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

# THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. V THE ELECTRIC MOMENTS OF CERTAIN ORGANIC MOLECULES IN CARBON DISULFIDE AND HEXANE SOLUTION

BY JOHN WARREN WILLIAMS AND EARL F. OGG

RECEIVED OCTOBER 18, 1927 PUBLISHED JANUARY 5, 1928

The utility of the Debye modification of the Clausius-Mossotti law for the calculation of the electric moments of certain molecules has been shown by several investigators.[1] At the present writing data for the moments of various types of organic molecules, calculated in the manner referred to above, are accumulating rapidly. In general, these figures are being obtained either from dielectric constant and density data for their solutions in benzene or from the temperature variation of the dielectric constant of their vapors. In this series of articles the dielectric constants of binary mixtures are being studied; therefore, it is concerned only with the first type of calculation, with the important modification, however, that other solvents besides benzene are being used. The third paper of this series[2] presented values for the electric moments of certain organic molecules, calculated from dielectric constant and density data of their solutions in carbon tetrachloride. The purpose of this paper is to show that carbon disulfide and hexane may also be used successfully as solvents for the purpose in hand. The electric moments of several organic molecules have been calculated from dielectric constant and density data in these solutions, data similar in all respects to those presented in previous papers of this series.

## Method

The method used for the determinations of the dielectric constants of the solvents, carbon disulfide and hexane, and their solutions, was the electrical resonance method described in the first paper of the series.[3] The same frequency, $10^6$ cycles per second, and the same temperature, 25°, were used for the measurements in every case.

Density determinations on the solutions were made at 25° using a 50cc. pycnometer of the Ostwald-Sprengel type. The usual precautions for precision work were observed throughout.

## Purification of Materials

**Carbon Disulfide.**—The carbon disulfide was agitated with mercury to remove

---

[1] (a) Lange, *Z. Physik*, **33**, 169 (1925); (b) Smyth and Morgan, THIS JOURNAL, **49**, 1030 (1927); (c) Sänger, *Physik. Z.*, **27**, 556 (1926); (d) **28**, 455 (1927); (e) Williams and Krchma, THIS JOURNAL, **49**, 1676 (1927).

[2] Krchma and Williams, THIS JOURNAL, **49**, 2408 (1927).

[3] Williams and Krchma, *ibid.*, **48**, 1888 (1926).

foreign sulfides. It was dried by means of phosphorus pentoxide, after which it was submitted to fractional distillation; boiling point 45.3–45.6°.

Hexane.—This liquid was obtained from the Eastman Kodak Company. It was thoroughly dried with phosphorus pentoxide and fractionally distilled; boiling point 67.5–70.5°. Owing to the difficulty of obtaining absolutely pure hexane, it was necessary to use the fraction as given. Since the material contained only saturated hydrocarbons, it served well as an electrically inert solvent.

Benzene.—The benzene was obtained in a thiophene free condition from the Eastman Kodak Company. It was dried and fractionated in the manner described by Richards and Shipley[4] and gave practically the same physical constants reported by these investigators.

Nitrobenzene.—The nitrobenzene used was obtained from the J. T. Baker Chemical Company. It was subjected to repeated fractional crystallizations and fractional distillations; boiling point 210.6–210.8°.

Chlorobenzene.—This material was obtained from the Eastman Kodak Company. It was carefully dried and fractionated; boiling point 130.7–131.0°.

Naphthalene.—Naphthalene, obtained from Merck and Company, was purified by crystallization and sublimation; melting point 80.1°.

Anthracene.—This material was purified by recrystallizing from toluene and washing with alcohol; melting point 217.6°.

Phenol.—Merck and Company "U. S. P.—C. P.—Loose Crystals" phenol was melted and fractionally distilled; boiling point 179.5–180.0°.

Benzoic Acid.—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; melting point 121.8°.

Cinnamic Acid.—Cinnamic acid, obtained from Kahlbaum, was purified by recrystallization from alcohol; melting point 132.6°.

Iodine.—The iodine, a Mallinckrodt product, was resublimed. It was used without further treatment.

## Experimental Results

The results of the experimental work are presented in Tables I and II. In Table I dielectric constant and density data for solutions in carbon disulfide are given and in Table II similar data for solutions in hexane. The columns of these tables give, from left to right, the mole fraction of the solvent, in Table I, M. F. $CS_2$, in Table II, M. F. $C_6H_{14}$; the density of the solution compared to water at 25°, $d_{25}^{25}$; the observed dielectric constant of the solution, $\epsilon$; 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 are accurate to within 0.1 of one per cent.

It will be noted that these data are somewhat different in certain respects. In the case of the binary liquid mixtures the two components are mutually soluble in all proportions, while in the case of the binary systems in which the solute is a solid substance, examples are presented

---

[4] Richards and Shipley, This Journal, 41, 2022 (1919).

which show widely varying solubilities. The solubilities of the benzoic acid, cinnamic acid and anthracene in carbon disulfide and the solubility of the benzoic acid in hexane were so slight that the calculation of their molar polarizations was not attempted. However, their dielectric constant and density data have been included in the tables.

Table I

Dielectric Constant and Density Data for Solutions in Carbon Disulfide

| | | Carbon Disulfide—Benzene | | |
|---|---|---|---|---|
| M. F., $CS_2$ | $d^{25}_{25}$ | $\epsilon$ | $P_{1,2}$, cc. | $P_2$, cc. |
| 1.00 | 1.2598 | 2.633 | 21.26 | 29.0 |
| 0.75 | 1.1200 | 2.531 | 23.11 | 28.4 |
| .50 | 1.0220 | 2.441 | 24.44 | 27.8 |
| .25 | 0.9450 | 2.358 | 25.54 | 27.0 |
| .0 | .8746 | 2.285 | 26.66 | 26.7 |
| | | Carbon Disulfide—Hexane | | |
| 1.00 | 1.2598 | 2.633 | 21.26 | 31.6 |
| 0.75 | 1.0110 | 2.319 | 23.71 | 30.8 |
| .50 | 0.8630 | 2.126 | 25.65 | 30.1 |
| .25 | .7550 | 2.003 | 27.68 | 29.6 |
| .0 | .6796 | 1.904 | 29.27 | 29.2 |
| | | Carbon Disulfide—Chlorobenzene | | |
| 1.00 | 1.2591 | 2.633 | 21.27 | 82.5 |
| 0.90 | 1.2320 | 3.087 | 26.54 | 75.4 |
| .75 | 1.1988 | 3.627 | 33.12 | 68.2 |
| .50 | 1.1572 | 4.449 | 43.52 | 66.4 |
| .25 | 1.1276 | 5.094 | 52.91 | 63.3 |
| .0 | 1.1011 | 5.610 | 61.81 | 62.0 |
| | | Carbon Disulfide—Nitrobenzene | | |
| 1.00 | 1.2591 | 2.633 | 21.26 | 346 |
| 0.95 | 1.2530 | 4.350 | 32.99 | 260 |
| .90 | 1.2465 | 6.060 | 40.64 | 216 |
| .75 | 1.2315 | 9.810 | 53.50 | 150 |
| .50 | 1.2173 | 17.34 | 69.14 | 117 |
| .25 | 1.2080 | 24.60 | 81.78 | 101 |
| .0 | 1.2022 | 36.10 | 94.30 | 94 |
| | | Carbon Disulfide—Phenol | | |
| 1.000 | 1.2591 | 2.633 | 21.28 | 83.6 |
| 0.996 | 1.2578 | 2.644 | 21.44 | 83.6 |
| .984 | 1.2544 | 2.714 | 22.11 | 83.6 |
| .969 | 1.2500 | 2.794 | 22.94 | 83.6 |
| .955 | 1.2464 | 2.868 | 23.63 | 83.6 |
| .931 | 1.2394 | 3.040 | 25.21 | 83.6 |
| .903 | 1.2320 | 3.246 | 27.04 | 83.6 |
| | | Carbon Disulfide—Naphthalene | | |
| 1.000 | 1.2591 | 2.633 | 21.27 | 54 |
| 0.999 | 1.258 | 2.641 | 21.37 | 54 |

TABLE I (*Concluded*)

| M. F., $CS_2$ | $d^{25}_{25}$ | $\epsilon$ | $P_{1,2}$, cc. | $P_2$, cc. |
|---|---|---|---|---|
| .994 | 1.255 | 2.646 | 21.55 | 54 |
| .983 | 1.246 | 2.654 | 21.93 | 54 |
| .973 | 1.240 | 2.663 | 22.25 | 54 |
| .965 | 1.235 | 2.673 | 22.59 | 54 |
| .935 | 1.225 | 2.680 | 23.30 | 54 |
| | | Carbon Disulfide—Anthracene | | |
| 1.0000 | 1.2591 | 2.633 | 21.27 | |
| .9998 | 1.2590 | 2.641 | 21.34 | |
| .9996 | 1.2590 | 2.646 | 21.41 | |
| .9992 | 1.2589 | 2.649 | 21.46 | |
| .9984 | 1.2588 | 2.662 | 21.57 | |
| .9981 | 1.2587 | 2.665 | 21.63 | |
| .9957 | 1.2581 | 2.674 | 21.79 | |
| | | Carbon Disulfide—Benzoic Acid | | |
| 1.0000 | 1.2591 | 2.633 | 21.28 | |
| 0.9998 | 1.2591 | 2.644 | 21.40 | |
| .9992 | 1.2590 | 2.651 | 21.47 | |
| .9985 | 1.2589 | 2.657 | 21.54 | |
| .9970 | 1.2588 | 2.663 | 21.56 | |
| .9947 | 1.2584 | 2.666 | 21.66 | |
| .9924 | 1.2580 | 2.668 | 21.70 | |
| | | Carbon Disulfide—Cinnamic Acid | | |
| 1.0000 | 1.2598 | 2.633 | 21.26 | |
| 0.9997 | 1.2594 | 2.645 | 21.39 | |
| .9992 | 1.2592 | 2.649 | 21.45 | |
| .9986 | 1.2586 | 2.663 | 21.55 | |
| .9972 | 1.2583 | 2.673 | 21.70 | |
| .9963 | 1.2581 | 2.679 | 21.76 | |
| | | Carbon Disulfide—Iodine | | |
| 1.000 | 1.2591 | 2.633 | 21.27 | 60.3 |
| 0.995 | 1.2763 | 2.669 | 21.53 | 60.3 |
| .993 | 1.2830 | 2.672 | 21.58 | 60.3 |
| .990 | 1.2910 | 2.684 | 21.65 | 60.3 |
| .987 | 1.3010 | 2.710 | 21.88 | 60.3 |
| .983 | 1.3115 | 2.718 | 21.96 | 60.3 |

TABLE II

DIELECTRIC CONSTANT AND DENSITY DATA FOR SOLUTIONS IN HEXANE

Hexane—Benzene

| M. F., $C_6H_{14}$ | $d^{25}_{25}$ | $\epsilon$ | $P_{1,2}$, cc. | $P_2$, cc. |
|---|---|---|---|---|
| 1.00 | 0.6800 | 1.904 | 29.25 | 27.8 |
| 0.91 | .695 | 1.931 | 29.11 | 27.6 |
| .75 | .717 | 1.981 | 28.84 | 27.4 |
| .50 | .757 | 2.054 | 28.20 | 27.0 |
| .25 | .810 | 2.160 | 27.49 | 26.8 |
| .0 | .875 | 2.283 | 26.65 | 26.7 |

TABLE II (*Concluded*)

| M. F., $C_6H_{14}$ | $d^{25}_{25}$ | $\epsilon$ | $P_{1,2}$, cc. | $P_2$, cc. |
|---|---|---|---|---|
| | | Hexane—Chlorobenzene | | |
| 1.00 | 0.680 | 1.904 | 29.25 | 84.0 |
| 0.90 | .720 | 2.167 | 34.51 | 81.0 |
| .75 | .774 | 2.605 | 41.68 | 78.7 |
| .50 | .874 | 3.462 | 51.10 | 72.8 |
| .25 | .984 | 4.508 | 57.99 | 67.4 |
| .0 | 1.104 | 5.610 | 61.70 | 61.7 |
| | | Hexane—Nitrobenzene | | |
| 1.00 | 0.680 | 1.904 | 29.25 | 346.0 |
| 0.95 | .700 | 2.624 | 44.08 | 322.0 |
| .90 | .724 | 3.474 | 55.92 | 293.0 |
| .75 | .794 | 6.300 | 76.61 | 218.4 |
| .51 | .915 | 14.68 | 93.40 | 156.8 |
| .0 | 1.202 | 36.10 | 94.32 | 94.3 |
| | | Hexane—Naphthalene | | |
| 1.000 | 0.6796 | 1.906 | 29.28 | 55.0 |
| 0.998 | .6809 | 1.919 | 29.61 | 55.0 |
| .987 | .6849 | 1.928 | 29.85 | 55.0 |
| .984 | .6861 | 1.930 | 29.93 | 55.0 |
| .977 | .6885 | 1.936 | 29.97 | 55.0 |
| .972 | .6899 | 1.939 | 30.10 | 55.0 |
| .964 | .6920 | 1.941 | 30.13 | 55.0 |
| | | Hexane—Benzoic Acid | | |
| 1.0000 | 0.6796 | 1.904 | 29.26 | |
| .9992 | .6803 | 1.912 | 29.40 | |
| .9980 | .6810 | 1.915 | 29.51 | |
| .9974 | .6811 | 1.915 | 29.60 | |
| .9964 | .6812 | 1.916 | 29.62 | |
| .9957 | .6814 | 1.917 | 29.62 | |
| .9950 | .6817 | 1.918 | 29.66 | |
| | | Hexane—Carbon Disulfide | | |
| 1.00 | 0.6796 | 1.904 | 29.27 | 29.2 |
| 0.75 | .7550 | 2.003 | 27.68 | 29.6 |
| .50 | .8630 | 2.126 | 25.65 | 30.1 |
| .25 | 1.0110 | 2.319 | 23.71 | 30 8 |
| .0 | 1.2598 | 2.633 | 21.26 | 31.6 |

## Calculation of the Electric Moments of the Various Solute Molecules

The dielectric constant and density data using carbon disulfide and hexane as non-polar solvents for certain organic molecules are exactly similar to those obtained for the binary systems considered in the three preceding papers of this series,[1d,2,5] in which either benzene or carbon tetrachloride was used as the solvent. The calculations of the electric moments of the various solute molecules to be presented in this article

---

[5] Williams and Allgeier, THIS JOURNAL, 49, 2416 (1927).

were made in the same manner and making the same assumptions, so that the details will be omitted.

The electric moments of the various solute molecules, calculated from dielectric constant and density data of their solutions in carbon disulfide, are given in Table III. In Table IV are given the results of similar calculations for the electric moments of certain solute molecules from like data in hexane solutions. The symbols of the previous articles have been retained throughout.

TABLE III

ELECTRIC MOMENTS OF SOLUTE MOLECULES (CARBON DISULFIDE AS SOLVENT) AT 25°

| | $P_2''$, cc. | $P_2'$, cc. | $\mu \times 10^{18}$ |
|---|---|---|---|
| Phenol | 27.5 | 56.1 | 1.63 |
| Naphthalene | 43.5 | 10.5 | 0.69 |
| Benzene | 25.8 | 2.7 | 0.09 |
| Nitrobenzene | 32 | 314 | 3.89 |
| Chlorobenzene | 31 | 51 | 1.52 |
| Hexane | 29.6 | 2 | 0.08 |

TABLE IV

ELECTRIC MOMENTS OF SOLUTE MOLECULES (HEXANE AS SOLVENT) AT 25°

| | $P_2''$, cc. | $P_2'$, cc. | $\mu \times 10^{18}$ |
|---|---|---|---|
| Carbon disulfide | 21.1 | 2 | 0.08 |
| Naphthalene | 43.5 | 11.5 | 0.72 |
| Benzene | 25.8 | 2 | 0.08 |
| Nitrobenzene | 32 | 314 | 3.89 |
| Chlorobenzene | 31 | 53 | 1.55 |

It is of interest also to consider benzene as the solvent in the case of the systems carbon disulfide-benzene and hexane-benzene. This permits a calculation of the electric moments of the carbon disulfide and hexane molecules, the results of which are given in Table V.

TABLE V

ELECTRIC MOMENTS OF CARBON DISULFIDE AND HEXANE (BENZENE AS SOLVENT) AT 25°

| | $P_2''$, cc. | $P_2'$, cc. | $\mu \times 10^{18}$ |
|---|---|---|---|
| Carbon disulfide | 21.1 | 1.1 | 0.06 |
| Hexane | 29.6 | 0.9 | 0.05 |

## Discussion of Tables of Electric Moments

One exceedingly important conclusion can now be drawn from the data made available by this series of articles, namely, that the value of the electric moment for the solute molecules, calculated from dielectric constant and density data in various non-polar solvents, is quite independent of the solvent used. This point is illustrated by the data collected in Table VI.

TABLE VI

ELECTRIC MOMENT DATA FOR CHLOROBENZENE AND NITROBENZENE IN VARIOUS SOLVENTS—TEMPERATURE, 25°

| Solvent | $\epsilon$ (solvent) | $P_2$ ($C_6H_5Cl$) | $\mu \times 10^{18}$ ($C_6H_5Cl$) | $P_2$ ($C_6H_5NO_2$) | $\mu \times 10^{18}$ ($C_6H_5NO_2$) |
|---|---|---|---|---|---|
| Carbon disulfide | 2.633 | 82.5 | 1.55 | 346 | 3.89 |
| Benzene | 2.283 | 82 | 1.55 | 344[a] | 3.84 |
| Hexane | 1.904 | 84 | 1.56 | 346 | 3.89 |

[a] The value for $P_2(C_6H_5NO_2)$ in benzene solution was taken from Miss Lange's work, Lange, *Z. Physik*, **33**, 169 (1925). This value has recently been checked in the Wisconsin Laboratory by Mr. C. H. Schwingel in the course of an investigation of the dielectric properties of certain nitro derivatives of benzene and toluene in benzene solution, the results of which will be published shortly.

It might have been predicted that since the dielectric constant of the solvent changes, a change in the molar polarization of the solute molecule, and therefore in its electric moment, should result. Indeed it may be said that from the meager data available to the time of these researches slight differences were indicated in the molar polarization values depending on the non-polar solvent used. The present authors believe that for the first time sufficiently accurate data have been accumulated to prove that such is not the case.

The data of this article have been used to calculate the electric moments of the molecules of the solvent media and their values have been included in the tables. The moments for benzene, carbon disulfide and hexane are practically zero; in other words they are non-polar in nature. This fact permits their use as solvents in studies of the type previously referred to.[1] The value $\mu = 0.08 \times 10^{-18}$ for benzene is of interest in connection with the article of Sänger,[6] in which this author shows from dielectric constant data on pure benzene and certain theoretical considerations that this molecule should have practically a zero moment.

The value found for the electric moment of naphthalene, $\mu = 0.70 \times 10^{-18}$, is of special interest to the organic chemist. If the structural formula for the substance is written in the conventional way, there results a molecule which appears to be symmetrical, or in the terms used here, it would appear to have a zero moment. The result presented above is not surprising since it is well known that the second benzene ring of the naphthalene behaves quite differently chemically from the first. The data for anthracene indicate that it has a much higher molar polarization, and therefore a higher electric moment, than naphthalene.

Phenol dissolved in carbon disulfide gave a value of $\mu = 1.63 \times 10^{-18}$, in excellent agreement with that found in benzene solution,[5] $\mu = 1.70 \times 10^{-18}$.

The agreement between the values of the electric moments found for

---

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

chlorobenzene and nitrobenzene in the various solvents used leaves nothing to be desired. This agreement is shown amply in Table VI.

## Summary

1. Using an electrical resonance method previously described, dielectric constant data have been obtained for carbon disulfide solutions of benzoic acid, phenol, cinnamic acid, iodine, naphthalene, anthracene, benzene, hexane, nitrobenzene and chlorobenzene, and for hexane solutions of benzoic acid, naphthalene, benzene, nitrobenzene and chlorobenzene. Corresponding density determinations have been made.
2. The data have been applied to the calculation of the electric moments of a majority of the solute molecules.
3. The data of this article prove that the molar polarization, and therefore the electric moment, of a solute molecule is independent of the non-polar solvent used.
4. The solvents benzene, carbon disulfide and hexane have been shown to be non-polar in character.

MADISON, WISCONSIN

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

# THE ENTROPY OF HYDROGEN CHLORIDE. HEAT CAPACITY FROM 16°K. TO BOILING POINT. HEAT OF VAPORIZATION. VAPOR PRESSURES OF SOLID AND LIQUID

BY W. F. GIAUQUE AND R. WIEBE

RECEIVED OCTOBER 20, 1927 PUBLISHED JANUARY 5, 1928

The results presented in this paper were obtained in the first of a series of researches on low temperature calorimetry of condensed gases. This research, which was started in 1922, is in active continuation. It is hoped that the more important substances of simple structure which are gases under ordinary conditions will be investigated, or perhaps we should say re-investigated since data exist in many cases. In addition to the data presented in this paper, measurements on hydrogen bromide and hydrogen iodide have been completed but will not be available until the completion of the laborious calculations.

Our immediate purpose is the testing of the third law of thermodynamics and more particularly the comparison of the entropy, as obtained from this law, with that obtained from various theories with the assistance of spectroscopic data It seems almost unnecessary to state that such a purpose imposes severe requirements on the accuracy of the measurements.

Hydrogen chloride was selected because of the reliability of band spectra measurements and their interpretation for this substance. While the measurements were in progress the results of a similar investigation