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# Dipole Moment Studies. I. Dipole Moments in Solution

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The solvent effect observed in the measurement of dipole moments in dilute solution may be ascribed to three factors: (1) incorrect assumptions inherent in the conventional methods of treatment, (2) anisotropy of the dipole molecule, and (3) specific solute–solvent or solute–solute interactions. A treatment using an electrostatic model which corrects for the first two factors is presented. The dipole molecule is regarded as an ellipsoid of uniform polarizability immersed in a medium of uniform dielectric constant. Equations applicable to solutions in both polar and nonpolar solvents are derived and used to recalculate moments for several representative polar molecules. Comparisons with other methods of calculation and with vapor state moments are made and discussed.

Recent studies of electron distribution and dipole moments for nonvolatile compounds of boron have directed our attention to old problems associated with measurement of dipole moments in solution.

Many methods have been proposed for obtaining dipole moments from dielectric constant measurements in the liquid state.[1–3] These can be divided into three categories: (1) methods based on the conventional Clausius–Mosotti–Debye equation, which assume additivity of the component molar polarizations and which differ from each other primarily in the procedure used to extrapolate the data to infinite dilution, (2) methods based on the Onsager approach, and (3) methods based on the Kirkwood approach. The deviation of solution moments, as calculated by the conventional equation, from moments obtained from measurements in the vapor state has been termed the "solvent effect."

It was first pointed out by Onsager[4] that the conventional equation is theoretically unsound in that it involves two incorrect assumptions: (1) that the reaction field is in the direction of the applied field rather than in the direction of the dipole and (2) that the effective dielectric constant inside the cavity occupied by the molecule is the same as that in the bulk of the solution. The superiority of the Onsager treatment was best demonstrated by application to pure polar liquids for which the conventional equation fails completely. For dilute solutions, however, the Onsager approach did not appear to offer significant improvement, and, in fact, in some cases gave corrections which were in the opposite direction from the "true" vapor state moments.[5]

Higasi[6] showed a relation between the solvent effect and the shape of the solute molecule. An ellipsoidal molecule with the dipole in the elongated direction appears to have a smaller moment in solution than in the vapor state, while a molecule such as $CHCl_3$ in which the dipole direction is shortened shows the opposite effect. Modifications of the Onsager approach which take into consideration the geometrical and/or optical anisotropy of the polar molecule have been derived and tested by Scholte,[7] by Abbot and Bolton,[8] and by Buckley and Maryott.[9] These methods of treatment will be considered in more detail below.

The most striking improvement in relating dielectric constants and dipole moments has been achieved when the environment of the polar molecule is no longer regarded as a continuous medium of uniform dielectric constant, but specific interaction energies with neighboring molecules are introduced, as in the method of Kirkwood.[10] However, the detailed information required for this method of calculation limits its application to the simplest and best understood molecules.

It appears that the worker who wishes to use dipole moment measurements as a routine chemical tool faces the dilemma of choosing between a method that is theoretically unsound or one in which the calculation

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[1] R. H. Cole, *Ann. Rev. Phys. Chem.*, **11**, 149 (1960).

[2] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

[3] C. J. F. Böttcher, "Theory of Electric Polarization," Elsevier Publishing Co., Amsterdam, 1952.

[4] L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).

[5] J. W. Smith and L. B. Witten, *Trans. Faraday Soc.*, **47**, 1304 (1951).

[6] K. Higasi, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **28**, 284 (1936).

[7] (a) Th. G. Scholte, *Physica*, **15**, 437 (1949); (b) **15**, 450 (1949); (c) *Rec. Trav. Chim.*, **70**, 50 (1951).

[8] J. A. Abbot and H. C. Bolton, *Trans. Faraday Soc.*, **48**, 422 (1952).

[9] F. Buckley and A. A. Maryott, *J. Res. Natl. Bur. Std.*, **53**, 229 (1954).

[10] J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).

is prohibitively complex. It is the purpose of this paper to present (hopefully) a treatment that is rigorously derived from a well-defined model, but with a calculation procedure that is sufficiently direct for routine use. It is recognized that no general method of calculation will eliminate completely the solvent correction since the forces involved are frequently specific. It should be advantageous, however, to sort out the solvent effect into its three component parts: (1) the effect of the erroneous assumptions of the conventional equation, (2) the effect of the shape of the solute molecule, and (3) effects due to deviations from the model such as irregularities in shape, localized dipoles, hydrogen bonding, etc. The model to be used in the presentation is a modified Onsager model in which the polar molecule is regarded as occupying an ellipsoidal cavity in a uniform medium whose dielectric constant is the macroscopic dielectric constant of the solution.

Derivations of equations for an ellipsoidal model have been given by Scholte,[7] Abbot and Bolton,[8] Buckley and Maryott,[9] and LeFevre and Rao.[11] Comparison of their conclusions shows them to be similar except for differences arising from the method of choosing: (1) the volume of the cavity and (2) the anisotropy of the polarizability of the molecule. Both of these effects are of great importance in determining the amount of interaction between the molecule and its environment and, hence, the solvent effect. The interaction increases with decreasing cavity size and with increasing eccentricity of the cavity. Since the detailed effects of nearest neighbors are regarded as "smeared out" to give a continuous medium, it would appear that a realistic choice for the boundary of the medium which would give an interaction approximately equivalent to that of the actual neighboring molecules would be obtained by taking the volume of the cavity as equal to the volume per molecule of the liquid, as was done by Onsager. Abbot and Bolton have used this procedure, but Scholte used a much smaller volume obtained from the variation of refractive index with temperature, compensating for this in the final result by using a correspondingly smaller value for the molecular polarizability obtained from the same plot. Buckley and Maryott used the variation of dielectric constant with temperature to show that more consistent results are obtained using a constant cavity volume rather than the apparent volume per molecule which varies with temperature, but their choice of the constant volume was arbitrary. LeFevre and Rao used the volume of the liquid at the melting point and obtained rather consistent results. Abbot and Bolton and Buckley and Maryott in their final results made no correction for the anisotropy of polarization, while Scholte and LeFevre and Rao obtained a greater polarizability in the direction of the major axis of the ellipsoid by considering the polarizability as uniformly distributed throughout the cavity.

In the present treatment, the cavity volume has been taken as the apparent molecular volume of the liquid, following Onsager, and the model of Scholte has been used for obtaining the anisotropy of polarization. The simplification of the calculation resulting from the above volume assumption permits application not only to pure polar liquid and dilute solution in nonpolar solvents, but also, without unreasonable complexity, to solutions in polar solvents. Further, the only data needed are commonly available in dipole measurements.

## Pure Polar Liquid

For a pure liquid, the ellipsoidal model leads to an equation which may conveniently be written in the form[12]

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{12\pi\epsilon} = N\left[\frac{\alpha}{1 - 2FB} + \frac{1 - FC}{(1 - FD)^2}\frac{\mu^2}{3kT}\right] \tag{1}$$

where $\epsilon$ is the macroscopic dielectric constant of the liquid, $N$ is the number of molecules per unit volume, $\alpha$ is the polarizability of the molecule averaged over all molecular orientations, $\mu$ is the permanent dipole moment of the molecule, $F$ is a function of the dielectric constant defined by

$$F = \frac{\epsilon - 1}{2\epsilon + 1} \tag{2}$$

and $B$, $C$, and $D$ are molecular parameters defined, along with the additional parameter, $A$, by the relations

$$A = \frac{abc}{2}\int_0^\infty \frac{\mathrm{d}s}{(s + a^2)^{3/2}(s + b^2)^{1/2}(s + c^2)^{1/2}} \tag{3}$$

$$B = \frac{\alpha}{abc} = \frac{\epsilon_\mathrm{i} - 1}{\epsilon_\mathrm{i} + 2} \tag{4}$$

$$C = 3A - 1 \tag{5}$$

$$D = (1 + C)(2 - C)\frac{\alpha_\mathrm{a}}{abc} + C = \frac{2(\epsilon_\mathrm{i} - 1) + C(2\epsilon_\mathrm{i} + 1)}{(\epsilon_\mathrm{i} + 2) + C(\epsilon_\mathrm{i} - 1)} = \frac{2B + C + BC}{1 + BC} \tag{6}$$

which $a$ is the semiaxis in the dipole direction and $b$ and $c$ are semiaxes perpendicular to $a$, $s$ is a variable of integration, $\alpha_a$ is the polarizability of the molecule in the direction of the dipole axis, and $\epsilon_\mathrm{i}$ is the "internal dielectric constant," that is, the dielectric constant of an equivalent ellipsoid having the same size, shape, and polarizability as the molecule, but with uniform polarizability throughout the ellipsoid. Imposing the condition that the volume of the cavity be equal to the volume per molecule of the liquid gives

$$\frac{4}{3}\pi abc = \frac{1}{N} = \frac{Mv}{N_0} \tag{7}$$

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(11) R. J. W. LeFevre and D. A. A. S. N. Rao, *Australian J. Chem.*, **8**, 329 (1955).

(12) *Cf.* ref 7 and 8 and also ref 3, pp 72 and 319–321. Our eq 1 is equivalent to eq 9.54 or ref 3 applied to a pure polar liquid. The second equality of our eq 6 follows from eq 14 of ref 7a.

where $M$ is the molecular weight, $v$ the specific volume, and $N_0$ is Avogadro's number. Equation 1 may then be written as

$$\frac{4\pi N_0}{9kT}\mu^2 = Mv\frac{(1 - FD)^2(2 + 1)^2(\epsilon - \epsilon_i)}{(1 - FC)9\epsilon(2\epsilon + \epsilon_i)} \qquad (8)$$

If the cavity is spherical, $C$ vanishes, and Onsager's equation results

$$\frac{4\pi N_0}{9kT}\mu^2 = Mv\frac{(2\epsilon + \epsilon_i)(\epsilon - \epsilon_i)}{\epsilon(\epsilon_i + 2)^2} \qquad (9)$$

The conditions for eq 8 may be recapitulated as follows: (1) the molecule is considered as an ellipsoid immersed in a uniform medium of dielectric constant $\epsilon$; (2) the ellipsoid itself has a uniform dielectric constant $\epsilon_i$; (3) the volume of the ellipsoid is the volume per molecule of the pure liquid; and (4) there is a fixed point dipole of moment, $\mu$, located near the center of the ellipsoid[13] and oriented in the direction of one of the axes. It may be noted that with the adoption of condition 3, the quantity $\epsilon_i$ becomes that part of the macroscopic dielectric constant due to distortion polarization. The right-hand member of eq 8 may be termed the "corrected orientation polarization" of the substance.

## Dilute Solutions in Nonpolar Solvents

For a dilute solution of a polar solute in a nonpolar solvent, the dielectric constant is given by an equation analogous to eq 1

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{12\pi\epsilon} = \frac{N_1\alpha_1}{1 - 2FB_1} + N_2\left[\frac{\alpha_2}{1 - 2FB_2} + \frac{1 - FC_2}{(1 - FD_2)^2}\frac{\mu^2}{3kT}\right] \qquad (10)$$

where the subscripts 1 and 2 refer to solvent and solute, respectively. $N_1$ and $N_2$ are the number of molecules of each component contained in unit volume of the solution and may be expressed in terms of $w_2$, the weight fraction of solute

$$N_1 = \frac{N_0}{M_1v}(1 - w_2) \qquad N_2 = \frac{N_0}{M_2v}w_2 \qquad (11)$$

A differential form of eq 10 applicable at infinite dilution may be obtained by substituting for $N_1$ and $N_2$ from (11), differentiating with respect to $w_2$, and then taking the limit as $w_2$ approaches zero. Indicating by primes the limiting value of the derivatives with respect to $w_2$, the result is

$$\frac{1}{12\pi N_0}\left[\frac{2\epsilon^2 + 1}{\epsilon^2}v\epsilon' + \frac{(\epsilon - 1)(2\epsilon + 1)}{\epsilon}v'\right] = \frac{\alpha_1}{M_1(1 - 2FB_1)^2}[2B_1(F + F') - 1] + \frac{1}{M_2}\left[\frac{\alpha_2}{1 - 2FB_2} + \frac{1 - FC_2}{(1 - FD_2)^2}\frac{\mu^2}{3kT}\right] \qquad (12)$$

where $\epsilon$, $v$, and $F$ are now simply the values of these quantities for the pure solvent. From the definition of $F$ in eq 2

$$F' = \frac{3\epsilon'}{(2\epsilon + 1)^2} \qquad (13)$$

As before considerable simplification is achieved by assigning the volume of the cavity for each molecule equal to the apparent molecular volume for that component. For the solute the volume occupied will be considered to be the limiting value of the partial molal volume. Then

$$\frac{4}{3}\pi a_1b_1c_1 = \frac{M_1v}{N_0} \quad \text{and} \quad \frac{4}{3}\pi a_2b_2c_2 = \frac{M_2(v + v')}{N_0} \qquad (14)$$

Furthermore, under this condition, the value of $\epsilon_i$ for the solvent becomes simply $\epsilon$, and with the introduction of eq 13 and 14 and the definitions in eq 2 and 4, eq 12 becomes

$$\frac{M_2v}{3}\left[\left(\frac{2\epsilon + 1}{3\epsilon}\right)^2\epsilon' + \frac{2\epsilon + 1}{3\epsilon}(\epsilon - 1)\frac{(v + v')}{v}\right] = M_2(v + v')\frac{B_2}{1 - 2FB_2} + \frac{1 - FC_2}{(1 - FD_2)^2}\frac{4\pi N_0}{9kT}\mu^2 \qquad (15)$$

Since the volume of the cavity for the solute is obtained from the limiting value of the partial molal volume, it will probably be most consistent to obtain $B_2$, the polarization of the solute, from $\epsilon_i'$, the limiting value that $\epsilon'$ would have if the solute molecule had no permanent dipole moment. Experimentally, $\epsilon_i'$ can be obtained from refractive index measurements on the solution, with a correction for atomic polarization. The relation of $B_2$ and $\epsilon_i'$ may be obtained by setting $\mu = 0$ in eq 15, substituting $\epsilon_i'$ for $\epsilon'$, and solving for $B_2$

$$B_2 = \frac{3(v + v')\epsilon(\epsilon - 1) + v(2\epsilon + 1)\epsilon_i'}{3(v + v')\epsilon(\epsilon + 2) + 2v(\epsilon - 1)\epsilon_i'} \qquad (16)$$

or

$$\epsilon_i' = 3\frac{v + v'}{v}\epsilon\frac{B_2(\epsilon + 2) - (\epsilon - 1)}{(2\epsilon + 1) - 2B_2(\epsilon - 1)} \qquad (16a)$$

The interrelation of volume and polarization is demonstrated by showing the relation of $B_2$ to the distortion component of the molar polarization of the solute

$$P_{E+A} = M_2B_2(v + v') \qquad (17)$$

Combining eq 15 and 16 yields as the final equation for the case of a solute in a nonpolar solvent

$$\frac{4\pi N_0}{9kT}\mu^2 = \frac{(1 - FD_2)^2}{1 - FC_2}\frac{M_2v}{3}\left(\frac{2\epsilon + 1}{3\epsilon}\right)^2(\epsilon' - \epsilon_i') \qquad (18)$$

If the solute molecule is spherical, $C_2$ vanishes, $D_2$ becomes $2B_2$, and thus

$$\frac{4\pi N_0}{9kT}\mu^2 = \frac{3M_2v(\epsilon' - \epsilon_i')}{\left[\epsilon + 2 + \frac{2v(\epsilon - 1)\epsilon_i'}{3(v + v')\epsilon}\right]^2} \qquad (19)$$

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[13] See ref 8 for restrictive conditions on the location of the point dipole in the model.

This differs from a differential form of the conventional equation only by the last term in the bracket.[14] It is precisely the $\epsilon + 2$ in the denominator of the conventional equation which arises as a result of the incorrect assumption previously mentioned.

Designating the moment calculated by eq 18 as $\mu_{\mathrm{ell}}$, by eq 19 as $\mu_{\mathrm{sph}}$, and by the conventional procedure as $\mu_{\mathrm{conv}}$, the relations among the three, for this case of solution in a nonpolar solvent, are found to be

$$\mu_{\mathrm{sph}} = \frac{\mu_{\mathrm{conv}}}{\left[1 + \dfrac{2v(\epsilon - 1)\epsilon_{\mathrm{i}}'}{3(v + v')\epsilon(\epsilon + 2)}\right]} \qquad (20a)$$

$$= \frac{1 - 2FB_2}{1 - 2FB_1}\mu_{\mathrm{conv}} \qquad (20b)$$

$$\mu_{\mathrm{ell}} = \frac{1 - FD_2}{(1 - 2FB_2)\sqrt{1 - FC_2}}\mu_{\mathrm{sph}} \qquad (21a)$$

$$= \frac{1 - FD_2}{(1 - 2FB_1)\sqrt{1 - FC_2}}\mu_{\mathrm{conv}} \qquad (21b)$$

### Dilute Solution in a Polar Solvent

Just as the conventional equation fails completely for pure polar liquids, it also gives highly erroneous results for solutions in polar solvents. A generalized form of eq 10 applicable to a solution of several components, all of which may be polar, may be written in terms of the polarizability $\alpha_{\mathrm{j}}$, the permanent dipole moment $\mu_{\mathrm{j}}$, and the molecular parameters $B_{\mathrm{j}}$, $C_{\mathrm{j}}$, and $D_{\mathrm{j}}$ for each molecular species as

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{12\pi\epsilon} = \sum_{\mathrm{j}} N_{\mathrm{j}}\left[\frac{\alpha_{\mathrm{j}}}{1 - 2FB_{\mathrm{j}}} + \frac{1 - FC_{\mathrm{j}}}{(1 - FD_{\mathrm{j}})^2}\frac{\mu_{\mathrm{j}}^2}{3kT}\right] \qquad (22)$$

For a two-component system, a differential form of eq 22, applicable as component 2 becomes infinitely dilute, may be obtained by a process similar to that in the preceding section. The following differences will occur. Since the solvent is polar, $\epsilon_{\mathrm{i}}$ no longer becomes equal to $\epsilon$ at infinite dilution, so that in substituting for $B_1$ the subscript i must be retained. Similarly, the expression for $B_2$ in eq 16 becomes

$$B_2 = \frac{3(v + v')\epsilon_{\mathrm{i}}(\epsilon_{\mathrm{i}} + 1) + v(2\epsilon_{\mathrm{i}} + 1)\epsilon_{\mathrm{i}}'}{3(v + v')\epsilon_{\mathrm{i}}(\epsilon_{\mathrm{i}} + 2) + 2v(\epsilon_{\mathrm{i}} - 1)\epsilon_{\mathrm{i}}'} \qquad (23)$$

$\mu_1$, the permanent moment of the solvent, may be eliminated by the use of eq 8. Thus, writing eq 22 for two components, substituting the expressions in (11) for $N_1$ and $N_2$, differentiating with respect to $w_2$, taking the limit as $w_2$ approaches zero, and simplifying by the use of eq 4, 8, 14, 13, and 2 in the solvent terms and of eq 23, 14, and 2 in the polarizability term for the solute yields an expression which may be put in the form

$$\frac{4\pi N_0}{9kT}\mu_2^2 = \frac{(1 - FD_2)^2}{1 - FC_2}\frac{M_2 v}{3}[G_1\epsilon' + H_{12}] \qquad (24)$$

where $G_1$ is a function of solvent characteristics alone and is given by

$$G_1 = \frac{2\epsilon^2 + 1}{3\epsilon^2} - \frac{\epsilon - \epsilon_{\mathrm{i}}}{\epsilon(2\epsilon + \epsilon_{\mathrm{i}})}\left[\frac{2D_1}{1 - FD_1} - \frac{C_1}{1 - FC_1}\right] - \frac{2(\epsilon_{\mathrm{i}} - 1)^2}{(2\epsilon + \epsilon_{\mathrm{i}})^2} \qquad (25)$$

and $H_{12}$ contains the $v'$ and $\epsilon_{\mathrm{i}}'$ terms and is given by

$$H_{12} = \frac{3(v + v')\epsilon_{\mathrm{i}}(\epsilon - \epsilon_{\mathrm{i}}) - v(\epsilon + 2\epsilon_{\mathrm{i}})\epsilon_{\mathrm{i}}}{3(v + v')\epsilon_{\mathrm{i}}(2\epsilon - \epsilon_{\mathrm{i}}) - 2v(\epsilon - \epsilon_{\mathrm{i}})\epsilon_{\mathrm{i}}'} \times \frac{(2\epsilon + 1)^2}{3\epsilon}\frac{v + v'}{v} \qquad (26)$$

If the solvent molecule is spherical, $G_1$ reduces to

$$G_1 = \frac{(2\epsilon + 1)^2(2\epsilon^2 + \epsilon_{\mathrm{i}}^2)}{3\epsilon^2(2\epsilon + \epsilon_{\mathrm{i}})^2} \qquad (27)$$

If the solvent is nonpolar, eq 24 reduces to eq 18. If $\epsilon'$, $\epsilon_{\mathrm{i}}'$, and $v'$ are zero, it becomes identical with (8), the equation for a pure polar liquid section.

### Experimental Verification

The application of the model to experimental data requires two additional considerations: (1) the methods of obtaining the shape of the molecular cavity and (2) the assignment of a value for the atomic polarization. Since thermal motion causes the cavity to be considerably larger than the molecule, it is probable that it also causes it to be more nearly spherical. However, to avoid any arbitrary assumption on this rather critical point, in the present calculations the cavity shape was taken as geometrically similar to that of the molecule as calculated from internuclear distances and angles and van der Waals[7] radii. When the ratio of axes of the ellipsoid has been determined, it is necessary to obtain the value of the integral in eq 3. If the ellipsoid is a spheroid, that is, if $a = c$ or $b = c$, the integral can be obtained in a closed form.[7] A tabulation of the resulting function in terms of the ratio $b/a$ is shown in Table I. In most of the equations given above, the eccentricity enters through the parameter $C$, which, it may be observed from the table, is negative when the dipole is in the direction of a major axis and positive when it is in the direction of a minor axis.

The molecular parameter $B$ is related to the distortion polarization and requires an assumption as to the atomic polarization. For comparison with other methods of calculation where the atomic polarization has been taken as a certain fraction of the electronic polarization, it is convenient to have an expression relating this fraction, which will be designated $\Delta B/B$, to the difference between $\epsilon_{\mathrm{i}}$ and $n^2$ (either $n_\infty{}^2$ or $n_{\mathrm{D}}{}^2$, whichever was used in the original calculation). $\Delta B$ is obtained as the change in eq 4 when $n^2$ is substituted for $\epsilon_{\mathrm{i}}$. To a first approximation

$$\epsilon_{\mathrm{i}} - n^2 = \frac{(n^2 - 1)(n^2 + 2)}{3}\frac{\Delta B}{B} + \ldots \qquad (28)$$

In a similar fashion, the difference between $\epsilon_{\mathrm{i}}'$ and $n^{2\prime}$ may be written in terms of the assumed fraction of

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[14] J. W. Smith, *Trans. Faraday Soc.*, **46**, 394 (1950).

TABLE I

THE ECCENTRICITY PARAMETERS $A$ AND $C$ (EQ 3 AND 5) AS FUNCTIONS OF THE RATIO BETWEEN AXES OF THE SPHEROIDAL CAVITY IN THE DIELECTRIC

| | $c = b$ | | $c = a$ | |
|---|---|---|---|---|
| $b/a$ | $A$ | $C$ | $A$ | $C$ |
| 0.100 | 0.0203 | −0.9391 | 0.0696 | −0.7912 |
| 0.200 | 0.0558 | −0.8326 | 0.1248 | −0.6256 |
| 0.300 | 0.0954 | −0.7138 | 0.1693 | −0.4921 |
| 0.400 | 0.1352 | −0.5944 | 0.2059 | −0.3823 |
| 0.500 | 0.1736 | −0.4792 | 0.2364 | −0.2908 |
| 0.600 | 0.2100 | −0.3700 | 0.2621 | −0.2137 |
| 0.700 | 0.2441 | −0.2677 | 0.2839 | −0.1483 |
| 0.800 | 0.2760 | −0.1720 | 0.3027 | −0.0919 |
| 0.900 | 0.3048 | −0.0856 | 0.3190 | −0.0430 |
| 1.000 | 0.3333 | 0.0000 | 0.3333 | 0.0000 |
| 1.111 | 0.3617 | 0.0851 | 0.3475 | 0.0425 |
| 1.250 | 0.3944 | 0.1832 | 0.3620 | 0.0860 |
| 1.429 | 0.4322 | 0.2966 | 0.3779 | 0.1337 |
| 1.667 | 0.4758 | 0.4274 | 0.3950 | 0.1850 |
| 2.000 | 0.5272 | 0.5816 | 0.4132 | 0.2396 |
| 2.500 | 0.5882 | 0.7646 | 0.4324 | 0.2972 |
| 3.337 | 0.6613 | 0.9839 | 0.4523 | 0.3569 |
| 5.000 | 0.7505 | 1.2515 | 0.4721 | 0.4163 |
| 10.000 | 0.8608 | 1.5824 | 0.4898 | 0.4685 |

atomic polarization for the solvent $\Delta B_1/B_1$ and for the solute $\Delta B_2/B_2$

$$\epsilon_i' - n^{2\prime} = g_{12}\frac{v + v'}{v}\left[\frac{\Delta B_2}{B_2} - \frac{\Delta B_1}{B_1}\right] + n^{2\prime}\left[g_2\frac{\Delta B_2}{B_2} + g_1\frac{\Delta B_1}{B_1}\right] \quad (29)$$

where

$$g_{12} = \frac{(n^2 - 1)(n^2 + 2)}{3}$$

$$g_2 = \frac{4n^4 + n^2 + 4}{9n^2}$$

$$g_1 = \frac{2(n^2 - 1)(n^2 + 2)}{9n^2} \quad (30)$$

Since $n^{2\prime}$ is usually small, the last term in (29) is often negligible. If, furthermore, the same fraction of atomic polarization is assumed for solvent and solute, the first term is zero, and $\epsilon_i' = n^{2\prime}$. A tabulation of values for $g_{12}$, $g_2$, and $g_1$ for several values of $n^2$ is given in Table II.

TABLE II

VALUES OF COMPUTATIONAL PARAMETERS (EQ 29) FOR DISTORTION POLARIZATION

| $n$ | $g_{12}$ | $g_2$ | $g_1$ |
|---|---|---|---|
| 1.8 | 1.02 | 1.16 | 0.38 |
| 1.9 | 1.17 | 1.19 | 0.41 |
| 2.0 | 1.33 | 1.22 | 0.44 |
| 2.1 | 1.50 | 1.26 | 0.48 |
| 2.2 | 1.68 | 1.29 | 0.51 |
| 2.3 | 1.86 | 1.33 | 0.54 |
| 2.4 | 2.05 | 1.36 | 0.57 |
| 2.5 | 2.25 | 1.40 | 0.60 |

The procedure for application of the method may be summarized as follows. (1) The shape of the molecular cavity is estimated, and the shape parameter $C$ is obtained from Table I or from eq 3 and 5. (2) A value is assigned for the atomic polarization, and $\epsilon_i$, $\epsilon_i'$, and the polarization parameters $B$ and $D$ are obtained from the appropriate equations. (3) The moment $\mu$ is calculated using (8), (18), or (24), whichever is applicable. In step 2, the equation used will depend on the data available; *e.g.*, if $P_{E+A}$ can be estimated, eq 17, 16a, and 6 could be used for the dilute solution case; if, on the other hand, the distortion polarization of the solute is to be obtained from $n^{2\prime}$ and an estimate of the fraction of atomic polarization, eq 29 and Table II give $\epsilon_i'$ and (16) and (6) give $B$ and $D$.

For recalculation of dilute solution moments from results previously obtained by the conventional procedure, eq 21b is useful; $C_2$ is obtained as in step 1 above, $D_2$ from (17) and (6), $F$ from (2), and $B_1$ from (4).

Tables III–V show results obtained by recalculation of literature data for several polar liquids whose shapes can be approximated as ellipsoids of revolution or whose shape parameters can be calculated, for three solutes, *t*-butyl chloride, acetonitrile, and nitrobenzene, in a number of nonpolar solvents, and for two solutes, benzonitrile and nitrobenzene, in a few polar solvents. The last three columns of Table III show a comparison of $\mu_{\text{sph}}$ (the Onsager model), $\mu_{\text{ell}}$ (the present model), and $\mu_{\text{gas}}$ for a variety of pure polar liquids. Dielectric constants were obtained from the compilation of Maryott and Smith.[15] $\epsilon_i$ values were calculated in most cases from the intercept of the vapor phase polarizations.[16] Where these did not appear consistent, atomic polarizations were estimated using principles outlined by Smyth.[2] All molecular cavities were regarded as either prolate or oblate spheroids, except chlorobenzene, nitrobenzene, and benzonitrile, for which the value ($A$ = 0.178) calculated by Scholte[7] was used.

The results for pure polar liquids indicate that, for a number of substances, the anisotropic correction is of the right order of magnitude and that the assumed model is adequate for interpreting the dielectric behavior of these liquids. Striking exceptions are hydrogen cyanide and the three oxygen-containing molecules, nitrobenzene, acetone, and ethyl ether, all of which give $\mu_{\text{ell}}$ values that are much too high, indicating a degree of parallel orientation in excess of that due to dipole–dipole interaction as predicted from the model. Smaller relative deviations are shown by *t*-butyl chloride, for which $\mu_{\text{ell}}$ is high, while methyl iodide, methyl bromide, and phosphorus trichloride have $\mu_{\text{ell}}$ less than $\mu_{\text{gas}}$, indicating either a smaller amount of interaction than predicted or specific intermolecular forces tending to orient neighboring molecules in directions other than parallel with respect to

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[15] A. A. Maryott and E. R. Smith "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular 514, U. S. Government Printing Office, Washington, D. C., 1951.

[16] A. A. Maryott and F. Buckley, "Table of Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State," National Bureau of Standards Circular 537, U. S. Government Printing Office, Washington, D. C., 1953.

TABLE III

DIPOLE MOMENTS FOR PURE POLAR LIQUIDS

| | $T$, °K | $\epsilon$ | $n_D$ | $v$ | $\epsilon_i$ | $b/a$ | $A^a$ | $B^a$ | $C^a$ | $D^a$ | $\mu_{sph}$ | $\mu_{ell}$ | $\mu_{gas}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3Cl$ | 253 | 12.6 | | 1.004 | 2.12 | 0.76 | 0.263 | 0.272 | −0.210 | 0.293 | 1.68 | 1.84 | 1.87 |
| | 223 | 14.88 | | 0.950 | 2.42 | 0.76 | 0.263 | 0.322 | −0.210 | 0.393 | 1.64 | 1.82 | 1.87 |
| $CHCl_3$ | 293 | 4.806 | 1.445 | 0.670 | 2.39 | 1.34 | 0.413 | 0.316 | 0.240 | 0.882 | 1.10 | 1.02 | 1.013 |
| $(CH_3)_3CCl$ | 293 | 9.85 | 1.386 | 1.188 | 1.99 | 1.13 | 0.367 | 0.249 | 0.100 | 0.608 | 2.40 | 2.30 | 2.13 |
| $C_6H_5Cl$ | 293 | 5.708 | 1.525 | 0.904 | 2.51 | $b$ | 0.178 | 0.335 | −0.466 | 0.057 | 1.37 | 1.66 | 1.70 |
| $CH_3Br$ | 223 | 12.63 | | 0.539 | 2.42 | 0.74 | 0.258 | 0.324 | −0.230 | 0.347 | 1.46 | 1.65 | 1.78 |
| | 273 | 9.83 | | 0.578 | 2.30 | 0.74 | 0.258 | 0.302 | −0.230 | 0.327 | 1.50 | 1.66 | 1.78 |
| $CH_3I$ | 293 | 7.00 | 1.529 | 0.438 | 2.43 | 0.76 | 0.263 | 0.323 | −0.210 | 0.395 | 1.28 | 1.40 | 1.65 |
| $CH_3CN$ | 283 | 37 | 1.346 | 1.278 | 1.86 | 0.57 | 0.199 | 0.223 | −0.400 | −0.047 | 3.43 | 4.02 | 3.94 |
| $C_6H_5CN$ | 298 | 25.5 | | 0.994 | 2.54 | $b$ | 0.178 | 0.339 | −0.466 | 0.052 | 3.43 | 4.45 | 4.42 |
| $C_6H_5NO_2$ | 298 | 36.0 | | 0.831 | 2.63 | $b$ | 0.178 | 0.352 | −0.466 | 0.088 | 4.00 | 5.26 | 4.27 |
| $(CH_3)_2CO$ | 298 | 20.7 | | 1.272 | 2.01 | 0.8 | 0.276 | 0.252 | −0.172 | 0.303 | 2.98 | 3.21 | 2.88 |
| $(C_2H_5)_2O$ | 298 | 4.21 | 1.350 | 1.390 | 1.95 | $2.0^c$ | 0.413 | 0.241 | 0.240 | 0.737 | 1.35 | 1.26 | 1.15 |
| $PCl_3$ | 293 | 3.47 | 1.518 | 0.636 | 2.76 | 1.37 | 0.420 | 0.369 | 0.260 | 1.068 | 0.61 | 0.55 | 0.78 |
| $N(CH_3)_3$ | 298 | 2.44 | | 1.597 | 1.82 | 1.8 | 0.496 | 0.214 | 0.489 | 0.925 | 0.73 | 0.67 | 0.65 |
| HBr | 206 | 6.22 | | 0.361 | 2.36 | 0.85 | 0.290 | 0.311 | −0.129 | 0.447 | 0.69 | 0.74 | 0.80 |
| HCN | 293 | 114.9 | 1.264 | 1.455 | 1.57 | 0.61 | 0.213 | 0.160 | −0.360 | −0.106 | 5.87 | 6.77 | 2.95 |

[a] $A$, $B$, $C$, and $D$ are molecular parameters used in calculating $\mu_{ell}$ as defined in eq 3–6. [b] $b/a = 0.80$; $c/a = 0.39$. [c] Calculated for the most extended position of the ethyl groups.

TABLE IV

DIPOLE MOMENTS MEASURED IN DILUTE SOLUTIONS OF NONPOLAR SOLVENTS

| | | Solute | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $t$-Butyl chloride | | | | Acetonitrile | | | | | Nitrobenzene | | |
| | | $\mu_{gas}$ = 2.13 D. | | | $\mu_{ell}$ | $\mu_{gas}$ = 3.94 D. | | | $\mu_{ell}$ | | $\mu_{gas}$ = 4.27 D. | | $\mu_{ell}$ |
| Solvent | $\epsilon$ | $B_2$ | $\mu_{conv}$ | $\mu_{sph}$ | $b/a$ = 1.12 | $B_2$ | $\mu_{conv}$ | $\mu_{sph}$ | $b/a$ = 0.57 | $b/a$ = 0.50 | $\mu_{conv}$ | $\mu_{sph}$ | $b/a$ = 0.80 $c/a$ = 0.39 |
| $n$-Hexane | 1.883 | 0.236 | 2.17 | 2.16 | 2.12 | 0.210 | 3.34 | 3.35 | 3.54 | 3.62 | 4.04 | 3.83 | 4.16 |
| $n$-Heptane | 1.910 | 0.241 | 2.16 | 2.16 | 2.13 | | | | | | 4.06 | 3.84 | 4.18 |
| Diisoamyldecane | 1.976 | | | | | | | | | | 3.98 | 3.80 | 4.15 |
| Cyclohexane | 2.016 | | | | | | | | | | 3.97 | 3.79 | 4.15 |
| Decalin | 2.162 | | | | | | | | | | 3.92 | 3.78 | 4.17 |
| Dioxane | 2.205 | 0.250 | 2.20 | 2.24 | 2.20 | 0.225 | 3.55 | 3.67 | 3.90 | 4.00 | 3.91 | 3.78 | 4.18 |
| Carbon tetrachloride | 2.226 | 0.247 | 2.17 | 2.12 | 2.18 | 0.226 | 3.43 | 3.55 | 3.78 | 3.87 | 3.93 | 3.80 | 4.21 |
| $p$-Xylene | 2.260 | | | | | | | | | | 3.92 | 3.80 | 4.22 |
| Carbon tetrachloride + $p$-dichlorobenzene | 2.266 | 0.248 | 2.17 | 2.22 | 2.18 | 0.222 | 3.42 | 3.56 | 3.80 | 3.90 | | | |
| Dioxane + $p$-dichlorobenzene | 2.270 | 0.248 | 2.16 | 2.22 | 2.18 | 0.221 | 3.51 | 3.65 | 3.89 | 4.00 | | | |
| Benzene | 2.273 | 0.249 | 2.13 | 2.18 | 2.14 | 0.221 | 3.49 | 3.61 | 3.85 | 3.96 | 3.97 | 3.85 | 4.28 |
| Toluene | 2.380 | | | | | | | | | | 3.80 | 3.72 | 4.16 |
| Carbon disulfide | 2.634 | | 2.01 | 2.14 | 2.10 | | 3.21 | 3.48 | 3.75 | 3.86 | 3.66 | 3.66 | 4.13 |
| Tetralin | 2.752 | 0.253 | 1.95 | 2.10 | 2.06 | 0.223 | 3.08 | 3.38 | 3.64 | 3.76 | | | |

TABLE V

DIPOLE MOMENTS MEASURED IN DILUTE SOLUTIONS IN POLAR SOLVENTS

| | | | Benzonitrile | | | | Nitrobenzene | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $\mu_g$ = 4.35 | | | | $\mu_g$ = 4.27 | | | |
| Solvent or solute | $\epsilon$ | $G_1$ | $H_{12}$ | $\epsilon'$ | $\mu_{sph}$ | $\mu_{ell}$ | $H_{12}$ | $\epsilon'$ | $\mu_{sph}$ | $\mu_{ell}$ |
| Ether | 4.25 | 0.580 | | | | | 0.733 | 15.12 | 3.94 | 4.72 |
| Chloroform | 4.724 | 0.555 | | | | | 1.59 | 30.5 | 3.77 | 4.53 |
| Chlorobenzene | 5.612 | 0.632 | 2.26 | 20.9 | 3.58 | 4.35 | 1.72 | 17.10 | 3.50 | 4.26 |
| Benzonitrile | 25.50 | 0.658 | 15.20 | 0 | 3.43 | 4.45 | 12.59 | 5.4 | 3.77 | 4.88 |
| Nitrobenzene | 35.95 | 0.659 | 26.35 | −21.2 | 2.78 | 3.64 | 22.05 | 0 | 4.00 | 5.26 |

each other. Some speculation on this effect will be given after consideration of the dilute solution results.

In Table IV, the moments for $t$-butyl chloride and acetonitrile are calculated from the data of Smith and Witten,[5] and for nitrobenzene, from the $\epsilon'$ and $v'$ (their $\alpha$ and $\beta$) values of Smith and Cleverdon[17] recalculated by them from the data of several workers. The $\mu_{conv}$ values are their moments. $\mu_{sph}$ and $\mu_{ell}$ were calculated using eq 20b and 21b and checked by eq 18. For $t$-butyl chloride and acetonitrile, values of $B_2$ were calculated with results as shown. For nitrobenzene, $B_2$ was taken as 0.352 (Table III). Two $b/a$ values were tried for acetonitrile because of the uncertainty in the best equivalent ellipsoidal cavity for this pear-shaped molecule.

An examination of the $\mu_{ell}$ columns in Table IV shows that for these three very different solutes, the elliptical model gives solution moments which are, for the most part, within 0.1 D. of the vapor phase values. Neither the Onsager correction alone nor the anisotropy correction alone would have given marked

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(17) J. W. Smith and D. Cleverdon, *Trans. Faraday Soc.*, **45**, 109 (1949).

improvement on the $\mu_{\mathrm{conv}}$ values. The systematic decrease of the solution moment with increasing dielectric constant of the solvent, noted by many authors,[2] is quite adequately accounted for, the greater part of the variation being due to the Onsager correction (*e.g.*, for nitrobenzene in *n*-hexane and carbon disulfide the difference in $\mu_{\mathrm{conv}}$ is 0.38, in $\mu_{\mathrm{sph}}$ 0.17, and in $\mu_{\mathrm{ell}}$ 0.03).

A more detailed analysis of the $\mu_{\mathrm{ell}}$ values reveals two interesting observations: (a) For all three of the solutes, the moments in dioxane, carbon tetrachloride, and benzene are higher than the moments in carbon disulfide, the aliphatic hydrocarbons, and most of the branched aromatic hydrocarbons. (2) For the five solvents that are common to all three solutes, the average deviation of $\mu_{\mathrm{ell}}$ from $\mu_{\mathrm{gas}}$ is $+0.02$ for *t*-butyl chloride, $-0.18$ ($b/a = 0.57$) and $-0.08$ ($b/a = 0.50$) for acetonitrile, and $-0.08$ for nitrobenzene. This second observation may indicate that the anisotropy correction is about 20–30% too small. Since it is not reasonable to assume a greater cavity eccentricity, this greater interaction would appear to require a smaller cavity volume, as assumed by Scholte.

An alternative hypothesis, however, appears very attractive because it explains (qualitatively) both of these observations as well as some of the observed deviations for pure liquids. As noted in the introduction of this paper, the most significant improvement in interpretation of experimental results has been achieved by taking into account in detail the interactions between solvent and solute molecules and between one solvent molecule and another. In the present theory this interaction is "smeared out" to give a continuous medium of uniform dielectric constant. Dioxane with highly polar oxygens near the surface of the molecule is assigned the same interaction as a molecule of equal dielectric constant in which the polarizable groups lie in the interior of the molecule well protected by other atoms. At first thought it might seem that the aliphatic hydrocarbons would conform most closely to the model, but when one notes that the model requires that the macroscopic dielectric constant must extend up to the surface of the cavity, it appears that a solvent molecule which can, at least in some of its orientations, present its more polarizable regions to the solute molecule will more nearly satisfy this requirement. Benzene should be such a molecule, and it may not be a coincidence that for all three solutes, the $\mu_{\mathrm{ell}}$ values in benzene are almost identical with the vapor phase moments. For molecules in which the polarizable portions are shielded, a quantitative treatment might be attempted in which three dielectric constants are defined: $\epsilon_1$, the macroscopic dielectric constant; $\epsilon_{\mathrm{i}}$, the effective internal dielectric constant; and $\epsilon_{\mathrm{ex}}$, the effective external dielectric constant. It can be anticipated, however, that a correct derivation would lead to the following conclusions: (1) the calculated moment would become greater for a shielded molecule since a smaller amount of the total polarization would be assigned to the induced moment;[18] (2) for different solutes, the correction should be greatest when the solute molecule is small and has a large permanent moment. Applied to the data of Table IV, this hypothesis would explain not only the low values for the *n*-hexane solution but also the order of their deviations (acetonitrile > nitrobenzene > *t*-butyl chloride). The low values for carbon disulfide are explained by partial shielding of the highly polarizable carbon–sulfur bond by the rather large groups, yielding effective dielectric constants that are lower than the macroscopic value but probably still much higher than the constant for benzene. For dioxane and carbon tetrachloride, the order of $\mu_{\mathrm{ell}}$ values is different for the three solutes, but one might predict that dioxane should have an effective constant somewhat larger than its macroscopic value, while carbon tetrachloride should be somewhat lower. This order is observed for acetonitrile. The value for dioxane with nitrobenzene is anomalously low.

In Table III the deviations noted for the methyl halides which become increasingly negative from the chloride to the iodide are consistent with the screening explanation. Conversely, nitrobenzene, acetone, and ether might be regarded as demonstrating constants larger than the macroscopic value although it is probably more realistic to ascribe the deviations of these substances, as well as those of HCN and PCl, to forces of association other than dipole interaction. The high value for *t*-butyl chloride in the pure liquid remains unexplained.

To illustrate the calculation for dilute solution in polar solvents, two solutes were selected: benzonitrile, which is "well-behaved" both in the pure liquid and in nonpolar solvents ($\mu_{\mathrm{ell}} = 4.32$ in benzene and 4.31 in carbon tetrachloride; $\mu_{\mathrm{gas}} = 4.35$), and nitrobenzene, which gave good values in nonpolar solvents, but not in the pure liquid. For each of the solvents, the coefficient $G_1$ was calculated using the data in Table III. Values of $\epsilon'$ and the data for $H_{12}$ were obtained for nitrobenzene in ether from Higasi,[19] for nitrobenzene in chloroform and chlorobenzene from LeFevre and Russell,[20] and for the remaining solute–solvent combinations from Pilpel.[21]

Both solutes in chlorobenzene give $\mu_{\mathrm{ell}}$ values in agreement with vapor state values. All other values for nitrobenzene showed large positive deviations while benzonitrile in nitrobenzene showed a large negative deviation. Specific interaction of nitrobenzene with itself and with other molecules appears to be indicated. It is reasonable to suppose that a similar association of nitrobenzene with solvent molecules takes place in nonpolar solvents also, but in that case it has only a slight effect on the observed moment.

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(18) It might appear that a smaller interaction would lead to a smaller correction from the conventional moment. This is not the case since the conventional calculation assumes a value $\epsilon$ for both the internal and the external dielectric constants. The Onsager correction is positive if $\epsilon_{\mathrm{i}} < \epsilon$ because the induced moment must be less than assumed in the conventional calculation. For $\epsilon_{\mathrm{ex}} < \epsilon$ the correction would be more positive.

(19) K. Higasi, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **24**, 63 (1934).

(20) R. J. W. LeFevre and P. Russell, *J. Chem. Soc.*, 491 (1936).

(21) N. Pilpel, *J. Am. Chem. Soc.*, **77**, 2949 (1955).

Table VI

A Comparison of Different Methods for Calculating Dipole Moments in Solution Using Nonspherical Cavities

| | Data[a] | | | | Calculated dipole moments by method of | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Compd | $T$, °K | $\epsilon$ | Density, g/cc | $P_{E+A}$ | Scholte[7] | LeFevre[11] | Abbot[8] | Buckley[9] | This work[b] | Gas |
| $CHCl_3$ | 393 | 4.813 | 1.489 | 24.8 | 1.08 | 0.99 | 0.92 | 0.92 | 1.00 | 1.01 |
| $C_6H_5Cl$ | 302.2 | 5.475 | 1.096 | 31.5 | 1.63 | 1.67 | 1.80 | 1.82 | 1.71 | 1.70 |
| $C_6H_5NO_2$ | 298 | 34.89 | 1.199 | 37.2 | 5.04 | 4.93 | 5.44 | 5.45 | 5.15 | 4.27 |

[a] From ref 11. [b] Values differ slightly from those in Table III because of use of different experimental data.

## Comparison with Other Methods

In order to observe the effect of varying the assumptions as to the nature of the cavity and the anisotropy correction, it is of interest to compare our results with those of previous workers, all of whom used somewhat different procedures. However, this presents some difficulty since the published results are not strictly comparable because of variations in the original data. Some of the methods used data not ordinarily obtained as part of a normal dipole measurement. Some are applied to pure liquids only, and others to dilute solutions.

LeFevre and Rao[11] compared their results for three compounds–chloroform, chlorobenzene, and nitrobenzene—with Scholte's[7] results. Since these compounds represent nearly the extremes in eccentricity, a considerable range in polarity, and include one which shows large deviations from all of the equations, they appear to be a good selection for comparison on a limited basis. Table VI shows these values of Scholte and Le Fevre and Rao, along with values calculated from these same basic data and using the same shape parameter by the methods of Abbot and Bolton,[8] Buckley and Maryott,[9] and by the present method.

The important conclusions to be drawn would appear to be: (1) If the correction is made for cavity shape alone without including the anisotropy in polarizability, the result will be over-corrected as in the work of Abbot and Bolton and Buckley and Maryott. (2) The use of a cavity size much smaller than the apparent molecular volume, as in the work of Scholte, does not lead to any improvement in agreement with gas values. From a theoretical point of view, the results of LeFevre and Rao should be superior to the others since values for the individual polarizabilities along the minor axes were introduced, but the difference from this work where these effects are averaged is not great.

The best results for nonassociated liquids are obtained by using for cavity volumes the average molecular volume and by including anisotropy of polarization along the dipole axis.

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# Dipole Moment Studies. II. The Dipole Moments of the Ethylphosphines

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The dipole moment of monoethylphosphine, as measured in the gas phase with a high-precision heterodyne beat apparatus, is 1.17 ± 0.02 D. The moments of monoethyl-, diethyl-, and triethylphosphine, measured in benzene solution and corrected for solvent effect, are 1.15 ± 0.05, 1.36 ± 0.06, and 1.35 ± 0.05 D., respectively. These data plus microwave values for $CH_3PH_2$ and $(CH_3)_3P$ lead to a value of 1.22 ± 0.05 D. for the dipole moment of dimethylphosphine. This compares favorably with a recently reported experimental value of 1.23 D. The moment of the ethyl–phosphorus bond is about 0.11 D. larger than that of the corresponding methyl–phosphorus bond. It is assumed that the size of the carbon–phosphorus moment increases as one goes from trialkylphosphine to monoalkylphosphine while the size of the phosphorus–hydrogen moment remains constant in the series.

At the time that this study was initiated, the literature contained no reliable dipole moment data for the *alkyl*phosphines. On the other hand, a study of the Stark effect in the microwave region of phosphine, $PH_3$, had permitted Sirvetz and Weston[1] to obtain a dipole moment value of 0.579 ± 0.012 D. for $PH_3$. More recently, using microwave techniques, Kojima, Breig, and Lin[2] obtained a value of 1.100 ± 0.010 for $CH_3PH_2$, while Lide and Mann,[3] also using microwave methods, obtained a value of 1.192 ± 0.005 for $(CH_3)_3P$. In cases where microwave methods are applicable, a large amount of detailed data of high precision is obtained.

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(1) M. H. Sirvetz and R. E. Weston, *J. Chem. Phys.*, **21**, 898 (1953).

(2) T. Kojima, E. Breig, and C. C. Lin, *ibid.*, **35**, 2139 (1961).

(3) D. R. Lide and D. E. Mann, *ibid.*, **29**, 914 (1958).