1, in which electric shields are represented by dotted lines. The oscillator, bridge and detector were each in separate galvanized iron boxes, fitting closely against one another and grounded. The oscillator tube was a Western Electric 216-A type operated with 135 volts on the plate and giving a direct current in the plate circuit of approximately 30 milliamperes. The three coupling coils (L_1, L_2, L_3) were wound beside one another on the same fiber core. The setting of the variable condensers (C_1 and C_2) across the fixed grid and plate inductances (L_1 and L_2) determined the frequency of the oscillations, 5×10^5 cycles corresponding to a wave length of 600 meters being adopted as suitable for the bridge and checked occasionally by means of a wave meter. The condensers (C_3 and C_4, C_5) across the power and detector coils (L_3 and L_4, L_5) were for tuning, by means of which it was possible to increase two- or three-fold the deflection of the galvanometer used as null instrument for a given capacity change in either arm of the bridge. The power was brought from the oscillator to one corner of the bridge by a heavy, shielded wire, the circuit being completed by grounding the opposite corner of the bridge. In order to maintain the symmetry of the bridge, this power lead was carried beneath the bottom of the box containing the bridge and brought vertically up to the corner shown between R_1 and R_2. The bridge consisted of two resistance arms, R_1, R_2, of 1000 ohms each, specially wound non-inductively on the same Bakelite cylinder and shielded from the rest of the bridge, and two capacity arms, the balancing condenser C_B, a 2000 $\mu\mu$f shielded air condenser, and the standard condenser C_S, a General Radio Company type 222 precision instrument of 1500 $\mu\mu$f capacity. These condensers were connected to the grounded shield through General Radio Company decade resistance boxes, R_B and R_S, non-inductively wound. The resistance in series with C_B was used to balance any conductance in the measuring cell C_x, which could be connected in parallel with C_S, while that in series with C_S was rarely used, having been inserted largely with the object of maintaining the symmetry of the bridge as far as possible. The ends of R_1 and R_2, remote from one another and forming opposite corners of the bridge were connected through a small honey-comb coil, L_4, loosely coupled through a grounded electrostatic shield to another coil, L_5, current through which was rectified by a crystal detector, D, and passed through a Leeds and Northrup high sensitivity galvanometer G, minimum deflection of which indicated balance of the bridge. A switch, S, which could be operated without opening the box, was used to close the detector circuit. The galvanometer was critically damped and a variable shunt was used to protect the galvanometer while bringing the bridge approximately to balance.

A balance of the bridge was obtained when the capacity and conductance were the same in each arm. When the conductance in the opposite arms was different there was a current flowing in the galvanometer, even though the capacity in both arms was the same.

The method of operation was to vary the standard condenser and the balancing resistance until practically zero current was obtained in the galvanometer, both conductance and capacity being then balanced. The condenser containing the liquid to be measured was then connected in parallel with the variable standard condenser and the bridge balanced again by varying the standard condenser and balancing resistance. The capacity of the measuring condenser was equal to the change of the variable standard condenser required to bring the bridge back to balance. With the liquids used in this work, it was unnecessary to change the balancing resistance by more than a few tenths of an ohm.

The measuring condenser C_x consisted of two concentric gold-plated brass cylinders closed at both ends, separated by a distance of 1 mm. on the sides, and insulated from each other and held rigidly by quartz disks set in bushings at the ends. A slightly larger gold-plated cylinder with a cover served as container. Twenty-five cc. of liquid were required to fill this container and the air capacity of the condenser was 34 $\mu\mu$f.

The capacity of the measuring condenser was made up of two parts, the fixed capacity due to the leads and insulation, which did not vary with the dielectric constant of the liquid in the cell, and the capacity between the plates, which was directly proportional to the dielectric constant of the liquid in the condenser. The condenser was calibrated by determining its capacity filled with air and again filled with a liquid whose dielectric constant was well known. The calibrating liquid was benzene, for which a mean value of $\epsilon = 2.273$ at 25° was adopted from the work of Isnardi,[9] Graffunder[10] and Lertes.[11]

---

[9] Isnardi, *Z. Physik*, **9**, 153 (1922).

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

[11] Lertes, *Z. Physik*, **6**, 257 (1921).

Ether, toluene, chloroform and carbon tetrachloride were also measured with a view to calibration and the agreement obtained with the most probable values for the dielectric constants of these substances was satisfactory, but, as the benzene value appeared to be the most accurate, it seemed best to rely wholly on it.

The precision condenser C_S, after being fixed in position in the bridge, was recalibrated in terms of a fixed capacity, that of the empty measuring cell serving as a convenient unit, and this calibration was checked from time to time.

The densities of the liquids were determined with an Ostwald-Sprengel pycnometer, the ends of which were fitted with caps to prevent evaporation. For measurements at 0°, the cell and pycnometer were immersed in cracked ice and water, and, at 25 and 50°, in carefully regulated thermostats. The probable error of the dielectric constant measurements was 0.5% and of the density determinations 0.03%.

Preparation of Materials

The hexane used was Eastman Kodak Company petroleum hexane, b. p. 65–70°. The first lot was treated with acid and alkaline permanganate as recommended by Castelli and Henri[12] and then fractionated. The middle fraction differed from the unpurified material so little in its dielectric properties that, in the work which followed, the untreated hexane was used.

Merck's crystallizable benzene was shaken three times with concentrated sulfuric acid and then with water. It was dried over phosphorus pentoxide and fractionated.

The monochlorobenzene was shaken several times with concentrated sulfuric acid, then with water, dried over fused calcium chloride and fractionated.

The dichlorobenzenes were Eastman Kodak Company products. The ortho and meta isomers were fractionated under reduced pressure, only the middle fraction being used. The para compound was crystallized twice from ethyl alcohol and thoroughly dried over calcium chloride.

Results

Table I gives the experimentally determined dielectric constants and densities of the liquid mixtures at 0, 25 and 50°, together with the values

TABLE I

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS OF BINARY MIXTURES

Mole fraction of	ϵ			d			P_{12}		
	0°	25°	50°	0°	25°	50°	0°	25°	50°
C_6H_5Cl in C_6H_6									
0	...	2.273	2.226	....	0.8727	0.8458	...	26.63	26.84
0.0786	2.710	2.621	2.518	0.9214	.8973	.8713	31.80	31.58	31.13
.1988	3.140	2.994	2.853	.9485	.9227	.8963	37.28	36.80	36.16
.4007	3.879	3.659	3.443	.9986	.9712	.9441	45.09	44.45	43.70
.6020	4.650	4.332	4.050	1.0435	1.0178	.9907	52.00	51.14	50.37
.7048	5.039	4.665	4.339	1.0663	1.0393	1.0125	55.10	54.20	53.30
1.000	6.088	5.628	5.226	1.1272	1.1006	1.0737	62.84	62.06	61.25

---

[12] Castelli and Henri, *Bull. soc. chim. biol.*, **6**, 299–302 (1924).

TABLE I (*Concluded*)

Mole fraction of	ϵ			d			P_{12}		
	0°	25°	50°	0°	25°	50°	0°	25°	50°
o-$C_6H_4Cl_2$ in C_6H_6									
0	...	2.273	2.226	....	0.8727	0.8458	...	26.63	26.84
0.0205	...	2.453	2.373	....	.8837	.8570	...	29.34	29.10
.054	2.873	2.724	2.607	0.9243	.9022	.8792	33.97	33.05	32.44
.1156	3.331	3.153	2.998	.9621	.9328	.9063	39.11	38.54	37.93
.2015	4.023	3.777	3.561	1.0016	.9748	.9476	46.06	45.34	44.67
.5010	6.520	5.988	5.547	1.1367	1.1094	1.0826	64.22	63.50	62.73
1.000	11.130	9.930	8.900	1.3251	1.2973	1.2699	85.53	84.80	83.90
m-$C_6H_4Cl_2$ in C_6H_6									
0	...	2.273	2.226	....	0.8727	0.8458	...	26.63	26.84
0.0372	2.497	2.414	2.342	0.9184	.8916	.8648	29.22	28.97	28.80
.1008	2.719	2.629	2.533	.9494	.9234	.8966	32.61	32.40	32.04
.2703	3.283	3.130	2.989	1.0314	1.0033	.9761	40.48	40.02	39.48
.6837	4.552	4.254	3.997	1.2014	1.1702	1.1427	56.47	55.67	54.76
1.000	5.403	5.039	4.703	1.3085	1.2799	1.2523	66.80	65.90	64.80
p-$C_6H_4Cl_2$ in C_6H_6									
0	...	2.273	2.226	....	0.8727	0.8458	...	26.63	26.84
0.1354	2.372	2.323	2.266	0.9673	.9407	.9135	28.34	28.49	28.37
.1483	2.389	2.341	2.276	.9735	.9466	.9198	28.70	28.79	28.65
.3860	...	2.359	2.313	....	1.0555	1.0280	...	30.92	31.00
.6741	...	...	2.369	....	...	1.1421	...	...	34.16
.7335	...	...	...	....	....	1.1703	...	...	...
C_6H_5Cl in C_6H_{14}									
0.0	1.960	1.908	1.839	0.6882	0.6656	0.6426	30.32	30.07	30.04
0.0293	2.060	1.989	1.922	.6990	.6761	.6528	32.47	31.87	31.28
.0792	2.201	2.122	2.039	.7177	.6940	.6707	35.13	34.59	33.83
.1470	2.419	2.312	2.221	.7430	.7191	.6952	38.89	38.07	37.43
.2903	2.870	2.727	2.543	.7981	.7748	.7505	45.14	44.26	42.61
.4979	3.690	3.453	3.249	.8860	.8601	.8353	52.98	51.94	50.92
.7540	4.824	4.467	4.153	1.0027	.9770	.9511	59.28	58.19	57.13
.8477	5.370	4.953	4.602	1.0502	1.0222	.9962	61.24	60.36	59.40
1.000	6.088	5.628	5.226	1.1278	1.1008	1.0741	63.03	62.26	61.62
o-$C_6H_4Cl_2$ in C_6H_{14}									
0	1.960	1.908	1.839	0.6882	0.6656	0.6426	30.32	30.07	30.04
0.0255	2.100	2.035	1.966	.7037	.6805	.6572	33.50	33.14	32.58
.0739	2.382	2.292	2.190	.7327	.7084	.6848	39.09	38.51	37.63
.1320	2.783	2.630	2.503	.7684	.7425	.7184	45.73	44.66	43.73
.3406	4.370	4.030	3.744	.8935	.8715	.8463	63.30	61.66	60.29
.5881	6.498	5.873	5.384	1.0527	1.0238	.9978	74.88	73.75	72.60
1.000	11.130	9.930	8.900	1.3251	1.2973	1.2699	85.53	84.80	83.90
m-$C_6H_4Cl_2$ in C_6H_{14}									
0	1.960	1.908	1.839	0.6882	0.6656	0.6426	30.32	30.07	30.04
0.0204	2.024	1.969	1.900	.7056	.6818	.6587	31.57	31.36	30.30
.0245	...	...	...	.7061	.6840	.6608	...	...	...
.0684	2.168	2.087	2.014	.7318	.7085	.6850	34.64	34.03	33.40
.2084	2.602	2.480	2.337	.8140	.7926	.7682	42.24	41.21	39.64
.4324	3.270	3.090	2.948	.9477	.9235	.8980	51.22	50.07	49.36
1.000	5.403	5.039	4.703	1.3085	1.2799	1.2523	66.80	65.90	64.80

of the polarization, P_{12}, calculated by means of equation (2). Typical curves showing the variation of these quantities with the composition of the mixture are given in Figs. 2, 3 and 4. For the sake of brevity, the actual values calculated for P_2, the molar polarization of the polar substance, at the different concentrations are omitted but the results obtained for benzene solutions at 50° are plotted in Fig. 5. The P_2 curves obtained for the solutions in hexane were similar in character to those for the ben-

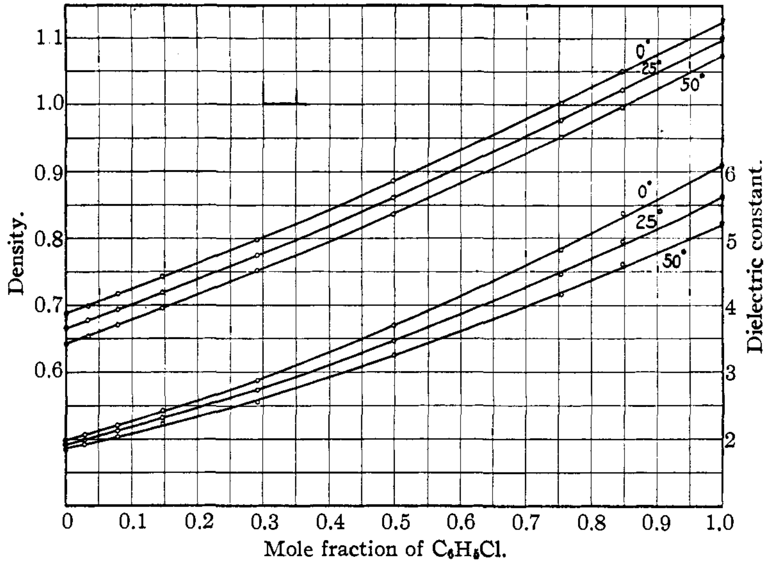

Fig. 2.—Densities and dielectric constants of chlorobenzene-hexane mixtures.

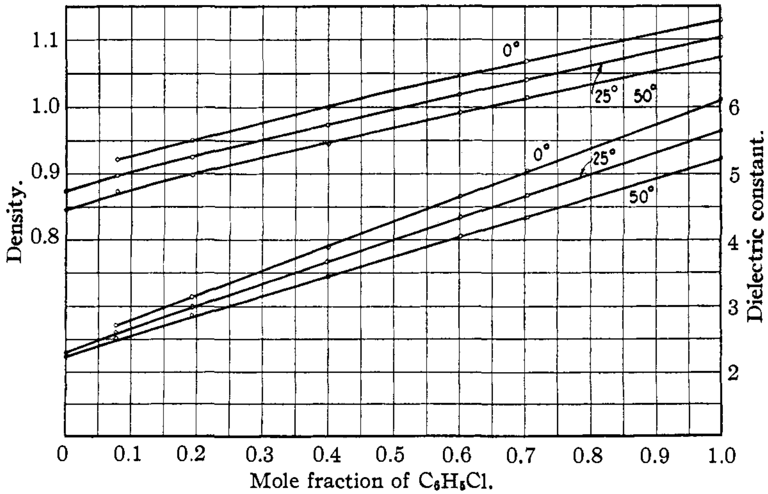

Fig. 3.—Densities and dielectric constants of chlorobenzene-benzene mixtures.

zene solutions, which are shown in preference to the former because *p*-dichlorobenzene was measured only in benzene. The values of P_2 at infinite dilution at 25° obtained by extrapolation to zero concentration ($c_2 = 0$) of the polar substance are given in Table II as P_∞, together with the values of P_E calculated from data in "International Critical Tables" in agreement with the calculations of Errera,[6] P_A obtained by Errera for the dichlorobenzenes, P_M calculated as $P_M = P_\infty - (P_E + P_A)$, and the electric moment calculated from P_M. Solid monochlorobenzene has not been investigated but an approximate value, 3.3, may be calculated for P_A from results to be described in our next paper. This value is, therefore, inserted here and used to obtain P_M and μ.

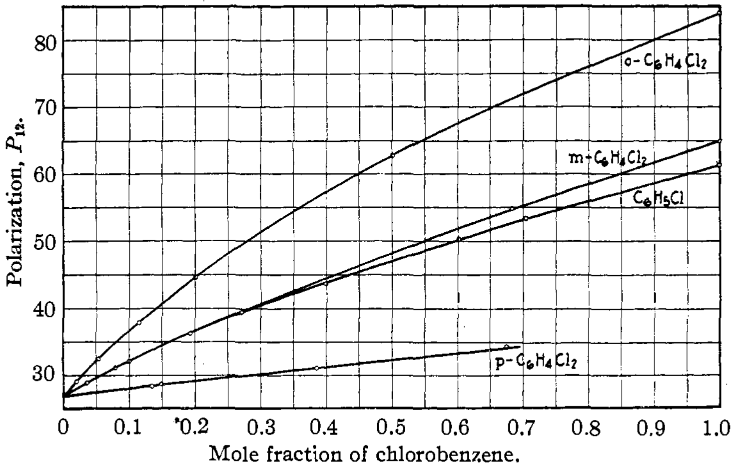

Fig. 4.—Polarization (P_{12}) of mixtures of chlorobenzenes with benzene at 50°.

TABLE II

POLARIZATION CONTRIBUTIONS AT 25° AND ELECTRIC MOMENTS OF THE CHLOROBENZENES

	P_∞	P_E	P_A	P_M	$\mu \times 10^{18}$
C_6H_5Cl	83.6	29.9	3.3	50.4	1.56
o-$C_6H_4Cl_2$	145	34.4	5.8	104.8	2.25
m-$C_6H_4Cl_2$	84.3	34.6	4.4	45.3	1.48
p-$C_6H_4Cl_2$	37.8	34.8	3.4	0	0

Discussion of Results

The value for the moment of monochlorobenzene agrees well with the figure 1.58×10^{-18} recently published by Höjendahl[13] and by Williams and Krchma,[14] who, being unable to take into account the small quantity P_A, obtained a slightly high value. It also differs by less than the possible

---

[13] Höjendahl, *Nature*, **117**, 892 (1926).

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

error from the value, 1.52×10^{-18}, obtained by the more accurate method to be described in Part II of this series. All the values of the moment in Table II are, of course, slightly lower than those first published[1] when no data were available for the calculation of P_A. The values of the polarizations of pure *o*- and *m*-dichlorobenzene are in satisfactory agreement with those of Errera and that for P_∞ of the para compound is identical with Errera's value. For this latter compound, P_M is given as 0 instead of the figure −0.4 actually obtained, which is less than the probable error and has no apparent physical significance. The values for P_∞ of the ortho and the meta compound and consequently of the moments are distinctly higher than those obtained by Errera, whose extrapolation was made at but one temperature and based upon measurements in only one solvent.

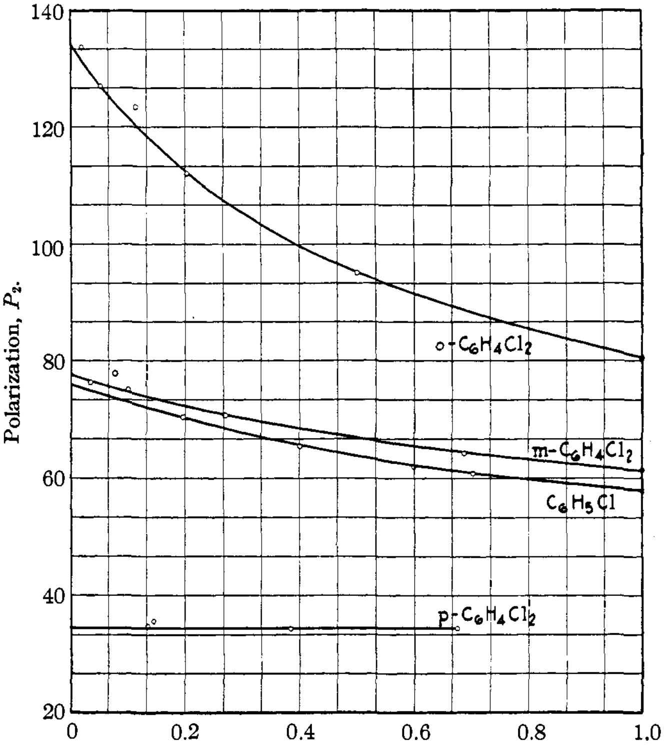

Fig. 5.—Polarization (P_2) of chlorobenzenes in benzene solutions at 50°.

The curves (Figs. 2 and 3 show typical curves) representing the variation of the dielectric constant and the density with the mole fraction c_2 of the polar substance are, in some cases, very nearly linear, but the dielectric constant curves usually possess marked curvature. The departure from linearity of both the dielectric constant and the density curves evidently depends upon the character not only of the polar substance but also of the non-polar. For a given set of mixtures at different temperatures, the density curves run much more nearly parallel than the dielectric constant curves, which spread apart with increasing content of the polar substance because of the high temperature coefficient of the latter indicated by equation (1). In Fig. 4 *p*-dichlorobenzene, which has no electric moment, is the only substance showing a linear variation of P_{12} with c_2 as required by equation (2) if P_1 and P_2 are constant and independent of c_2. The departure from linearity of the other curves is attributable to decrease in P_2, the polarization of the polar substance, because of increase in molecular orientation with increasing concentration. Monochlorobenzene and *m*-dichlorobenzene, which have nearly equal moments, have very similar curves, that for the latter lying a little higher in the more concentrated region because of its greater chlorine content, which gives a higher value for MR_∞. The relations are clear in Fig. 5, in which the P_2 curve for the para compound is a horizontal straight line showing independence of concentration when the moment is zero. For the other compounds, P_2 decreases rapidly with increasing concentration, particularly in the dilute region, the decrease being greatest in the case of the ortho compound which has the largest moment. The values at different temperatures, which have been omitted for the sake of brevity, show that P_2 decreases with rising temperature more rapidly in the dilute solutions than in the concentrated, where increasing thermal agitation gives increased freedom to the molecules, which can thus orient more freely in the applied field.

It may be concluded that the molecules of the chlorobenzenes tend to orient themselves in such a way that neighboring doublets oppose one another, thereby decreasing the polarization. This effect is greater, the greater the moment of the molecule, the lower the temperature and the smaller the distance between the doublets, that is, the greater the concentration. Measurements upon solutions of acetic acid in benzene and in ether, which, because of their preliminary character and uncertain interpretation, are not included in the present paper, indicate that, as might be expected, not only the magnitude of the field of force around the single molecule but also steric influences and highly localized valence forces may play an important part in determining the behavior of the molecules.

The writers wish to express their indebtedness to the National Academy of Sciences for a grant from the Joseph Henry Fund, and to thank Professor K. T. Compton for his helpful interest in the work.

Summary

A capacity bridge for the measurement of dielectric constants is described and the dielectric constants and densities of solutions of chloro-

benzene and *o*-, *m*- and *p*-dichlorobenzene in benzene and in hexane are given.

The polarization and electric moments calculated indicate that, as might be expected, the molecules affect one another more strongly, the greater their moments, the greater their concentrations and the lower the temperature.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS.
II. THE TEMPERATURE DEPENDENCE OF THE POLARIZATION IN CERTAIN LIQUID MIXTURES[1]

BY C. P. SMYTH AND S. O. MORGAN[2]

RECEIVED DECEMBER 30, 1927 PUBLISHED JUNE 5, 1928

As the results reported in Part I showed that the effect of polar molecules upon one another in dilute solution varied greatly with concentration and with temperature, it was evident that accurate determinations of dielectric constant and density over a wide range of temperature were needed.

Apparatus

The apparatus described in Part I was modified, although the same capacity bridge with the same wave length of 600 meters was used. The Western Electric 216-A tube in the oscillator was replaced by a 5-watt 104-DW power tube, upon the plate of which 250 volts were applied by means of a high speed motor generator. This increased the accuracy of the bridge balance by supplying more current. The measuring cell used in the earlier work was replaced by a condenser of approximately 200 $\mu\mu$f. capacity, which greatly reduced the relative error of a capacity measurement. Since the capacity of this cell when filled with a liquid of high dielectric constant was greater than that of the precision condenser which was used to measure it, a 1000 $\mu\mu$f. variable air condenser of the same type as that used in the balancing arm of the bridge was so arranged that, by means of interchangeable brass rods dipping into cups filled with mercury, it could be connected in series with the cell or in parallel with the precision condenser or could be totally disconnected. When the capacity of the cell was too great to be measured by direct substitution on the precision condenser, this variable air condenser was set at a convenient value, measured on the precision condenser, and then connected in series with the cell. The capacity of the cell and condenser, thus reduced by the series connection, was measured on the precision condenser and the capacity of the cell alone then calculated.

The measuring cell (Fig. 1) was designed in such a way as to have large electrical capacity, small internal volume and small temperature lag. It was made up of three concentric platinum cylinders (A), with diameters 1.95, 1.80 and 1.64 cm., respectively, open at the ends. The outer and inner cylinders, which were 9.2 cm. long, were con-

---

[1] A paper based upon the results of the present contribution was presented before the Physical and Inorganic Division of the American Chemical Society in Richmond, April, 1927.

[2] DuPont Fellow in Chemistry, 1926–27.