[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, COLLEGE OF ENGINEERING, CARNEGIE INSTITUTE OF TECHNOLOGY]

Molar Polarizations in Extremely Dilute Solutions. The Dipole Moments of *d*-Limonene, *d*-Pinene, Methyl Benzoate and Ethyl Benzoate[1]

BY W. J. SVIRBELY, JAMES E. ABLARD AND J. C. WARNER

Recently a number of investigators[2] have emphasized the need of obtaining reliable measurements of the dielectric constants and densities of very dilute solutions of polar solutes in non-polar solvents if the molar polarization of the solute at infinite dilution is to be accurately determined. An exact knowledge of the mole fractions of the constituents of these dilute solutions is also important. These investigators have examined the limits of error in measurements and the methods of extrapolating the polarization to infinite dilution. We have made a similar critical examination of our method and have been able to obtain reliable measurements in solutions more dilute than have been commonly used. To check our procedure, we have redetermined the dipole moment of nitrobenzene, obtaining a moment of 4.08 *D*, which is in good agreement with the results (μ = 4.05 to 4.10 *D*) of recent careful investigations.[2c,3]

Having tested our procedure, we determined the moments of *d*-limonene, *d*-pinene, methyl benzoate and ethyl benzoate from measurements of the dielectric constants and densities of very dilute solutions of these substances in benzene.

Materials

Eastman "Best Grade" benzene was refluxed over mercury for three hours and then twice fractionally distilled over phosphorus pentoxide, the first and last fractions being discarded. This procedure yielded benzene which was very constant in dielectric constant and density.

d-Pinene (chemically pure) was purchased from the E. deHaen Company and used without further purification: physical constant α^{26}_{5892} 46.30° compared to α^{23}_{5892} 43.94°.[4]

d-Limonene was prepared by the fractional distillation of a *d*-limonene rich fraction of orange oil under reduced pressure; physical constants, $d^{30}{}_4$ 0.8347 and α^{30}_{5892} 119.0° compared to values in the literature of $d^{20}{}_4$ 0.8468,[5] and α^{20}_{5892} 120.6[6] and 115.9.[7]

Eastman "Best Grade" methyl benzoate was dried over calcium chloride and fractionally distilled: $d^{25}{}_4$ 1.0833 compared to $d^{25}{}_4$ 1.0836.[8]

Eastman "Best Grade" ethyl benzoate was dried over anhydrous copper sulfate and fractionally distilled: $d^{25}{}_4$ 1.0434 compared to $d^{25}{}_4$ 1.0423 ±0.001.[9]

Method and Apparatus

The dielectric constants were determined by the heterodyne beat method.[10] The fixed oscillator, operated at a frequency of 10^6 cycles per second, was controlled by a General Radio Company Type 376 crystal mounted in a constant temperature copper box. The circuit for the variable oscillator[11] is shown in Fig. 1. The amplifier[12] was placed midway between the two oscillators, which were about eleven feet apart, and all were separately shielded. The standard condenser was a General Radio Company Precision Condenser, Type 222-L, of 1500 $\mu\mu$f capacitance with 2500 scale divisions. The beat note was matched with a 1000-cycle electrically driven tuning fork which was calibrated for constancy of frequency against a synchronous clock. The measuring cell was of the semi-circular plate type. The plates were gold plated but the body of the cell was brass. The stator was rigidly attached to the heavy brass lid through bakelite insulating studs. The rotor could be moved through about 50° between heavy studs fixed on the lid. The lid, rotor and body of the cell were at ground potential. The cell was placed in a copper jacket and mounted on a stand rigidly attached to the iron shield of the variable oscillator. This permitted the use of short leads. Water from a thermostat was circulated through the copper jacket maintaining the temperature of the cell constant to within ±0.015°.

Solutions were prepared as follows: 200 cc. of benzene was weighed to within 0.03 g. The solute (0.1 to 6.0 g.) was weighed out in a small glass-stoppered weighing bottle to within 0.2 mg. and the bottle then dropped into the benzene. Considering the error which might be made in weighing solute and solvent, the maximum error in composition was no greater than 0.25%; 150 cc. of this solution was transferred to the measuring cell and the remainder used for density determinations with an Ostwald–Sprengel pycnometer. All density measurements were checked at least twice with a maximum absolute variation of one significant figure in the fifth decimal place. The maximum error in density measurements was no greater than 0.006%. In filling the measuring cell, care was taken to displace any air bubbles trapped between the condenser plates. When the cell had attained constant temperature,

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[1] A portion of this paper is abstracted from a thesis presented by W. J. Svirbely to the Committee on Graduate Instruction in partial fulfilment of the requirements for the degree of Doctor of Science.

[2] (a) Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929); (b) Weissberger and Sängewald, *Physik. Z.*, **30**, 792 (1931); (c) Müller, *ibid.*, **34**, 689 (1933); (d) Rau and Narayanaswamy, *Z. physik. Chem.*, **B26**, 23 (1934).

[3] Bergmann, Engel and Sándor, *ibid.*, **B10**, 397 (1930); Jenkins, *Nature*, **133**, 106 (1934).

[4] Conant and Carlson, THIS JOURNAL, **51**, 3467 (1929).

[5] "I. C. T.," Vol. VII, p. 52.

[6] "I. C. T.," Vol. VII, p. 410.

[7] Landolt–Börnstein, "Tabellen," 1923, p. 1002.

[8] Beilstein, Band 9, p. 110.

[9] "I. C. T.," Vol. III, p. 29.

[10] Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, 1931, p. 54.

[11] The authors take this opportunity to thank Dr. W. Work and Mr. R. T. Gabler of the Department of Electrical Engineering for valuable assistance in the design of the variable oscillator.

[12] Williams, THIS JOURNAL, **52**, 1831 (1930).

the rotor plates were set in one of the fixed positions and the precision condenser adjusted to zero beat (against the 1000-cycle tuning fork). The rotor was then moved to the other fixed position and the precision condenser again adjusted to zero beat. This procedure was repeated until several difference readings were made. Using this procedure, the capacity balance is

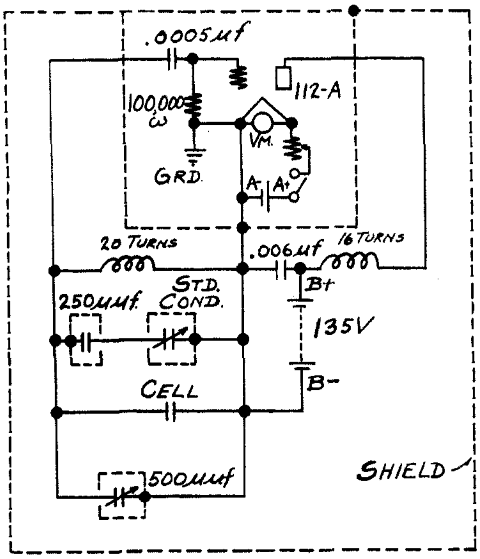

Fig. 1.—Circuit for variable oscillator.

$$C'_x + \left(\frac{C_f C'_p}{C_f + C'_p}\right) = C_x + \left(\frac{C_f C_p}{C_f + C_p}\right) \qquad (1)$$

C_x and C_p are the capacities of the measuring cell and the precision condenser for one fixed position of the measuring cell and C'_x and C'_p the corresponding capacities for the other fixed position. C_f is the capacity of the fixed condenser in series with the precision condenser. Equation (1) may be transformed into

$$\Delta C_x = \frac{C_f^2\,(\Delta C_p)}{(C_f + C_p)\,(C_f + C'_p)} \qquad (2)$$

Using Equation (2), the values of ΔC_x were calculated separately for the several readings obtained on each sample and the average value of ΔC_x was used for calculating the dielectric constant. The value of C_f was determined by the substitution method over the whole range of the precision condenser. The maximum absolute deviation of any individual result for C_f from the mean value of 263 μμf was less than 0.15%. The absolute values of C_p and C'_p were taken from the calibration chart furnished with the precision condenser. Using $\epsilon = 2.2830$[2c,13] for benzene at 25°, the dielectric constant of a solution was calculated by the relation

$$\epsilon(\text{soln.}) = 2.2830\ \Delta C_x(\text{soln.})/\Delta C_x(\text{benz.}) \qquad (3)$$

Based upon the reproducibility of ΔC_x for benzene, the maximum error in dielectric constant measurements was not greater than 0.03%.

The molar polarizations of the solutions (P_{12}) and the molar polarizations of the solute (P_2) were calculated by the usual relationships

$$P_{12} = \left(\frac{\epsilon - 1}{\epsilon + 2}\right)\frac{M_1N_1 + M_2N_2}{d} \qquad (4)$$

$$P_2 = \frac{P_{12} - P_1(1 - N_2)}{N_2} \qquad (5)$$

Considering the contribution of errors in densities, composition and dielectric constant to error

TABLE I

SUMMARY OF EXPERIMENTAL DATA

N_2	ϵ	d	P_{12}	P_2
		d-Pinene in Benzene at 25°		
0.00000	2.2830	0.87335	P_1 = 26.771	
.000432	2.2860	.87331	26.823	147
.000574	2.2874	.87331	26.846	157
.0007878	2.2887	.87332	26.872	155
.002262	2.2900	.87329	26.920	93
.00626	2.2907	.87314	27.014	66
.01038	2.2936	.87301	27.144	63
.01458	2.2952	.87290	27.256	60
.01726	2.3010	.87283	27.465	61
.02099	2.3003	.87275	27.464	55
1.00000	2.6428			
		d-Limonene in Benzene at 30°		
0.000000	2.2750	0.86808	P_1 = 26.815	
.000662	2.2765	.86801	26.853	84
.0008109	2.2770	.86799	26.864	87
.0021632	2.2773	.86790	26.898	66
.003155	2.2777	.86777	26.928	66
.011182	2.2788	.86706	27.127	55
.01474	2.2803	.86676	27.230	55
.01691	2.2807	.86658	27.285	54.6
.02042	2.2815	.86631	27.376	54.3
		Methyl Benzoate in Benzene at 25°		
0.0000	2.2830	0.87335	P_1 = 26.771	
.000669	2.2887	.87350	26.863	163
.001888	2.2967	.87385	26.992	143
.002769	2.3033	.87412	27.086	141
.003322	2.3048	.87428	27.126	134
.006601	2.3185	.87525	27.348	116
.009555	2.3364	.87615	27.649	118
.0134	2.3552	.87727	27.961	116
.0137	2.3552	.87737	27.965	114
.0174	2.3721	.87848	28.240	111
		Ethyl Benzoate in Benzene at 25°		
0.0000	2.2830	0.87335	P_1 = 26.771	
.001099	2.2916	.87363	26.915	157
.001767	2.2957	.87383	26.997	154
.002334	2.2996	.87396	27.052	147
.003481	2.3071	.87427	27.180	144
.005316	2.3157	.87480	27.334	133
.007752	2.3298	.87547	27.577	131
.01123	2.3492	.87648	27.911	128
.01521	2.3696	.87753	27.270	125

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(13) Williams and Schwingel, THIS JOURNAL, **50**, 362 (1928); Smyth and Stoops, *ibid.*, **51**, 3312 (1929).

in P_2, we estimate that the maximum error in P_2 should be about 3.0 cc. This estimate is supported by the fact that only one experimental point (Fig. 2) lies more than 3.0 cc. from the smooth P_2 curve.

Experimental Results

The experimentally determined dielectric constants and densities and the calculated values of P_{12} and P_2 for the various solutions of *d*-limonene, *d*-pinene, methyl benzoate and ethyl benzoate are given in Table I. In Fig. 2, P_2 for each of these four substances is plotted against mole fraction.

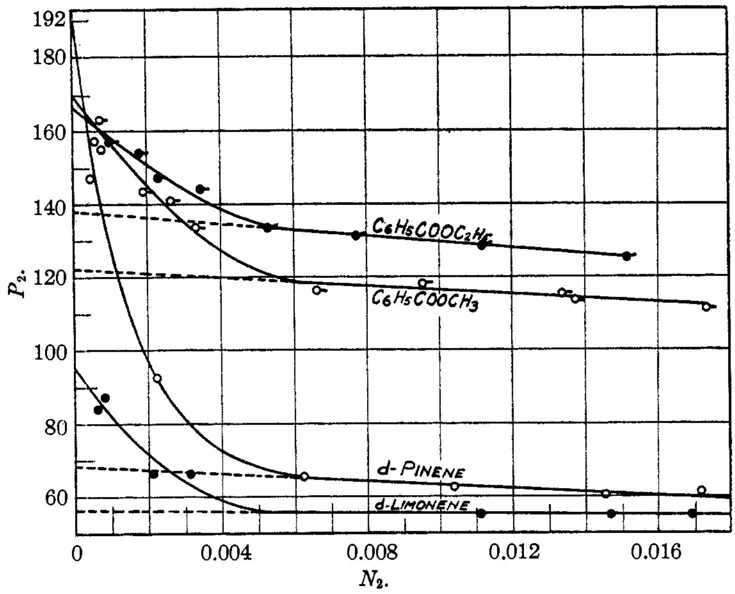

Fig. 2.—Variation of P_2 with mole fraction of solute.

Discussion

A number of investigators have used the equation developed by Hedestrand[2a] to calculate the molar polarization of solutes at infinite dilution.

$$P_\infty = A(M_2 - \beta d_1(M_1/d_1)) + B\alpha\epsilon_1 \quad (6)$$

A and *B* are constants depending upon the solvent and α and β are constants in the equations

$$\epsilon = \epsilon_1^\circ(1 + \alpha N_2) \quad (7)$$

$$d = d_1^\circ(1 + \beta N_2) \quad (8)$$

The average values of α and β are calculated from the experimental data and P_∞ is then obtained by Equation (6). This method was very satisfactory when applied to our data on nitrobenzene (N_2 = 0.00066–0.00256), where Equation (6) yields P_∞ = 379 cc. and graphical extrapolation yields 382 cc. However, when Equation (6) is applied to the calculation of P_∞ from our data on solutions of *d*-limonene, *d*-pinene, methyl benzoate and ethyl benzoate unsatisfactory results are obtained. An average value of $\alpha\epsilon_1$ (Eq. 6) cannot be obtained because α drifts to decidedly higher values at mole fractions of solute below 0.004. The failure of the Hedestrand method in these solutions is obviously due to the fact that the dielectric constants and densities are not linear functions of the mole fraction in the dilute solution region, as is implied in Equations (7) and (8). At mole fractions above 0.004, the dielectric constants and densities of these solutions are approximately linear functions of the mole fraction. As a consequence, in this higher concentration region, P_2 is approximately a linear function. At lower concentrations, however, there is a rather rapid increase in P_2 with decrease in concentration. This behavior indicates that in these solutions some orientation of dipoles, such as has been shown to exist in solutions of alcohols,[14] persists to very low concentrations. The rapid increase in P_2 with decrease in concentration was not observed in solutions of nitrobenzene over a similar concentration range.

Owing to the inapplicability of Hedestrand's equation to our data, P_∞ for the four substances investigated has been obtained by direct graphical extrapolation (Fig. 2). One extrapolation makes use of all experimental points and the other (broken lines in Fig. 2) uses only the experimental points at higher concentrations where P_2 is approximately a linear function of the composition.

TABLE II

Compound	*d*-Pinene	*d*-Limonene	Benzoates Methyl	Ethyl
$P_{2\infty}$ high concn. only, cc.	68	56	122	138
$P_{2\infty}$ all exptl. points, cc.	192	95	170	166
P_M molar refraction, cc.	43.99[a]	45.30[b]	37.82[c]	45.54[b]
μ high concn. only × 10^{18}, e. s. u.	1.10	0.70	2.01	2.14
μ all exptl. points × 10^{18}, e. s. u.	2.67	1.56	2.52	2.43

[a] Landolt-Börnstein, "Tabellen," 1923, p. 981. [b] *Ibid.*, p. 980. [c] *Ibid.*, p. 979.

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(14) For a detailed discussion of association in dilute solution, the reader is referred to Smyth's Monograph,[1e] Chapter IX.

These extrapolated values of P_∞ and the moments calculated by the relation $\mu = 0.0127 \times 10^{-18} \sqrt{(P - P_M)\,T}$ are listed in Table II. The moments obtained for methyl and ethyl benzoates are definitely higher than the values[15] (1.8 *D*) previously reported. The moments obtained for *d*-limonene and *d*-pinene are surprisingly high.

Summary

Measurements have been made of the dielectric constants and densities of solutions of *d*-pinene, *d*-limonene, methyl benzoate and ethyl benzoate in benzene to mole fractions as low as 0.0006. The sources of error in the experimental determinations were carefully examined and evaluated. From the data obtained, the dipole moments of the above substances were calculated by graphical extrapolation of the molar polarization to infinite dilution. The non-linearity of the curves relating ϵ_{12} to N_2 and d_{12} to N_2 for the more dilute solutions does not permit the use, in these cases, of Hedestrand's method of extrapolation and suggests that this method should not be considered of general applicability.

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[15] Estermann, *Z. physik. Chem.*, **B1**, 422 (1928).

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The Directive Influence of the Electric Moment on Substitution in the Benzene Ring[1]

BY W. J. SVIRBELY AND J. C. WARNER

Latimer and Porter[2] predict whether a second group or atom will substitute in the meta or in the ortho and para positions to a group or atom already substituted in the benzene ring by estimating the polarity of the bond between the carbon atom of the ring and the "key" atom of the substituted group. The success of the Latimer–Porter rule made it seem logical to expect that a more satisfactory rule could be developed which would relate the directive influence to the electric moment of the mono substituted compound. Such a rule would have the advantage of being based upon a measurable property of the molecule which is determined by its structure. In Table I we have listed the mono substituted benzene derivatives whose moments have been determined. The compounds are divided into two groups depending upon whether the second substituted group is directed to the ortho and para or to the meta position. An examination of the data in Table I yields the interesting information that all compounds which direct substitution to the ortho and para positions have electric moments of 2.04 *D* or less while compounds which direct to the meta position have moments of 2.10 *D* or higher. This leads to the rule: *In general: if the electric moment of a mono substituted benzene derivative is greater than ∼ 2.07 D, the next substituted group will be directed to the meta position; if the moment is less than ∼ 2.07 D, the next group will be directed to the ortho and para positions.* Of the mono substituted benzene derivatives, whose moments had been determined, only three appeared as well-defined exceptions to the rule. These were benzoic acid, methyl benzoate and ethyl benzoate. It seemed entirely possible that the moments reported for these compounds were too low due to the fact that measurements of dielectric constants were not made in dilute enough solutions in non-polar solvents to eliminate all dipole interactions. The two esters have been reinvestigated in this Laboratory[3] with the result that moments decidedly higher than those previously reported were obtained. They are, therefore, no longer exceptions to the rule. This suggests that the moment of benzoic acid should be redetermined. It must be emphasized that factors such as the nature of the solvent, concentration, temperature, nature of reagent and the possibility of intermediate complex formation may cause a change in the effective electric moment of molecules and serve to cause exceptions to the simple rule based upon the electric moments of molecules in the gaseous state or in such dilute solution that all dipole interactions are absent. For example, according to the experiments of Hammick and Illingworth,[4] nitrosobenzene directs substitution

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[1] Abstracted from a part of the thesis submitted by W. J. Svirbely to the Committee on Graduate Instruction in partial fulfilment of the requirements for the degree of Doctor of Science.

[2] Latimer and Porter, THIS JOURNAL, **52**, 206 (1930).

[3] Svirbely, Ablard and Warner, *ibid.*, **57**, 652 (1935).

[4] Hammick and Illingworth, *J. Chem. Soc.*, **133**, 2358 (1930).