tion was cooled, filtered, and carefully acidified. The precipitate was recrystallized from benzene–ethanol and melted at 207–208°. Mixed melting point determinations showed this substance to be identical with samples obtained in earlier experiments as described above.

2-Hydroxy-4-methoxyallylbenzene.—One and three-tenths grams of 2-allyloxy-4-methoxybenzoic acid dissolved in 12 cc. of N,N-dimethylaniline was refluxed for six hours, cooled, and poured into ether. The amine was removed from the ether layer by extraction with hydrochloric acid. Evaporation of the ether gave an oil which was soluble in

sodium hydroxide and completely insoluble in sodium bicarbonate. A positive ferric chloride test was obtained. The structure of this oil was established by methylation, isomerization with alkali, and oxidation to 2,4-dimethoxybenzoic acid; m. p. and mixed m. p. 108°.

Summary

A number of reactions leading to the formation of substituted coumarans have been described.

Solvent Polarization Error and its Elimination in Calculating Dipole Moments

BY I. F. HALVERSTADT[1,2] AND W. D. KUMLER

An old idea in dipole moment literature is that P_{12}–N_2 (or p_{12}–ω_2) curves would be straight lines in the absence of intermolecular action[3] or molecular association. This idea is implicit in the usual methods of calculating the degree of molecu-

Fig. 1.—Theoretical polarization–concentration curves calculated by use of the Debye–Clausius–Mosotti equation for solutions in which ϵ_{12} is taken as linear with ω_2 (absence of association). β is taken in all cases as −0.2 and α has been varied from 5 to 40.

lar association from polarization concentration curves, and in the calculation of dipole moments by a linear extrapolation of P_2–N_2 curves, a method still used by a number of authors.

Considerable evidence has accumulated which indicates that the dielectric constant ϵ_{12} is a linear function of the weight fraction of solute ω_2[4,5,6,7] in dilute solutions.

We have examined over fifty compounds of widely different nature and have found ϵ_{12} to be linear with ω_2 in every case as long as ω_2 is less than 0.01. Now it can be shown from the nature of the relation

$$p_{12} = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \frac{1}{d_{12}}$$

that if ϵ_{12} is linear with respect to ω_2, p_{12} is not linear with ω_2. The extent of this deviation is shown in Fig. 1. The corresponding p_2–ω_2 curves are given in Fig. 2 and it is to be observed that the latter curves are neither horizontal nor straight. It is thus obvious that a linear extrapolation of p_2–ω_2 or P_2–N_2 curves introduces an error which is small in case of compounds with a low dipole moment and comparatively larger with compounds of high dipole moment.

This error is eliminated by the method of extrapolation proposed by Hedestrand.[8] However, serious errors may result even with the use of Hedestrand's method if it is not realized that the dielectric constant of the solvent in the solution sometimes differs considerably from the measured dielectric constant of the pure solvent.
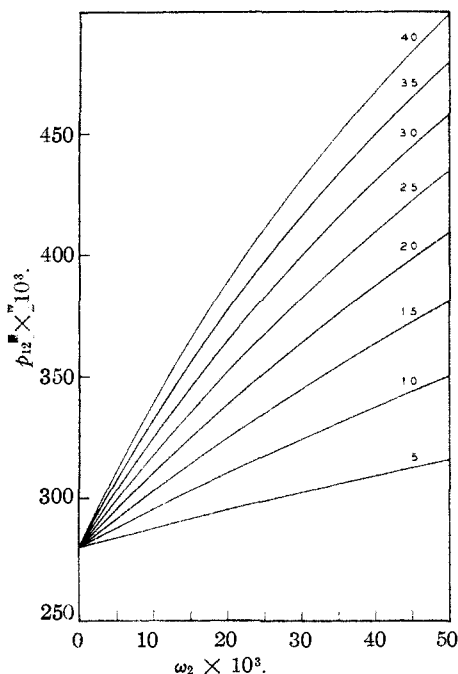
(1) Abraham Rosenberg Fellow in Pharmaceutical Chemistry, 1941–1942.

(2) Present address: American Cyanamid Company, Stamford, Conn.

(3) Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, N. Y., 1931, p. 176.

(4) Muller, Physik. Z., 35, 346 (1934).

(5) Rodebush and Eddy, J. Chem. Phys., 8, 424 (1940).

(6) McCusker and Curran, THIS JOURNAL, 64, 614 (1942).

(7) Wyman, ibid., 58, 1482 (1936).

(8) Hedestrand, Z. physik. Chem., B2, 428 (1929).

Solvent Polarization Error

Two considerations are involved here. First, with the usual methods of handling, the solutions are exposed longer to air than is the pure solvent and consequently the solutions may absorb more water vapor than the solvent. Second, even if rigid methods are used to exclude moisture each $\Delta\epsilon$ value for the different solutions depends on a single solvent measurement of ϵ_1 and consequently the latter is much more heavily weighted than any single solution measurement of ϵ_{12}. Now since the ϵ_{12}–ω_2 curves are straight lines both of the factors giving rise to solvent polarization error can be essentially eliminated if the dielectric constant of the pure solvent is obtained by extrapolating the ϵ_{12}–ω_2 curves for the solution to $\omega_2 = 0$. By comparing the extrapolated value of ϵ_1 with the measured value one can also tell if there has been appreciable contamination of the solvent in handling the solutions. The method used to calculate p_{2_0} making use of the extrapolated value of ϵ_1 is as follows:

A Method of Calculating p_{2_0}[9]

In calculating p_{2_0} we use the equation

$$p_{20} = \frac{3\alpha v_1}{(\epsilon_1 + 2)^2} + (v_1 + \beta)\frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)} \quad (1)$$

which is derived from the expressions

$$p_{12} = \frac{(\epsilon_{12} - 1)}{(\epsilon_{12} + 2)} v_1 \quad (2)$$

$$\epsilon_{12} = \epsilon_1 + \alpha\omega_2 \quad (3)$$

$$v_{12} = v_1 + \beta\omega_2 \quad (4)$$

The corresponding equation in N_2 is

$$P_{20} = \frac{3\alpha' v_1}{(\epsilon_1 + 2)^2} M_1 + (M_2 v_1 + M_1\beta')\frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)} \quad (5)$$

This is essentially the same as the equation proposed by Hedestrand.[8]

The ϵ_{12}–ω_2 and v_{12}–ω_2 curves are plotted. If one point is considerably off the curve and all other points on, it suggests an experimental error and that point is rechecked. If the plots show curvature, they suggest some abnormal behavior and this method is not used, or the method is applied to the points in dilute solutions where they are linear. A straight line equation is fitted to the

(9) The symbols used are: subscripts 1, 2, and 12 refer to solvent, solute and solution, respectively; ϵ, dielectric constant; d, density; v, specific volume, $1/d$; V, molecular volume; M, molecular weight; p, specific polarization; p_{2_0}, specific solute polarization at infinite dilution; P, molar polarization; P_{2_0}, solute molar polarization at infinite dilution; P_{E_2}, solute molar electronic polarization; ω, weight fraction; W, weight; m, moles; N, mole fraction; $\alpha = d\epsilon_{12}/d\omega_2$; $\beta = dv_{12}/d\omega_2$; $\alpha' = d\epsilon_{12}/dN_2$; $\beta' = dv_{12}/dN_2$; μ, dipole moment in Debye units; T, absolute temperature.
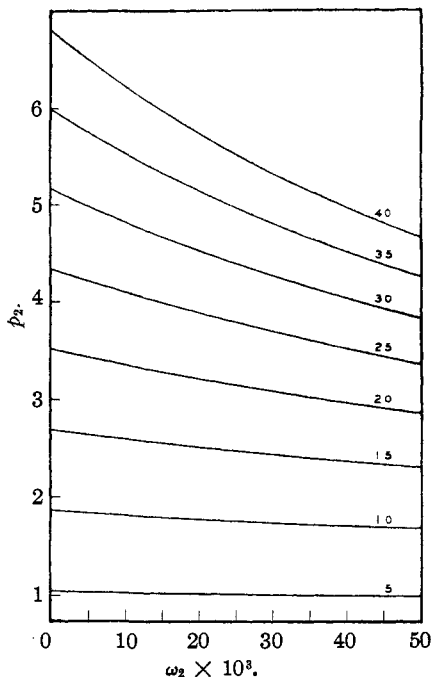

Fig. 2.—The theoretical p_2–ω_2 curves corresponding to the p_{12}–ω_2 curves in Fig. 1.

data by the method of least squares using the points for the solutions and omitting those for the pure solvent.[10] The constants of these equations give the values of ϵ_1, v_1, α and β which are substituted in equation (1).

This calculation can be done graphically by plotting the ϵ_{12}–ω_2 and v_{12}–ω_2 curves. These are straight lines and can easily be extrapolated to $\omega_2 = 0$. The intercept of the ϵ_{12}–ω_2 line gives ϵ_1 and its slope is α. The intercept of the v_{12}–ω_2 line gives v_1 and its slope is β.

The advantages of this method of calculation are: first, it eliminates errors due to a difference in the dielectric constant of the solvent in the solution and the measured dielectric constant of the pure solvent. Second, it is objective and does

(10) The usual statistical method of least squares was used; for example, to fit the straight line $\epsilon_{12} = \epsilon_1 + \alpha\omega_2$ to the dielectric constant data, the equations

$$\Sigma\epsilon_{12} = N\epsilon_1 + \alpha\Sigma\omega_2$$
$$\Sigma(\omega_2\epsilon_{12}) = \epsilon_1\Sigma\omega_2 + \alpha\Sigma(\omega_2)^2$$

in which N represents the number of observations, were set up and solved for ϵ_1 and α. In this method if the data are accurate to five places, the summations need to be carried only to five places, but all numbers derived from these during the solutions of the equations should be taken to eight or nine places if anomalous solutions are to be avoided. This is necessary because ϵ_1 and α are obtained as the ratios of small differences between relatively large numbers and if these large numbers are given only to five places the differences will very often be given only to three places, which, of course, will lead to incorrect results. The calculation of the dipole moment of a compound by this method requires less than an hour if an electric calculating machine is used.

not involve the judgment of the calculator. Third, all extrapolations are carried out with straight line functions. Fourth, if the solutions are absorbing water this is easily detected because the extrapolated and measured dielectric constants for the solvent will be different.

If a contaminant such as water gets into the solutions it will cause the p_2 values to be too high and the magnitude of the error thus introduced will be greater the higher the dilution.

An examination of the literature reveals a number of cases of an abnormal rise in p_2 or P_2 values at high dilution. The effect is usually either ignored, attributed to experimental error, or to that convenient explanation of anomalous behavior—molecular association. Application of our method of calculation to some of these cases reveals a solvent polarization error and the abnormality in the moment disappears when our method is applied. For example, a case of a very marked upward trend at high dilution is found in the paper of Svirbely, Ablard and Warner.[11] They obtain the following values: d-pinene 2.67, d-limonene 1.56, methyl benzoate 2.52, ethyl benzoate 2.43. The first two values are much too high (1 to 2 units) for hydrocarbons with one and two double bonds. The last two values are about half a unit high for esters. We have recalculated their data using our method and obtained the following values which are consistent with those obtained by other authors[12] for the same compounds. The recalculated values are as follows: d-pinene 0.80, d-limonene 0.61, methyl benzoate 1.86, ethyl benzoate 1.94. No correction has been made for atomic polarization which will have an appreciable effect on the moments of the first two compounds. These are still probably high by about 0.2 of a unit.

The high values obtained by the above authors in very dilute solutions we believe are without significance and result most probably from solvent polarization errors.

Lewis, Oesper and Smyth[13] have measured trimethyl- and triethyllead chloride at high dilutions and obtain a higher value, 4.47, for the trimethyl compound than for the triethyl compound, 4.39. This is contrary to expectation because the ethyl groups are more polarizable than methyl groups and the large lead–chlorine

moment should have a large polarizing effect. The trimethyl compound was measured in solutions about ten-fold more dilute than the triethyl compound so the effect of a small solvent polarization error on P_2 would be much greater for the trimethyl compound. A recalculation by our method gives values of the expected order, 3.81 for trimethyllead chloride and 4.27 for triethyllead chloride.

That solvent polarization errors can have an enormous effect on the observed moment of a compound as determined in very dilute solution is illustrated in the cases of urea and thiourea. The moments of these compounds as given in the literature were 8.6 and 7.6, respectively.[14] A redetermination of these moments under conditions in which solvent contamination was reduced and solvent polarization errors essentially eliminated by using our method of calculation gave values of 4.56 for urea and 4.89 for thiourea.[15]

Theoretically the dielectric constant of the solvent should be increased slightly[16] by the presence of a polar solute and the possibility exists that this effect is responsible for the abnormal increase of P_2 at high dilutions. There are, however, some serious objections to such an interpretation. First, the effect of the solute in increasing the dielectric constant of the solvent would be greater the higher the concentration of the solute. The observed effect is just the reverse, the P_2 values become more abnormal as the solutions become more dilute. Second, many investigators including ourselves do not always obtain the same measured value for the dielectric constant of the pure solvent and these variations are most noticeable with the very hygroscopic solvent dioxane and least noticeable with hexane. Third, where special precautions are taken to eliminate water[17] this sharp rise in P_2 curves at high dilutions is not present. The evidence thus points very strongly to absorption of water as the cause of the abnormally high P_2 values in dilute solutions.

A Test of Our Method of Calculation

A wide variation of dipole moment values in the literature is difficult to reconcile with the accuracy of the dielectric constant and density

(11) Svirbely, Ablard and Warner, THIS JOURNAL, **57**, 652 (1935).

(12) Estermann, Z. physik. Chem., **B1**, 422 (1928); Bergmann and Weizmann, THIS JOURNAL, **57**, 1755 (1935).

(13) Lewis, Oesper and Smyth, THIS JOURNAL, **62**, 3243 (1940).

(14) Bergmann and Weizmann, Trans. Faraday Soc., **34**, 783 (1938).

(15) Kumler and Fohlen, THIS JOURNAL, **64**, 1944 (1942).

(16) Onsager, ibid., **58**, 1486 (1936).

(17) Linton, THIS JOURNAL, **62**, 1945 (1940); Maryott, ibid., **63**, 3079 (1941).

TABLE I

Dielectric constants and specific volumes in Table I were plotted against N_2 the mole fraction of the solute, and total polarizations were calculated according to equation (5). All of these compounds were measured in benzene.

Compound	ϵ_1 measured	ϵ_1 calcu- lated	v_1 calculated	α'	β'	P_{2_0} old	P_{2_0} new	P_{E_2}	μ old	μ new
d-Pinene[a]	2.2830	2.2872	1.14504	0.660	0.0377	192	57.4	44.0	2.67	0.80
d-Limonene[a]	2.2750	2.2767	1.15199	.233	.1160	95	53.0	45.3	1.56	.61
Methyl benzoate[a]	2.2830	2.2876	1.14509	4.945	.3880	170	109.9	37.8	2.52	1.86
Ethyl benzoate[a]	2.2830	2.2866	1.14505	5.518	.3626	166	123.7	45.5	2.43	1.94
Trimethyllead chloride[b]	2.276	2.2777	1.14521	20.78	2.618	455	343.0	41	4.47	3.81
Triethyllead chloride[b]	2.276	2.2776	1.14491	26.13	2.667	455	434.0	55	4.39	4.27
Nitrobenzene[c]	2.2825	2.2818	1.13879	23.11	0.483	366	367.0	32.7	3.97	3.98
Nitrobenzene[d]	2.2826	2.2873	1.13916	23.20	.510	382	367.0	32.7	4.08	3.98
Nitrobenzene[e]	2.280	2.2752	1.14094	23.09	.488	348	368.2	32.7	3.93	4.00
Nitrobenzene[f]	2.2727	2.2704	1.14385	22.87	.476	354	367.0	32.6	3.94	4.01

[a] Data from Svirbely, Ablard and Warner, THIS JOURNAL, **57**, 652 (1935). [b] Data from Lewis, Oesper and Smyth, *ibid.*, **62**, 3243 (1940). [c] Data from Tiganik, *Z. physik. Chem.*, **B13**, 440 (1931). [d] Data from Bergmann, Engel and Sandor, *ibid.*, **B10**, 397 (1930). [e] Data from Plotz, *ibid.*, **B20**, 351 (1933). [f] Data from Jenkins, *J. Chem. Soc.*, 480 (1934).

measurements. Differences of 0.1–0.2 which represent errors of several per cent. are quite common. Most dielectric constant and density measurements are accurate to at least 0.5% when the total polarization is several times the electronic polarization, and measurements are made in solutions that are not too dilute. This discrepancy is evidently due to an error in the solvent polarization plus errors in extrapolation. If this is the case an application of our method to the data should reveal and correct such errors.

Nitrobenzene was chosen to test this point because it has been measured a number of times in benzene. Four sets of data were found in the literature in which the solutions were sufficiently dilute so that the dielectric constant values were linear with concentration. As seen in Table I the dipole moment values vary by 0.15 from 3.93 to 4.08. A recalculation by our method reduces the variation to 0.03. Part of this difference may be due to the decrease in the dielectric constant of the solvent with increase of temperature.

TABLE II

MEASUREMENTS IN DIOXANE AT 25°

Compound	ϵ_1 measured	ϵ_1 extra- polated	v_1 extrapolated	α	β	P_{2_0} old	P_{2_0} new	P_{E_2}	μ old	μ new
Tetronic acid	2.2023	2.2015	0.97379	28.98	0.2909	485	499.5	22.1	4.72	4.80
α-Chlorotetronic acid	2.2104	2.2086	.97364	32.09	.4244	700	733.1	26.0	5.69	5.83
α-Bromotetronic acid	2.2023	2.2029	.97393	26.01	.5162	777	793.6	28.5	6.00	6.07
Methyl α-bromo- tetronate	2.2023	2.2037	.97406	25.06	.4230	830	830.3	32.4	6.19	6.19
α-Iodotetronic acid	2.2023	2.2043	.97366	17.41	.4850	689	681.9	36.9	5.59	5.57
Methyl α-iodotetronate	2.2163	2.2188	.97363	19.71	.5069	820	834.4	39.7	6.12	6.22
l-Ascorbic acid	2.2137	2.2110	.97360	12.20	.4122	360	382.3	38.2	3.93	4.07
Aniline	2.2095	2.2120	.97383	4.412	.0129	106	93.4	31	1.90	1.73
Xenylamine	2.2099	2.2117	.97387	3.615	.0853	148	144.0	59	2.07	2.02
Xenylamine (in benzene)	2.2760	2.2746	1.14618	2.556	.2702	122	125.6	59	1.74	1.79
Benzenesulfonamide	2.2095	2.2074	0.97386	21.68	.2720	577	594.1	39	5.09	5.17
p-Phenylbenzenesulfon- amide	2.2099	2.2089	.97394	15.41	.2395	630	642.2	68	5.20	5.25
Sulfanilamide (operator 1)	2.2067	2.2065	.97367	32.75	.3059	960	964.1	45	6.63	6.65
Sulfanilamide (operator 2)	2.2104	2.2071	.97391	32.73	.3306	929	962.1	45	6.52	6.64
Metanilamide	2.2104	2.2097	.97375	24.48	.3070	705	728.0	45	5.63	5.73
p-(p-Aminophenyl)-ben- zenesulfonamide	2.2099	2.2076	.97378	24.78	.2552	1012	1066	75	6.71	6.90
Desoxycholic acid	2.2067	2.2053	.97385	3.493	.1015	314	324.7	108.8	3.15	3.22

Data from: Kumler, THIS JOURNAL, **62**, 3292 (1940); Kumler and Halverstadt, *ibid.*, **63**, 2182 (1941); Kumler and Halverstadt, *ibid.*, **64**, 1941 (1942).

Rau and Narayanaswamy[18] found experimentally that the apparent moment of nitrobenzene in benzene increases about 0.01 for an increase of 5°. Since the temperatures of the measurements we used range from 20 to 25° this would reduce the variation to 0.02 which is about the magnitude expected. Taking an average of the values corrected to 25° the dipole moment of nitrobenzene in benzene appears to be 4.00 ± 0.01, no correction being made for the atomic polarization.

In Table II the dipole moment values from two previous papers have been recalculated by the new method. There appear to have been no serious solvent polarization errors with the exception of aniline where the old moment value is high by 0.17. In thirteen of the seventeen cases the old values are lower by 0.02–0.19 than the new values. This we attribute to the linear extrapolation of the P_2-concentration curves which we have previously shown are concave upward, and to solvent polarization errors. The conclusions that were originally drawn from the old data hold for the new more accurate values.

To show further how the new method of calculation avoids exaggeration of experimental error we have included in Table II two measurements on sulfanilamide carried out by different operators using different samples of solute and solvent. The moment values calculated by the old method are 6.63 and 6.52, a difference of 0.11, while the new method gives 6.65 and 6.64, a difference of 0.01.

Summary

The available data indicate that the dielectric constant–weight fraction, ϵ_{12}–ω_2 curves for polar solutes in non-polar solvents are straight lines in dilute solutions. If this is the case it follows that the polarization p_{12} as defined by the Debye–Clausius–Mosotti (D-C-M) equation cannot be a linear function of the concentration. The p_2–ω_2 curves are neither horizontal nor straight and their curvature increases as ω_2 decreases. As a result, dipole moments calculated by a linear extrapolation of p_2 or P_2 to zero concentration are in error although the error is small for compounds with small moments. Per cent. association calculated by the assumption that p_{12}–ω_2 or p_2–ω_2 curves are linear in the absence of association is likewise in error.

A new method of calculating polarizations at infinite dilutions has been devised which, first, eliminates solvent polarization error, second, is objective and does not involve the judgment of the calculator, third, all extrapolations are made either statistically or graphically with straight line functions.

Evidence is presented to show that solvent polarization errors are responsible for some erroneous dipole moment values in the literature.

Our method of calculation has been applied to some of the anomalous cases and values are obtained which are more consistent with other determinations on the compounds or with the moment expected theoretically.

A test of this method of calculation has been applied to four sets of accurate data in the literature on nitrobenzene in benzene. The dipole moment values given by the authors have a variation of 0.15; our method gives a variation of 0.02. Another test was made on sulfanilamide measured by two operators and calculated by both methods. The linear P_2 extrapolation gave a variation of 0.11; our method, a variation of 0.01.

(18) Rau and Narayanaswamy, *Proc. Indian Acad. Sci.*, **1A**, 489 (1935). These authors obtained a value of 3.99 for the moment of nitrobenzene at 30° using Hedestrand's method of calculation. We did not recalculate their data because they measured only three solutions and one of these was at too high a concentration.