

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

## THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. II. THE ELECTRIC MOMENTS OF CERTAIN ORGANIC MOLECULES IN BENZENE SOLUTION

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RECEIVED APRIL 19, 1927

PUBLISHED JULY 5, 1927

### Theoretical Part

In the study of the dielectric constants of binary mixtures it has been the custom of most investigators to study the properties of the solutions from curves in which the dielectric constants of the mixtures have been plotted against the mole fractions of the constituents.<sup>1</sup> Following this custom, the results of the first paper of this series<sup>2</sup> were expressed in that manner. The application of the concept of molar polarization introduced by Debye,<sup>3</sup> has marked a distinct advance in the mathematical treatment of the properties of these binary mixtures, particularly in the case where one of the liquids, which may be termed the solvent, is known to have no electric moment. The reasons why this method of treatment is more desirable in the case of these mixtures have recently been discussed in detail by Ebert<sup>4</sup> and by Debye.<sup>5</sup>

The basis of this method of treatment is found in the familiar Clausius-Mosotti law,  $P = [(\epsilon - 1)/(\epsilon + 2)](M/d) = (4\pi/3)N\alpha$ , where  $P$  is the molar polarization,  $\epsilon$  the dielectric constant,  $M$  the molecular weight,  $d$  the density;  $N$  Avogadro's number =  $6.06 \times 10^{23}$  and  $\alpha$  the molecular polarizability.

The molar polarization,  $P$ , has been shown<sup>5</sup> to be a linear function of the reciprocal of the absolute temperature, so that the equation may be written in the form  $P = [(\epsilon - 1)/(\epsilon + 2)](M/d) = (4\pi/3)N[(\mu^2/3kT) + \alpha] = (B/T) + A$ , where  $B = (4\pi/3)N(\mu^2/3k) =$  effect of orientation of molecules in the field, and  $A = (4\pi/3)N\alpha =$  effect due to deformation of molecules. The quantity  $\mu$  in the above equations is a direct measure of the electric moment of the molecules.

**Application to Binary Mixtures.**—The molar polarization,  $P_{1,2}$ , of a binary mixture is given by the expression<sup>5</sup>

$$P_{1,2} = [(\epsilon - 1)/(\epsilon + 2)](f_1M_1 + f_2M_2)/d = f_1P_1 + f_2P_2$$

<sup>1</sup> (a) Linebarger, *Z. physik. Chem.*, **20**, 131 (1896). (b) Philip, *ibid.*, **24**, 18 (1897). (c) Schulze, *Z. Elektrochem.*, **18**, 77 (1912). (d) Kremann, "Die Eigenschaften der binären Flüssigkeitsgemische," F. Enke, Stuttgart, 1916.

<sup>2</sup> Williams and Krchma, *THIS JOURNAL*, **48**, 1888 (1926).

<sup>3</sup> Debye, *Physik. Z.*, **13**, 97 (1912); *Verhandl. deut. physik. Ges.*, **15**, 777 (1913).

<sup>4</sup> Ebert, *Z. physik. Chem.*, **113**, 1 (1924); **114**, 430 (1924).

<sup>5</sup> (a) Debye, *Handbuch der Radiologie (Marx)*, **6**, 625 (1925); (b) *Wisconsin Lectures*, Second Semester, 1926-1927.

where  $f_1$  and  $f_2$  = mole fractions of Components 1 and 2;  $M_1$  and  $M_2$  = molecular weights of Components 1 and 2;  $P_1$  and  $P_2$  = molar polarizations of Components 1 and 2;  $P_1 = (4\pi/3)N\alpha_1$ , and  $P_2 = (4\pi/3)N\alpha_2$ .

Measurements of the dielectric constants of binary systems in which the first component, the solvent, is known to have no electric moment, permit a calculation of the molar polarization, and therefore of the electric moment of the second component. Liquids such as carbon tetrachloride, carbon disulfide, pentane, hexane and benzene should serve as 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 of their solutions in benzene, calculated with the help of the equations given above, and to point out certain limitations to the general application of this method of treatment.

### Method

The method used for the determination of the dielectric constants of the binary mixtures was explained in detail in the first paper of this series<sup>2</sup> and will not be described here. It might be stated, however, that each of two dielectric cells similar to the one described in the previous paper was used for each measurement wherever possible. Since these two cells were of widely different capacitances, the fact that measurements on solutions of the same composition gave the same result within the limit of experimental error would vouch for their accuracy.

The refractive indices of the pure liquids and of the solutions were measured by means of a Pulfrich refractometer immediately after the dielectric-constant determination. Except when noted to the contrary, their densities were determined at 25° by means of an Ostwald-Sprengel pycnometer, taking the usual precautions for temperature regulation.

### Purification of Materials

An outline of the method of purification of each substance used is given below. The physical constants of each, density, and refractive index are included as part of Table I, under Experimental Results.

**Benzene.**—The benzene, obtained from the Eastman Kodak Company, was shaken with concd. sulfuric acid, washed with dil. sodium hydroxide solution and with distilled water. It was frozen out twice and fractionated, and showed no blackening with mercury. The drying agent used was phosphorus pentoxide. The liquid gave practically the same physical constants that are given by Richards and Shipley;<sup>6</sup> b. p., 80.10–80.15°.

**Toluene.**—This material was obtained from the Mallinckrodt Chemical Works. It was shaken with concd. sulfuric acid, washed with dil. sodium hydroxide and distilled water. After standing over mercury for a week it was dried with phosphorus pentoxide and fractionated; b. p., 110.60–110.80°.

***o*-Xylene.**—This liquid was obtained from Kahlbaum. It was shaken with concd.

<sup>6</sup> Richards and Shipley, *THIS JOURNAL*, **41**, 2002 (1919).

sulfuric acid, treated with dil. sodium hydroxide solution and washed with water. It was dried with phosphorus pentoxide and fractionated; b. p., 142.3–142.5°.

*p*-Xylene.—The xylene, also obtained from Kahlbaum, was subjected to a treatment similar to that of the *o*-xylene and fractionated; b. p., 138.3–138.4°.

Chloroform.—The material was obtained from the Eastman Kodak Company. It was treated with concd. sulfuric acid to remove alcohol and washed with dil. sodium hydroxide and water. It was dried over fused calcium chloride. After further drying with anhydrous copper sulfate, it was fractionally distilled; b. p., 61.10–61.20°.

Carbon Tetrachloride.—The preparation (obtained from Merck and Company) was refluxed over mercury and washed with concd. sulfuric acid to remove sulfides. It was then washed with dil. sodium hydroxide solution and water, dried over fused calcium chloride and fractionated; b. p., 76.45–76.52°.

Chlorobenzene.—This material was obtained from the Eastman Kodak Company. It was carefully dried and fractionated; b. p., 131.80–131.90°.

Ethyl Ether.—This material was obtained from the Mallinckrodt Chemical Company. It was treated with concd. sulfuric acid, washed, dried with calcium chloride and finally with sodium, and fractionated; b. p., 34.5–34.7°.

Phenol.—The phenol, obtained from Merck and Company, under the label "U. S. P. IX—'C.P.'—Loose Crystals," was simply melted and fractionated; b. p., 181.3–181.5°.

### Experimental Results

The results of the experimental determinations are summarized in Table I. The columns of this table give, from left to right: the mole fraction of the benzene which was used as the solvent,  $MFC_6H_6$ ; the refractive index of the solution,  $n_D^{25}$ ; the density of the solution,  $d_4^{25}$ ; the observed dielectric constant,  $\epsilon$ ; the molar polarization of the solution,  $P_{1,2} = [(\epsilon - 1)/(\epsilon + 2)](f_1M_1 + f_2M_2)/d = f_1P_1 + f_2P_2$ ; and the molar

TABLE I  
DIELECTRIC CONSTANT DATA FOR BINARY MIXTURES  
GROUP 1

Mole fraction of $C_6H_6$ , %	$n_D^{25}$	1. Benzene— <i>p</i> -xylene			
		$d_4^{25}$	$\epsilon$	$P_{1,2}$	$P_2$
100	1.49780	0.8731	2.282	26.73	36.68
50	1.49400	.8612	2.274	31.76	36.68
0	1.49286	.8567	2.265	36.68	36.68
		2. Benzene— <i>o</i> -xylene			
100	1.49752	0.8731	2.282	26.73	40.76
90	1.49753	.8727	2.302	28.03	40.76
75	1.49758	.8719	2.337	30.06	40.76
50	1.49766	.8712	2.398	33.57	40.76
0	1.49948	.8704	2.507	40.76	40.76
		3. Benzene—phenol <sup>a</sup>			
100	1.49807	0.8728	2.282	26.70	89.0
90	.....	.8924	2.722	32.53	89.0
75	.....	.9242	3.692	41.96	89.0
65	.....	.9447	4.672	48.65	89.0
0	.....	.....	...	89.0	89.0

TABLE I (Concluded)  
 4. Benzene—Carbon tetrachloride<sup>b</sup>

Mole fraction of C <sub>6</sub> H <sub>6</sub> , %	$n_D^{25}$	$d_4^{25}$	$\epsilon$	$P_{1,2}$	$P_2$
100	1.49780	0.8731	2.282	26.73	28.24
90	1.49738	.9498	2.274	26.83	28.24
75	1.48770	1.0624	2.267	27.09	28.24
50	1.47766	1.2433	2.253	27.46	28.24
25	1.46747	1.4159	2.240	27.85	28.24
0	1.45724	1.5835	2.230	28.24	28.24

## 5. Benzene—Ethyl ether

100	1.49807	0.8731	2.282	26.73	54.50
75	1.45846	.8297	2.713	33.73	54.50
50	1.42132	.7881	3.183	40.65	54.50
25	1.38496	.7465	3.691	47.52	54.50
0	1.35262	.7077	4.265	54.50	54.50

## GROUP 2

6. Benzene—toluene<sup>b,c</sup>

100	1.49780	0.8731	2.282	26.73	36.25
91.5	1.49724	.8715	2.304	27.54	34.90
75	1.49649	.8684	2.315	28.60	34.30
50	1.49553	.8651	2.337	30.27	33.84
25	1.49460	.8620	2.362	32.05	33.78
0	1.49392	.8593	2.378	33.66	33.66

## 7. Benzene—chlorobenzene

100	1.49752	0.8731	2.280	26.73	82.0
90	1.50014	.8993	2.623	31.80	77.4
75	1.50395	.9361	3.131	38.42	74.5
50	1.51012	.9946	3.979	47.71	68.7
0	1.52135	1.1011	5.610	61.84	61.8

8. Benzene—chloroform<sup>c</sup>

100	1.49780	0.8731	2.282	26.73	47.5
90	.....	.9292	2.460	28.95	48.9
80	.....	.9844	2.639	30.97	48.0
50	1.47066	1.1590	3.246	36.39	46.0
30	.....	1.2811	3.739	39.83	45.4
0	1.44394	1.4796	4.770	45.00	45.0

<sup>a</sup> Data of Mr. R. J. Allgeier, as yet unpublished. Another article of this series, on the dielectric constants of benzene solutions of certain solid substances, by Mr. Allgeier and the senior author of this paper, will be published in the near future.

<sup>b</sup> The dielectric-constant and refractive-index data for these systems were presented in the previous paper of this series.<sup>2</sup>

<sup>c</sup> Density data,  $d_4^{25}$ , taken from Linebarger [*Am. Chem. J.*, **18**, 429 (1896)] and calculated to  $d_4^{25}$ .

polarization of the second component,  $P_2 = (P_{1,2} - f_1 P_1)/f_2$ , and obtained by graphical methods.

The dielectric constants of the pure liquids and of the solutions were measured at 25°, using a frequency of the order 10<sup>6</sup> cycles per second.

### Discussion of Results

Experiments in binary liquid mixtures in which one of the components has no electric moment give results from which certain calculations concerning the electric moment of the other component can be made. The assumption is made in this method of treatment that the polarization due to the non-polar solvent (in this article, benzene) is always directly proportional to its mole fraction in solution. Although for such considerations benzene would appear to be an ideal solvent, and indeed has already been used as such by Lange,<sup>7</sup> this assumption may not be entirely borne out by experimental data on certain physical properties of the liquids. For example, benzene seems to show a somewhat abnormal behavior in solution with butane.<sup>8</sup> It shows evidence of a slight association in its specific heat-temperature curve.<sup>9</sup> It gives a slightly abnormal solution with carbon tetrachloride (a liquid whose moment is without doubt smaller than that of benzene) on the basis of specific-heat relations,<sup>10</sup> etc. It would seem that the assumption, while probably true in an infinitely dilute solution of the second component, fails to take into account what might be termed the chemistry of solution, that is, the changes which take place upon the addition of any finite quantity of the second component. These changes taking place upon solution have been discussed in a number of places,<sup>10,11</sup> and will not be presented here.

However, for the purpose of discussion, the above assumption will be made in the treatment of the binary mixtures whose constants were presented in Table I. It is convenient to divide the systems into two groups. Group 1 combines the systems in which the molar polarization of the second component,  $P_2$ , is constant throughout the whole range of concentration. These are benzene containing (1) *p*-xylene, (2) *o*-xylene, (3) phenol, (4) carbon tetrachloride, (5) ethyl ether. In Group 2,  $P_2$  is not a constant: benzene containing (6) toluene, (7) chlorobenzene, (8) chloroform.

In Group 1 are found what might be termed ideal solutions, since the molar polarization of the second component is exactly proportional to its mole fraction in the solution. As a typical example of a binary mixture of this type, curves showing the molar polarizations of the second component, and of the solution of benzene and ethyl ether, plotted against the mole fraction of benzene, are presented in Fig. 1. Curve I gives the product of  $f_1$  by  $P_1$ ; Curve II gives the molar polarization of the solution calculated from the relation  $P_{1,2} = [(\epsilon - 1)/(\epsilon + 2)](f_1M_1 + f_2M_2)/d$ ,

<sup>7</sup> Lange, *Z. Physik*, **33**, 169 (1925).

<sup>8</sup> Calingaert and Hitchcock, *THIS JOURNAL*, **49**, 750 (1927).

<sup>9</sup> Williams and Daniels, *ibid.*, **46**, 1569 (1924).

<sup>10</sup> Williams and Daniels, *ibid.*, **47**, 1490 (1925).

<sup>11</sup> Hildebrand, "Solubility," Chemical Catalog Co., New York, 1924.

and Curve III gives the molar polarization of ether,  $P_2$ , obtained from Curves I and II. It will be evident from Curve III that  $P_2$  is a constant. This may be interpreted to show that the electric moment of an ether molecule does not change, whether it be completely surrounded by benzene molecules (infinitely dilute solution in benzene), or by both benzene and ether molecules, or by other ether molecules.

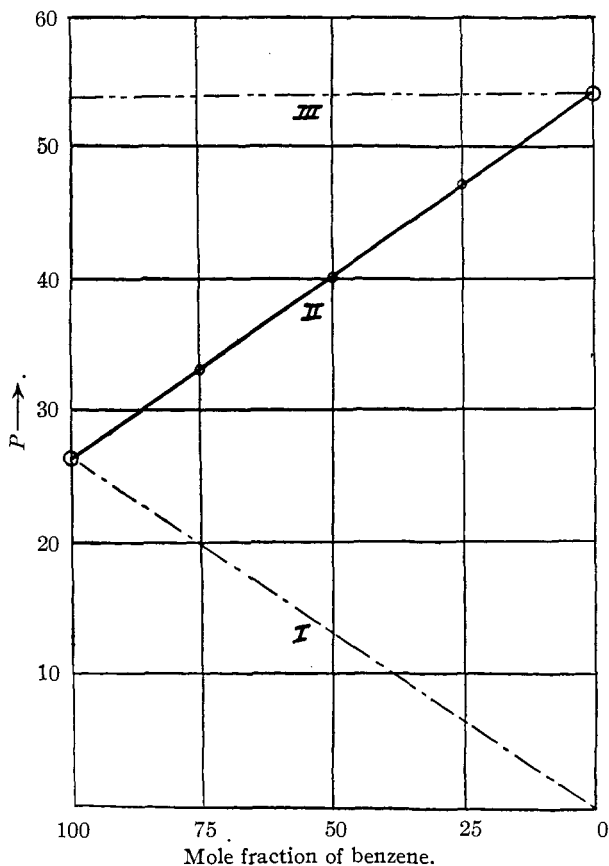


Fig. 1.—Benzene-ethyl ether. Ordinates: Curve I,  $f_1 P_1$ ; Curve II,  $P_{1,2}$ ; Curve III,  $P_2$ .

It should be emphasized that these solutions are ideal only with respect to their molar polarizations in solution. Vapor pressures, specific volumes and specific heats of these solutions may show considerable deviations from ideality, yet their dielectric properties may be normal. The liquids chosen, *o*-xylene, *p*-xylene, phenol, carbon tetrachloride and ethyl ether, represent four different types of organic compounds, only one of which is at all chemically similar to the solvent, benzene.

The binary mixtures in Group 2 give values of  $P_{1,2}$  which, when plotted against the mole fraction of the solvent, do not fall on a straight line. Since the molar polarization of the solvent is assumed to be directly proportional to its mole fraction in the solution, it is evident that  $P_2$  will no longer be a constant. These quantities are obtained in a manner exactly analogous to that of the solutions of Group 1.

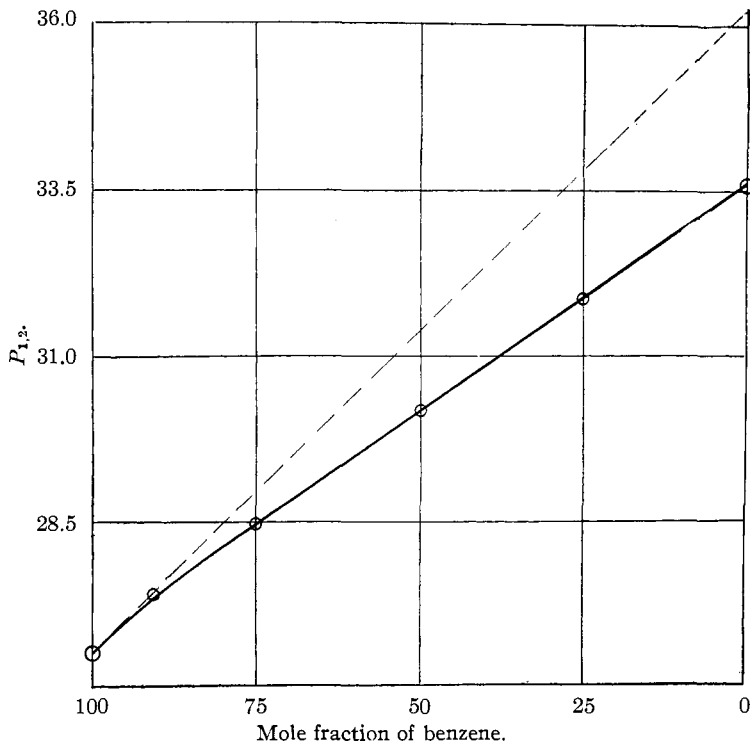


Fig. 2.—Benzene-toluene.

The type of curve obtained for these systems is illustrated by Figs. 2 and 3, in which the molar polarization of benzene-toluene solutions, and the molar polarization of the toluene in solution, respectively, are plotted against the mole fraction of benzene.

In the case of solutions of this group the value of  $P_2$  is obtained by taking a tangent to the  $P_{1,2}$  curve at the point where the mole fraction of the reference liquid is unity, and prolonging it until it cuts the axis where the mole fraction of the other component is unity, as shown in Fig. 2. For the intermediate concentrations, the values of  $P_2$  are obtained directly from those of  $f_2P_2$ , since  $P_{1,2} = f_1P_1 + f_2P_2$ , and  $P_{1,2}$  and  $f_1P_1$  are known.

The explanation of the form of curve obtained for systems of this group has been given by Debye.<sup>5</sup> It is at present a qualitative explanation,

comparable in many respects to the type of explanation given to account for the deviations from ideality of the physical properties of binary mixtures.<sup>10,11</sup>

### Calculation of the Electric Moments of the Molecules

The electric moment of a molecule surrounded by the inert molecules of a non-polar solvent may be calculated in the following manner. The molar polarization of the dissolved substance,  $P_2$ , contains two terms, one a polarization due to orientation,  $P_2'$ , the other a polarization due to deformation,  $P_2''$ , so that the equation  $P_2 = P_2' + P_2''$  may be written. Rearranging,  $P_2' = P_2 - P_2''$ . The term  $P_2$  has been calculated for each

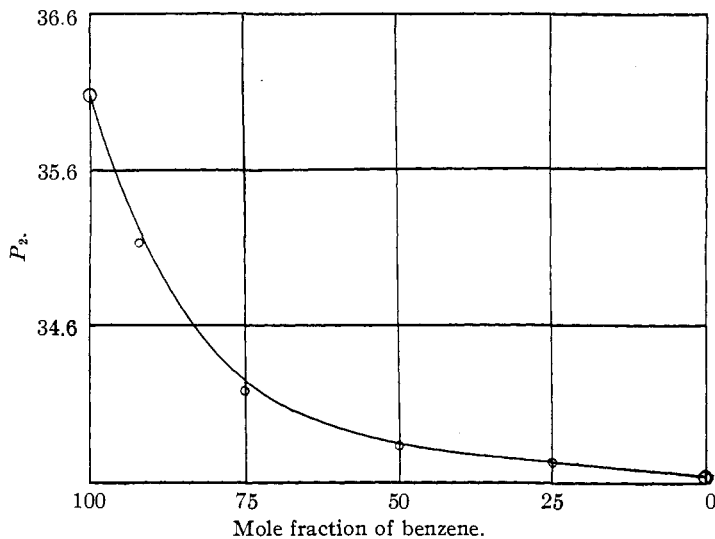


Fig. 3.—Benzene-toluene.

solute in benzene, and included in Table I. For all the calculations of this section the value of  $P_2$  is taken as that value determined in the infinitely dilute solution in benzene, given in the table for 100 mole fraction of benzene. This molar polarization is due, therefore, to a single solute molecule completely surrounded by benzene molecules. The term  $P_2''$  may be approximated by means of the familiar Lorenz-Lorentz<sup>12</sup> formula,  $P_2'' = [(N_0^2 - 1)/(N_0^2 + 2)](M/d)$ , where  $N_0$  is the refractive index of the substance extrapolated to zero frequency. This extrapolation, of course, can only be made when there is no interfering infra-red absorption. Although it cannot be considered as exact because experimental measurements of the relation between the refractive index and the frequency have not as yet been made in the longer infra-red regions, it gives a result of sufficient accuracy so that the deformation term may be calculated.

<sup>12</sup> Lorentz, *Wied. Ann.*, 9, 641 (1880).



The method of calculation of the electric moment of a molecule is illustrated by a sample computation for the ethyl ether molecule.  $P'_2 = P_2 - P''_2 = 54.5 - 23 = 31.5$  cc.  $P'_2 = (4\pi/3)N(\mu^2/3kT) = 31.5$ , where  $N$  is Avogadro's number,  $\mu$  the electric moment of the molecule,  $k$  the Boltzmann constant  $= 1.37 \times 10^{-16}$  and  $T$  is the absolute temperature,  $298^\circ$ . Making the substitutions,  $\mu = 1.22 \times 10^{-18}$ .

The electric moments of the several solute molecules, computed in the above manner, are presented in Table II.

TABLE II  
ELECTRIC MOMENTS OF SOLUTE MOLECULES AT  $25^\circ$

Molecule	$P''_2$ , cc.	$P'_2$ , cc.	$\mu \times 10^{18}$
Ethyl ether	23.0	31.5	1.22
Carbon tetrachloride	28.3	0	0.00
<i>p</i> -Xylene	35.5	1.0	.06
<i>o</i> -Xylene	35.0	5.8	.52
Chloroform	21.3	26.2	1.10
Toluene	30.3	5.9	0.52
Chlorobenzene	30.2	51.8	1.55
Phenol	27.7	61.3	1.70

### Discussion of Table of Electric Moments

Two of the molecules studied, carbon tetrachloride and *p*-xylene, are symmetrical in structure, in which case the electric moment should be zero. The values found indicate that if these molecules have any moment at all it must be of a very small magnitude. Indeed it could hardly be expected that the values of  $P''_2$  might not show an error of  $\approx 1$  cc. so that within the limits of the accuracy of the method used, the electric moments of these molecules may be considered to be zero. Since the dielectric constants of benzene and *p*-xylene are so nearly alike, it is difficult to calculate an exact moment for the latter substance in benzene solution.

The electric moments of the toluene and of the *o*-xylene molecule are perhaps somewhat larger than might have been predicted. Smyth<sup>13</sup> has calculated the electric moments of the toluene and the various xylene molecules "from the indices of refraction at two different wave lengths, the density of the substance under the conditions under which these indices were measured, the dielectric constant at one temperature, the density at this temperature, the value of the temperature itself, the molecular diameter and certain universal constants." These calculated moments are not in particularly good agreement with the experimental ones here presented. The values calculated by Smyth have been criticized by Sanger<sup>14</sup> and will not be discussed here. It is a fact<sup>2,10</sup> that when small amounts of toluene are dissolved in benzene at  $25^\circ$ , the solution

<sup>13</sup> Smyth, THIS JOURNAL, **46**, 2151 (1924).

<sup>14</sup> Sanger, *Physik. Z.*, **27**, 165 (1926).

behaves abnormally. Since the tangent to the molar polarization curve for an infinitely dilute solution of toluene in benzene gives the quantity  $P_2$ , it must be expected that the term  $P'_2$  will be comparatively large, thereby resulting in a large moment. It is interesting to note that in the case of the symmetrical xylene the electric moment is practically zero, while in the case of the unsymmetrical xylene the electric moment has a significant value.

The values obtained for ethyl ether and chloroform may be compared with others found in the literature. Lange<sup>7</sup> has determined the electric moment of ethyl ether, obtaining the identical result tabulated above. This investigator determined the dielectric constants of solutions of benzene and ether, using a modified Nernst bridge method. Sanger<sup>15</sup> has recently determined the moment of chloroform in the vapor state with the result  $\mu = 0.95 \times 10^{-18}$ . The value found in benzene solution is only slightly larger.

Kerr<sup>16</sup> determined the dielectric constants of a number of binary mixtures in which benzene was used as a solvent, among them the system benzene-chlorobenzene. Kerr did not calculate the electric moments of the solute molecules, so that the result given above cannot be compared with others as yet. Indeed, it is the opinion of the present authors that these data are of insufficient accuracy for this calculation, because of the manner of preparing the solutions and of the degree of reproducibility of the dielectric-constant data.

The value reported for phenol would seem to be of the right order of magnitude. It cannot be considered to be exact because certain approximations had to be made concerning the properties of a phenol in the liquid state at the temperature of the measurements.

### Conclusion

Although the method of treatment of certain binary systems described above was presented by Debye<sup>3</sup> a number of years ago, it is only within recent years that investigators, chiefly chemists, have begun to apply it. This paper and several to follow, using other non-polar liquids as solvents, attempt to show the utility of the Clausius-Mosotti law in the calculation of the electric moments of certain molecules dissolved in a non-polar solvent.

The authors take this opportunity to express their thanks to Professor Debye for his kindly interest, advice and encouragement in the interpretation of the experimental data.

### Summary

1. The application of the Clausius-Mosotti law to the treatment of dielectric-constant data of certain binary liquid mixtures has been discussed.

<sup>15</sup> Sanger, *Physik Z.*, **27**, 556 (1926).

<sup>16</sup> Kerr, *J. Chem. Soc.*, **128**, 2796 (1926).

2. The dielectric constants of six binary mixtures at 25° have been determined at various concentrations. The systems studied are benzene-*p*-xylene, benzene-*o*-xylene, benzene-ethyl ether, benzene-chloroform, benzene-chlorobenzene and benzene-phenol.

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

4. The electric moments of each of the solute molecules in benzene solution have been calculated. These results have been critically discussed.

NOTE—Since this paper was written there has appeared an article by Smyth and Morgan [THIS JOURNAL, 49, 1030 (1927)] in which the electric moments of certain substituted benzene molecules were calculated from dielectric-constant and density data. Smyth and Morgan have apparently obtained dielectric-constant and density data for but one system reported in this paper, namely, benzene-chlorobenzene. The data used for the calculations for the moment of phenol were taken from a paper by Philip and Haynes [*J. Chem. Soc.*, 87, 998 (1905)]. Since Smyth and Morgan have withheld their dielectric-constant data for a future publication, and since all the dielectric-constant data used by these authors were obtained using bridge methods rather than one of the newer and more accurate electrical resonance methods, the authors of the present paper have decided to submit their paper in its original form.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MICHIGAN AGRICULTURAL EXPERIMENT STATION]

## ADSORPTION FROM SOLUTION BY ASH-FREE ADSORBENT CHARCOAL. IV. THE NON-INVERSION OF SUCROSE BY ADSORBED ACIDS AND ITS SIGNIFICANCE FOR THEORIES OF ADSORPTION AND CATALYSIS<sup>1</sup>

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RECEIVED APRIL 23, 1927

PUBLISHED JULY 5, 1927

Information that will throw light on the properties and behavior of substances in the adsorbed state is much needed for a better understanding of the nature of adsorption, catalysis, and reactions at interfaces. In the present paper are presented the results of a study of the properties of acids when adsorbed on pure ash-free adsorbent charcoals.

In a previous paper<sup>2</sup> methods were described whereby adsorbed acids can be removed from pure ash-free charcoal and quantitatively estimated. By means of these methods it was demonstrated<sup>3</sup> with hydrochloric acid and pure charcoal that a certain amount of adsorbed acid is held so firmly

<sup>1</sup> Published by permission of the Director of the Experiment Station as Journal Article No. 41.

<sup>2</sup> Miller, THIS JOURNAL, 46, 1150 (1924).

<sup>3</sup> Miller, *ibid.*, 47, 1270 (1925).