Dipole Moments and Dielectric Polarization in Solutions

By Frank E. Harris and Stephen G. Brush

Received October 5, 1955

The statistical mechanical theory of dielectric polarization is extended to mixtures and applied to dilute solutions of polar molecules in non-polar solvents, which differs significantly from that of Debye, permits unambiguous experimental determination of a precisely defined effective dipole moment in solution. The relation between the solution moment and vacuum moment is discussed in terms of an ellipsoidal molecule—continuous solvent model, and it is shown that it is necessary to consider the induced polarization of both the polar molecule and surrounding solvent. The solvent effects calculated on the basis of this model differ from earlier results of others based on the same model, and are in qualitative agreement with experiment. Alternative ways of calculating the distortion polarization are discussed and it is concluded that the Clausius–Mossotti expression is, although not ideal, adequate for this purpose.

I. Introduction

It has been known for a long time that the electric dipole moments of polar molecules, as determined in dilute solutions in non-polar solvents, are inconsistent with moments resulting from gas phase studies. The gas measurements, whose interpretation is least ambiguous, are much more cumbersome than dilute solution studies, and are not applicable to as wide a range of polar molecules. It would therefore be very helpful to have a reliable way of relating dielectric polarization in such solutions to the dipole moment of the solute molecules. In view of the extensive development of the statistical mechanical theory of dielectric polarization in pure polar substances,[1-4] it would seem to be worthwhile to attempt to develop a parallel theory for mixtures at least one of whose components is polar. Such a theory would provide for the specific interaction of the individual polar molecules both with surrounding solvent and other polar solute molecules, as well as providing a proper accounting of the effect of the gross properties of the solution upon the local field acting on each molecule.

The present paper describes the formulation of the statistical mechanical theory of dielectric polarization in mixtures. Just as in the theory of systems composed of a single polar component, it is found that, even in the absence of specific short range forces between neighboring molecules, neither the Clausius–Mossotti nor the Onsager formulas[1] are applicable. Thus the well known and frequently used Debye equation for the dielectric polarization of solutions is found to lead to erroneous results, even at infinite dilution of the polar molecules. However, the more accurate first-order expression does lead to the Debye result in dilute gas solutions, for which the dielectric constant is very nearly unity and all interactions between molecules become negligible.

In the application of the theory to dilute solutions of polar molecules in a non-polar solvent, the various contributions to the orientation dependent part of the dielectric polarization can be separated into two parts. The first part, which describes the interaction between a polar molecule and surrounding solvent, can be regarded as causing a change in the effective dipole moment of the molecule, through polarization of both the polar molecule itself and the surrounding solvent. Even for spherical dipolar molecules, this interaction will not vanish except in dilute solutions in the gas phase. The second interaction, that between pairs of polar molecules, becomes negligible in sufficiently dilute solutions and can be treated by virial expansion methods.

In the past considerable attention has been paid to determining the relation between the effective dipole moment of a polar molecule and its permanent moment as measured at high dilution in the gas phase.[5] Although these studies were handicapped by lack of knowledge of the exact relationship between the dielectric constant and the effective moment, the main factors responsible for the "solvent effect" were at least qualitatively recognized. We show here that a consistent treatment of a simple model, in which the polar molecule is represented as a homogeneously polarized ellipsoid in a continuous medium, predicts solvent effects in reasonable agreement with experiment, but at variance with those calculated by earlier investigators on the basis of the same model.[6-8] Since our calculations involve no arbitrary parameters and are completely non-empirical, we believe that when large deviations from the calculated solvent effects occur, they are characteristic of specific interactions of a type not recognized by this simple model.

In order to evaluate the usual experimental results, it may be necessary to calculate the distortion polarization of the solution from quantities descriptive of the pure solute and solvent. An examination of the theory of distortion polarization in mixtures is carried out, and it is found that in general the application of the Clausius–Mossotti equation leads to a sufficiently accurate result. However, fluctuations in the instantaneous induced moments of the molecules make it difficult to improve upon the first-order expression for the distortion polarization.

II. Theory

The bulk of the theory of dielectric polarization as presented for one component systems does not depend upon the identity of all the molecules of the

(1) L. Onsager, This Journal 58, 1486 (1936).

(2) J. G. Kirkwood, J. Chem. Phys., 7, 911 (1939).

(3) F. E. Harris and B. J. Alder, ibid., 21, 1031 (1953).

(4) F. E. Harris, ibid., 23, 1663 (1955).

(5) For a review, see R. J. W. Le Fevre, "Dipole Moments," Methuen & Co., London, 1953, Chapter III.

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

(7) I. G. Ross and R. A. Sack, Proc. Phys. Soc. (London), B63, 893 (1950).

(8) Th. G. Scholte, Rec. trav. chim., 70, 50 (1951).

system. A basic equation of the theory, applicable to isotropic and non-ferroelectric media, is[9]

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} + \left(\frac{3}{\epsilon + 2}\right)\left(\frac{3\epsilon}{2\epsilon + 1}\right)\left(\frac{4\pi <M_0^2>}{9VkT}\right) \quad (1)$$

where ϵ is the static dielectric constant of the solution and ϵ_∞ is the dielectric constant at frequencies so high that molecular orientation does not have time to take place. The high frequency dielectric constant ϵ_∞ differs from the square of the optical index of refraction in that the former includes the effect of atomic polarization whereas the latter does not. V is the volume containing the molecules for which $<M_0^2>$ is to be calculated, k is Boltzmann's constant, and T the absolute temperature.

The quantity $<M_0^2>$ is the statistical mechanical average, computed in the absence of an external applied electric field, of the square of the instantaneous electric dipole moment of a macroscopic portion of an infinite and boundless specimen of the dielectric whose properties are under consideration. Since the average moment, $<\overrightarrow{M_0}>$, vanishes under the conditions prescribed here, $<M_0^2>$ is seen to be a fluctuation quantity descriptive of the tendency of a sample to become polarized under the influence of an external force. Since $<M_0^2>$ is proportional to the volume of dielectric for which it is computed, eq. 1 does not depend upon the size or shape of the region selected for its computation. Both $<M_0^2>$ and $(\epsilon_\infty - 1)/(\epsilon_\infty + 2)$ may be expressed in terms of parameters of the individual molecules of which the dielectric is composed. For a mixture, these expressions may be obtained by an obvious generalization of the corresponding equations for one-component systems. The resulting equations are exhibited in Appendix 1. It is important to note that the distortion polarization term, $(\epsilon_\infty - 1)/(\epsilon_\infty + 2)$, is not assumed by the theory to be the result obtained by application of an approximate equation, but is, if not obtained from experiment, in principle to be calculated by the exact method first due to Kirkwood.[10] However, in actual practice the distortion polarization may be estimated from a simple model for the mixture, as the uncertainty thereby introduced will be smaller than that involved in the computation of the orientation polarization.

The orientation polarization term $<M_0^2>$ can be simplified considerably in the important case of a dilute solution of polar molecules in non-polar solvent. Expanding the formula given in Appendix 1, it is possible to separate the terms into those which involve but one polar molecule, those involving two, etc. The terms involving one polar molecule describe the interaction between polar molecules and solvent, and at high dilution constitute the major contribution to $<M_0^2>$, while those terms involving larger numbers of polar molecules describe solute–solute interactions and only become important as the concentration of polar molecules is increased. We shall here consider only the interaction between polar molecules and solvent. Further simplification may be obtained by introducing an effective dipole moment m, which will dif-

(9) Eq. 14 of reference 4.
(10) J. G. Kirkwood. *J. Chem. Phys.*, **4**, 592 (1936).

fer from the vacuum moment μ in that m will include the average induced moment of the molecule, plus the average net moment induced in the surrounding solvent which has previously been assumed to be boundless. As indicated in more detail in Appendix 1, $<M_0^2>$ now assumes the form

$$<M_0^2> = N_2 m^2 + \ldots \quad (2)$$

where N_2 is the number of polar solute molecules in the volume V. In eq. 2, the omitted terms describe only the effect of fluctuations in the average moment m. These fluctuation terms will usually be expected to be quite small relative to the indicated result, because the main contribution to m is the non-fluctuating quantity μ, and because the fluctuations arise from motions of only the non-polar solvent molecules. Equation 2 indicates that $<M_0^2>$ may be written in the form of independent contributions from each polar solute molecule, and that the contribution of each such molecule involves the entire moment associated with its presence, irrespective of the effect various parts of this total moment have upon the electric field at the polar molecule. There is, then, no ambiguity arising from the distinction between the field exerting a torque on the polar molecule and the field tending to polarize it further in the direction of its permanent moment. It must be emphasized that (2) has been obtained without the necessity of introducing any particular model for the dielectric.

Substitution of eq. 2 into eq. 1 leads to the main result of this section

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} + \left(\frac{3}{\epsilon + 2}\right)\left(\frac{3\epsilon}{2\epsilon + 1}\right)\left(\frac{4\pi N_2 m^2}{9VkT}\right) \quad (3)$$

It will be noticed that (3) differs from the Debye equation frequently applied to mixtures

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} + \frac{4\pi N_2 m^2}{9VkT} \quad (4)$$

in that the contribution of the orientation polarization is altered by the factor $[3/(\epsilon + 2)] [3\epsilon/(2\epsilon + 1)]$. This difference will result in an apparent dependence of the dipole moment on the dielectric constant of the solvent, superimposed upon any simultaneously occurring real change in m. The dipole moment as computed by (3) will be identical with that computed by (4) in dilute gas, where $\epsilon \sim 1$, but m as computed from experimental data in common solvents, whose dielectric constants range from 2 to 2.5, will be from 5 to 12% higher when computed by (3) rather than by (4).

III. The Effective Dipole Moment in Solution

Although the foregoing theory in principle leads to a definite value of the effective moment m in terms of molecular properties, in practice the expressions involved are too difficult to evaluate properly. The main difficulty is in the lack of reasonably accurate distribution functions with which to describe the relative positions of molecules in the solution. It therefore remains of interest to introduce simple models for calculating the relationship between m and the permanent moment μ. Let us consider the simplest such model containing the most important features of a polar molecule in a dilute solution. Each polar molecule will be represented as a homogeneously polarized ellipsoid, and

the solution shall consist of such ellipsoids embedded in a continuous medium with the dielectric properties of the solvent. The axes of the ellipsoids can be chosen so as to reproduce either the geometric shape of the polar molecule, or its optical anisotropy. Both these quantities describe ellipsoids of nearly the same shape.

In accord with the definition of m, we see that two effects must be considered, namely, the polarization of the polar molecule and of the surrounding solvent. Let us first consider the former. As was pointed out by Onsager,[1] a molecule in a cavity in a dielectric will induce polarization in the surrounding material which will, in turn, produce a "reaction field" within the cavity. Onsager obtained an expression for the reaction field of a dipole in a spherical cavity and, subsequently, Scholte[11] extended the calculation to cavities of ellipsoidal shape. A homogeneously polarized ellipsoid of total moment $\overrightarrow{m'}$,[12] embedded in material of dielectric constant ϵ, will induce a reduction field at the ellipsoid of magnitude $f\overrightarrow{m'}$, where the reaction field factor f is given by

$$f = \frac{3A(1 - A)(\epsilon - 1)}{abc[\epsilon + (1 - \epsilon)A]} \qquad (5)$$

The quantities a, b and c are the principal semi-axes of the ellipsoid, with the moment $\overrightarrow{m'}$ assumed to be in the direction of the axis described by a, with

$$A = \frac{abc}{2} \int_0^\infty \frac{ds}{(s + a^2)^{1/2}(s + b^2)^{1/2}(s + c^2)^{1/2}} \qquad (6)$$

For a sphere, A assumes the value $1/3$, while, in general, smaller values of A are associated with ellipsoids elongated in the a direction. Ross and Sack[7] have evaluated A as a function of a/b and a/c, and have summarized the results in convenient graphical form.

Equation 5 permits computation of the total moment m' of the ellipsoidal molecule itself. For, a molecule of moment $\overrightarrow{m'}$ will create a reaction field $f\overrightarrow{m'}$. But the total moment $\overrightarrow{m'}$ can be expressed as the sum of the permanent moment μ' and an induced moment $\alpha_2 f\overrightarrow{m'}$, where α_2 is the mean polarizability of a solute molecule. It is consistent to use the mean polarizability here rather than that in the dipole direction since in the present model anisotropy is accounted for by the shape assumed for the solute molecules. Rearranging the relationship between m' and μ

$$m' = \mu \left(\frac{1}{1 - \alpha_2 f} \right) \qquad (7)$$

In evaluating (7), it is convenient to note that since the solute molecular volume is $4 \pi abc/3$, the factor α_2/abc may be written $P_{\mathrm{D}}\rho_2/M_2$, where P_{D} is the molar distortion polarization, ρ_2 the density and M_2 the molecular weight of the solute. This replace-

(11) Th. G. Scholte, *Physica.* **15**, 437 (1949).

(12) The reaction field of a point dipole in a spheroidal cavity has been considered by F. Buckley and A. A. Maryott. *J. Research Natl. Bur. Standards,* **53**, 229 (1954). They obtain a relatively complicated approximate result. Inasmuch as the point dipole model is not necessarily more realistic than the extended polarization model we are using, we use Scholte's simpler result.

ment involves the assumption that the volume occupied by a solute molecule is approximately the same in both pure solute and solution. To this approximation, P_{D} is given by

$$P_{\mathrm{D}} = \left(\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right)_2 \frac{M_2}{\rho_2} \qquad (8)$$

where the subscript 2 refers to measurements on pure solute.

We must now compute the net moment of the solvent surrounding an ellipsoidal molecule. By methods discussed in detail in Appendix 2, it can be shown that an ellipsoid of homogeneously polarized material of total moment m', embedded in a medium of dielectric constant ϵ, gives rise to a total moment (m' plus the moment of the surroundings)

$$m = m' \left(\frac{2\epsilon + 1}{3} \right) \left(\frac{1}{\epsilon + A(1 - \epsilon)} \right) \qquad (9)$$

The result (9), when combined with (7), leads to the following relation between μ and m

$$m = \mu \left(\frac{2\epsilon + 1}{3} \right) \left(\frac{1}{\epsilon + (1 - \epsilon)A - \frac{3P_{\mathrm{D}}\rho_2}{M_2}A(1 - A)(\epsilon - 1)} \right) \qquad (10)$$

The result (10) differs from those obtained by previous investigators. Prior to Onsager's work,[1] attention was paid only to the polarization of the solvent around a polar molecule in dilute solution. The two most widely recognized studies of this effect were those of Frank,[13] and of Higasi.[6] Frank considered six solvent molecules around each solute, arranged as the nearest neighbors on a cubic lattice molecule. He then observed that if all these neighbors were present, their induced moments added up to a vanishing resultant, but that if one of the neighbors were missing, as would be the case if the solute were assumed to occupy more than one site, a non-vanishing net moment would result. Higasi considered the moment induced in a continuum by a dipole at the center of an ellipsoidal cavity therein. However, he neglected the effect of the dielectric material upon the field inducing the polarization, and therefore obtained incorrect results. It should be noticed that Ross and Sack's correction of Higasi's formula[7] consisted merely of inserting a factor ϵ, and therefore is also in error because the presence of the dielectric material does not merely require introduction of a constant scale factor in the expression for the field within it, but alters the field distribution materially due to the behavior at the boundary between cavity and dielectric.

Since Onsager's paper, computations of the effective moment have been made, neglecting the polarization of the solvent and including instead only the reaction field contribution.[7,11] These treatments are apparently based on the premise that a sufficiently refined discussion of the type originally made by Onsager suffices to account for all contributions to the polarization of the solution. It is difficult to decide exactly what contributions must be included to make this approach consistent, but fortunately no such decision is required, since

(13) F. C. Frank. *Proc. Roy. Soc. (London).* **A152**, 171 (1935).

the statistical mechanical approach is unambiguous.

Let us now consider the qualitative behavior implied by (10). Equation 10 contains two contributions, the first of which, the reaction field polarization, always tends to increase the total moment. Numerical calculations for solvents of dielectric constant near 2 indicate that this contribution is not very sensitive to the molecular shape. On the other hand, the second contribution, that of the polarization of the solvent, is strongly shape dependent, tending to reduce the total moment for elongated ellipsoids $(A < {}^1/_3)$, and tending to increase the total moment for flattened ellipsoids $(A > {}^1/_3)$. This contribution is frequently larger than the first contribution and can account for both negative and positive solvent effects of a considerable range of magnitudes. For a spherical molecule $(A = {}^1/_3)$, the net solvent polarization vanishes, so that in that important special case Onsager's original contribution[1] is identical with the present development.

It has been pointed out that the Onsager model for computing the total dipole moment of a molecule is only appropriate to condensed phases, leading in fact to an incorrect dependence upon density in the limit of low densities.[4,14] This failure arises from the fact that at low densities the volume available per molecule is much larger than that of any reasonable cavity from which surrounding molecules should be regarded as excluded. However, in the liquid solutions to which the foregoing remarks apply, there is little free volume and the Onsager model should be adequate.

IV. Distortion Polarization

In view of the multiplicity of methods suggested[14] for the computation of the distortion polarization term $(\epsilon_\infty - 1)/(\epsilon_\infty + 2)$, it is desirable to discuss some aspects of the distortion polarization of solutions. Just as in the computation of the moment m, we have an intractable formal expression for the distortion polarization term. An examination of the various computations of the distortion polarization of pure substances indicates two approaches which appear to lead to different results in media of finite density. The first approach, due to Kirkwood,[10] consists of the neglect of all fluctuations in the instantaneous moment of the molecules under the influence of an applied field. Kirkwood was able to show that in this limit, the distortion polarization of an assembly of spherical molecules attains the Clausius–Mossotti result

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi N\alpha}{3V} \qquad (11)$$

where α is the polarizability of the molecules and N is the number of molecules in the volume V. Kirkwood also considered non-spherical molecules, and pointed out that (11) may be expected to reproduce to within a few per cent. the distortion polarization of such systems.

The second approach, due to Bottcher,[14] is based on the observation that the local field is not the same at all points within a non-polar dielectric, and in particular will depend upon whether any mole-

(14) C. J. F. Bottcher, "Theory of Electric Polarization," Elsevier. Amsterdam, 1952.

cules near the point under consideration are at known positions. Since the consistent introduction of this idea into the theory requires consideration of the fluctuations in dipole moments, it is difficult to improve the statistical calculations in a simple way. Bottcher proposes instead to consider each molecule of the dielectric to be in the center of a spherical cavity of a radius, a, equal to that of the molecule. He is then able to derive the relation for spherical molecules[15]

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi N\alpha}{3V}\left[\frac{9\epsilon_\infty}{(\epsilon_\infty + 2)\left[2\epsilon_\infty + 1 - \dfrac{2\alpha}{a^3}(\epsilon - 1)\right]}\right] \qquad (12)$$

Equation 12 reduces to (11) if the volume of the cavity is chosen to be V/N rather than the molecular volume. Since the molecular volume is smaller than V/N, Bottcher's formula is equivalent to regarding the fluctuations as causing an increase in the local field over its value calculated assuming their absence. The difference between (11) and (12) vanishes in both the limiting cases of low and high density, as at low density, the local field effect is negligible, and at high density, V/N approaches the molecular volume. Liquids are near this latter limit, so (11) may be used without serious error.

We have just seen that a suitable continuum model corresponds to the neglect of fluctuations in a one component system of spherical molecules. However, similar considerations do not apply for mixtures, as in different relative positions in the solution the moments of the various molecules can vary much more than they can in pure substances. For, in a pure substance, a molecule always has identical molecules for neighbors, whereas in solution, the kinds as well as the positions of the neighbors can vary.

If the fluctuations in dipole moment are ignored, the statistical expression given in Appendix 1 for the distortion polarization may be reduced to

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi}{3V}(N_1\alpha_1 + N_2\alpha_2) \qquad (13)$$

where α_1 and α_2 are the polarizabilities of solvent and solute, and the N_i are the numbers of such molecules in the volume V. Equation 13 is the extension of the Clausius–Mossotti formula to solutions. On the other hand, Bottcher's procedure now leads to a result which always differs from (13). His formula may be expressed in the form

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi}{3V}[N_1\alpha_1 g_1(\epsilon_\infty) + N_2\alpha_2 g_2(\epsilon_\infty)] \qquad (14)$$

with

$$g_i(\epsilon_\infty) = \frac{9\epsilon_\infty}{(\epsilon_\infty + 2)\left[2\epsilon_\infty + 1 - \dfrac{2\alpha_i}{a_i^3}(\epsilon_\infty - 1)\right]} \qquad (15)$$

In (15), a_i is the radius of a molecule designated by i.

To see the relationship between the use of (14) and (12) as opposed to that of (13) and (11), let us substitute into (13) the polarizabilities of solvent and solute by (11), and into (14) the polarizabilities as given by (12). Then, (13) becomes

(15) Bottcher. ref. 14. pp. 205ff.

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{N_1}{N_1{}^0}\left(\frac{\epsilon_1 - 1}{\epsilon_1 + 2}\right) + \frac{N_2}{N_2{}^0}\left(\frac{\epsilon_2 - 1}{\epsilon_2 + 2}\right) \quad (13')$$

where $N_i{}^0$ is the number of molecules of i in a volume V of pure i, with high frequency dielectric constant ϵ_i. Similar treatment of (14) leads to the result

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{N_1}{N_1{}^0}\left(\frac{\epsilon_1 - 1}{\epsilon_1 + 2}\right)\frac{g_1(\epsilon_\infty)}{g_1(\epsilon_1)} + \frac{N_2}{N_2{}^0}\left(\frac{\epsilon_2 - 1}{\epsilon_2 + 2}\right)\frac{g_2(\epsilon_\infty)}{g_2(\epsilon_2)}$$
$$(14')$$

In dilute solutions, $\epsilon_\infty \sim \epsilon_1$, $g_1(\epsilon_\infty) \sim g_1(\epsilon_1)$ and the distortion polarization due to the solvent will be the same according to both (13') and (14'). However, the distortion polarization of the solute will be altered by the approximate inclusion of the fluctuations to the extent of the factor $g_2(\epsilon_\infty)/g_2(\epsilon_2)$. An examination of values obtainable for various values of the parameters determining g_2 indicates that this factor will only rarely alter the solute distortion polarization by more than about 5%. Since $(\epsilon_\infty - 1)/(\epsilon_\infty + 2)$ is usually less than half of $(\epsilon - 1)/(\epsilon + 2)$, this 5% uncertainty ordinarily corresponds to less than a 5% uncertainty in m^2, or of the order of 2% in m itself. For this reason there appears to be no great objection to the use of (13'). We prefer to use (13') inasmuch as it is the first approximation to an in principle exact theory, whereas (14') contains an approximation whose exact extent it is difficult to assess.

Let us now pause to contrast the influence of fluctuations and anisotropy upon the distortion polarization with their influence upon the orientation polarization as computed in the preceding section. Here we have found the fluctuations in the instantaneous dipole moment to be of considerable importance, while fluctuations in the effective dipole moment were dismissed as insignificant in computing the orientation polarization. The difference between the two cases is considerable. The entire distortion moment is induced, and therefore subject to fluctuations, while the bulk of the moment for orientation polarization is just the permanent moment of the molecule. In addition, the main source of the fluctuations in distortion polarization arises from the variety of environments a solvent molecule may experience, whereas the solute molecules, whose environments primarily determine the effective moment m, all possess approximately equivalent environments at high dilution. The role of anisotropy, on the other hand, is governed by different considerations. In the present section anisotropic contributions are small, because even though the molecules may be far from spherically symmetric, the polarization must be averaged over all orientations relative to the applied field. However, in computing m, the source of the polarizing field is the anisotropic molecule itself, and the anisotropy enters directly rather than only appearing in an average with respect to orientations which to first order nullifies its effect.

V. Discussion

Many measurements of the dielectric properties of dilute solutions of polar solute in non-polar solvents have been reported.[16] With the aid of eqs. 3

and 4, the values of the moment m computed from the Debye equation by the original authors can be converted into values computed according to the theory here presented. The values of m thereby obtained are, as pointed out elsewhere in the paper, independent of the model used for the dielectric. From dielectric polarization measurements in the gas phase, values of the permanent moment μ have been obtained for many molecules by methods whose validity is affirmed in the present study. For polar molecules which have been studied in both solution and gas, it is thus possible to obtain experimental values of m/μ. By a comparison of these experimental values with theoretical values, calculated on the basis of a model, it is possible to ascertain to what extent the model reproduces the experimental situation.

Values of m/μ computed both from experimental data and from the ellipsoidal molecule—continuum solvent model of section III are exhibited in Table I. The values of the parameter A of the model were taken from calculations by Ross and Sack,[7] and by Buckingham and LeFevre.[17,18] The values of A were estimated for some of the solutes both from the geometrical shapes of the molecules and from their polarizability ellipsoids; in these cases the values of m/μ reported represent the average of values obtained by the two alternative procedures. These values in most cases differed by less than 2%, and in no case by more than 5%. The values of m/μ reported as "observed" consist of the present authors' evaluation of the data cited in the table. In some cases there remains an uncertainty of several per cent. in the values of the solution moments. The molecules represented in the table cover a wide range of molecular shapes and polarizabilities, and for this reason constitute a reasonable basis for evaluating a model predicting solvent effects.

The comparison between the experimental and predicted m/μ is qualitatively very gratifying, as the model reproduces the wide range of the observed ratios. A more quantitative comparison, however, indicates that discrepancies still remain, and in some cases these are considerably larger than either experimental error or uncertainty in the model parameter. The average discrepancy is somewhat less than twice as great as that obtained by Buckingham and LeFevre[17] by use of their most recently proposed empirical relation. It is of interest to note that Buckingham and LeFevre were only able to achieve good correspondence with experiment by introducing a parameter descriptive of the shape of the solute, so that their equation includes, in an empirical manner, the same fundamental quantities which were employed here. None of the empirical relations not incorporating such a shape-dependent parameter have been conspicuously successful in correlating a wide range of data.

The failure of the simple model of this paper to quantitatively explain the solvent effect must of course be due to shortcomings of the model. Further examination of Table I indicates that the

(16) For a relatively complete listing up to 1948, see L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, Mass. Inst. of Technology. Cambridge. 1948.

(17) A. D. Buckingham and R. J. W. LeFevre. J. Chem. Soc., 1932 (1952).

(18) The parameter A is denoted by ξ in references 7 and 17.

TABLE I

THE RATIO m/μ OF THE ELECTRIC MOMENT IN DILUTE SOLUTION, m, TO ITS VALUE IN GAS, $\mu^{a,b}$

Solvent → Dielectric constant of solvent → Solute	Hexane 1.91		Decalin 2.16		CCl₄ 2.23		Benzene 2.28		CS₂ 2.64	
	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.
Methyl chloride					1.08	0.99	1.08	1.02		
Methyl bromide					1.08	1.00				
Nitromethane							1.05	0.97		
Acetonitrile					1.00	0.91	1.00	0.91		
Methylene chloride	1.15	1.12	1.17	1.11	1.18	1.12	1.18	1.12	1.22	1.08
Chloroform	1.17	1.25	1.20	1.29	1.21	1.20	1.21	1.21	1.25	1.21
Acetone	1.06	1.03	1.07	1.02	1.07	1.08	1.07	1.03	1.09	1.04
Paraldehyde					1.42	1.47	1.43	1.40		
Ethyl ether					1.20	1.24	1.20	1.08		
Toluene					1.00	0.97	1.00	1.00		
Chlorobenzene	1.01	0.98	1.01	0.97	1.01	1.00	1.01	0.99	1.01	0.94
Nitrobenzene	1.03	1.01	1.03	1.03	1.03	1.01	1.03	1.01	1.04	0.98
Benzonitrile					0.96	0.98	0.96	0.98		
Trimethylamine							1.25	1.45		
Sulfur dioxide							1.12	1.07		

ᵃ Some of the observed ratios are at 20°, and some at 25°. The calculated ratios are in each case for the same temperature as the corresponding observed ratio.   ᵇ An index to values for μ is provided by A. A. Maryott and F. Buckley, "Table of . . . Dipole Moments . . . in the Gaseous State," National Bureau of Standards Circular 537, U. S. Printing Office, Washington, D. C., 1953. An index to solution data is given by reference 16. Some more recent data are cited in reference 17. Other relevant work includes the following: C. J. LeFevre and R. J. W. LeFevre, *Aust. J. Chem.*, **7**, 33 (1945); R. J. W. LeFevre and D. A. A. S. N. Rao, *ibid.*, **8**, 140 (1955); N. Pilpel, THIS JOURNAL, **77**, 2949 (1955).

model is most satisfactory for the symmetric solvent molecules CCl₄, and relatively unsatisfactory for the more asymmetric or optically anisotropic solvent molecules, particularly carbon disulfide. We have attempted some calculations of solvent–solute interaction in which the discrete molecular structure of the solvent was recognized. These calculations indicated that fairly reliable values of the distribution functions in solutions of non-spherical molecules would be required to provide meaningful results. We therefore conclude that it will not be a simple task to refine the model we have used here.

VI. Practical Application

The theory and solution model presented here suggest some specific indications with regard to the measurement of dipole moments in dilute solution. As discussed excellently by LeFevre,[19] the quantities which should be measured are the dielectric constants of the solvent, ϵ_1, and of the solution, ϵ, at various mole fractions, x_1, x_2, of solvent and solute. Also needed are the densities of the same systems. By using eq. 13′ in conjunction with the fundamental equation of the theory, (3), one may obtain the computationally useful form

$$\bar{V}\left(\frac{\epsilon-1}{\epsilon+2}\right) - V_1\left(\frac{\epsilon_1-1}{\epsilon_1+2}\right) = x_2\left[P_D + \left(\frac{3}{\epsilon+2}\right)\left(\frac{3\epsilon}{2\epsilon+1}\right)\left(\frac{4\pi N_0 m^2}{9kT}\right)\right] \quad (16)$$

where N_0 is Avogadro's number, V_1 is the molar volume of the solvent, and $\bar{V}$ that of the solution. P_D represents the molar distortion polarization of the solute. It may be seen from (16) that if the quantity

$$Q(x_2) = \frac{1}{x_2}\left[\bar{V}\left(\frac{\epsilon-1}{\epsilon+2}\right) - V_1\left(\frac{\epsilon_1-1}{\epsilon_1+2}\right)\right]$$

is extrapolated to $x_2 = 0$, it will approach the limit

$$\lim_{x_2 \to 0} Q(x_2) = P_D + \left(\frac{3}{\epsilon_1+2}\right)\left(\frac{3\epsilon_1}{2\epsilon_1+1}\right)\left(\frac{4\pi N_0 m^2}{9kT}\right) \quad (17)$$

(19) LeFevre, ref. 5, Chaps. I and II.

Note that the extrapolated orientation polarization term involves the dielectric constant of the solvent only. The quantity P_D can be written in terms of an effective index of refraction of the pure solute as in eq. 8 ($n^2_{eff} = \epsilon_\infty$), or estimated by the methods discussed by LeFevre.[19] Equation 17 can therefore be solved unambiguously for the effective dipole moment m.

The relation of m to the vacuum moment μ may be made by the use of eq. 10. In the evaluation of (10), ϵ is the dielectric constant of the solvent, ρ_2 and M_2 are the density and molecular weight of solute, and A is a geometrical parameter characterizing the solute. The determination of A and the range of validity of eq. 10 have been discussed in preceding sections of the paper.

Appendix 1. Extension of Statistical Mechanical Theory to Mixtures

The statistical mechanical expressions for the quantities $<M_0^2>$ and $(\epsilon_\infty - 1)/(\epsilon_\infty + 2)$, descriptive of the orientation and distortion polarization, respectively, are of just the same form for a mixture as for a one-component system. The pertinent equations are[4]

$$<M_0^2> = \sum_{n,n'=0}^{\infty} \sum_{i,k,i',k'} <\vec{\mu}_{i'} \cdot [(-\mathrm{T}\cdot\alpha)^{n'}]_{k'i'} \cdot [(-\alpha\cdot\mathrm{T})^n]_{ik} \cdot \vec{\mu}_k> \quad (A-1)$$

$$\left(\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\right) = \frac{4\pi}{3V} \sum_{n=0}^{\infty} \sum_{i,k} <\hat{e}\cdot[(-\alpha\cdot\mathrm{T})^n]_{ik}\cdot\alpha^{(k)}\cdot\hat{e}> \quad (A-2)$$

The indices i, k, i' and k' refer to the individual molecules within the volume V, and all summations involving these indices are over all molecules of all kinds. The quantities $\vec{\mu}_i$ and $\alpha^{(i)}$ represent the permanent electric moment and polarizability tensor of molecule i, and $\hat{e}$ is an arbitrary constant unit vector. The angular brackets indicate statistical mechanical averages, which are to be computed using distribution functions for the system

in the absence of an applied electric field. The average (A-2) is to be computed for a spherical group of molecules *in vacuo*, but (A-1) is to be evaluated for a group of molecules embedded in an infinite and boundless dielectric of similar properties. These conditions, which arise in the development of the theory, make (A-1) and (A-2) converge rapidly when expanded in powers of α. The quantity $(-\alpha\cdot\mathbf{T})$ is a tensor (in the space spanned by the molecule indices) whose i, k element is $-\alpha^{(i)}\cdot\mathbf{T}_{ik}$. $\mathbf{T}_{ik}$ is itself a dyadic in ordinary space, and relates a dipole moment at the position of molecule k to its field at molecule i

$$\mathbf{T}_{ik} = \frac{1}{r_{ik}^3}\left[1 - \frac{3\vec{r}_{ik}\vec{r}_{ik}}{r_{ik}^2}\right] \quad i \neq k$$
$$= 0 \quad i = k \quad (A\text{-}3)$$

where 1 is the unit dyadic and $\vec{r}_{ik}$ is the vector distance from the center of molecule i to that of molecule k.

For a dilute solution of polar molecules in a nonpolar solvent, many of the terms of (A-1) vanish, and the remaining terms may be grouped according to the number of polar molecules involved. Since all averages involving more than 1 polar molecule will vanish at high dilution, we will by arranging terms according to the number of polar molecules they contain, have an expansion valid at low concentrations of solute. We shall introduce the following notation: The number of solvent and solute molecules in the sample will be represented by N_1 and N_2, respectively. Specific solvent molecules will be assigned numbers 1, 2, . . . as indices, while specific solute molecules will be designated by letters a, b, . . . Expanding (A-1), grouping similar terms wherever possible, and keeping only a few powers of α

$$<M_0^2> = N_2(\mu^2 - 2N_1<\vec{\mu}_a\cdot\mathbf{T}_{a1}\cdot\alpha^{(1)}\cdot\vec{\mu}_a> +$$
$$2N_1<\vec{\mu}_a\cdot\mathbf{T}_{a1}\cdot\alpha^{(1)}\cdot\mathbf{T}_{1a}\cdot\alpha^{(a)}\cdot\vec{\mu}_a> +$$
$$2N_1(N_1 - 1)<\vec{\mu}_a\cdot\mathbf{T}_{a1}\cdot\alpha^{(1)}\cdot\mathbf{T}_{12}\cdot\alpha^{(2)}\cdot\vec{\mu}_a> +$$
$$N_1<\vec{\mu}_a\cdot\mathbf{T}_{a1}\cdot\alpha^{(1)}\cdot\alpha^{(1)}\cdot\mathbf{T}_{1a}\cdot\vec{\mu}_a> +$$
$$N_1(N_1 - 1)<\vec{\mu}_a\cdot\mathbf{T}_{a1}\cdot\alpha^{(1)}\cdot\alpha^{(2)}\cdot\mathbf{T}_{2a}\cdot\vec{\mu}_a> - \cdots) +$$
$$N_2(N_2 - 1)(<\vec{\mu}_a\cdot\vec{\mu}_b> - 2<\vec{\mu}_a\cdot\mathbf{T}_{ab}\cdot\alpha^{(b)}\cdot\vec{\mu}_b> -$$
$$2N_1<\vec{\mu}_a\cdot\mathbf{T}_{a1}\cdot\alpha^{(1)}\cdot\vec{\mu}_b> + \cdots) + \cdots \quad (A\text{-}4)$$

The term of (A-4) involving but one polar molecule may be further simplified by introducing an effective dipole moment $\vec{m}$, defined such that $\vec{m}$ is the average moment of the solute molecule plus the average moment induced in the remainder of the dielectric. The formal definition of $\vec{m}$ therefore is

$$\vec{m} = \frac{\vec{\mu}}{\mu^2}\sum_{n=0}^{\infty}\sum_{i,k}<\vec{\mu}_a\cdot[(-\alpha\cdot\mathbf{T})^n]_{ik}\cdot\vec{\mu}_k> \quad (A\text{-}5)$$

Equation (A-5) only defines $\vec{m}$ as the total moment when the polar molecules possess sufficient symmetry that $\vec{m}$ and $\vec{\mu}$ are parallel. In any event, the following discussion formally applies, but the fluctuations appearing in (A-7) will not be small

if $\vec{m}$ and $\vec{\mu}$ are far from parallel. Expanding (A-5), keeping only terms involving but one polar molecule and not more than quadratic in the polarizabilities, one may find

$$\vec{m} = \frac{\vec{\mu}}{\mu^2}(\mu^2 - N_1<\vec{\mu}_a\cdot\alpha^{(1)}\cdot\mathbf{T}_{1a}\cdot\vec{\mu}_a> +$$
$$N_1<\vec{\mu}_a\cdot\alpha^{(a)}\cdot\mathbf{T}_{a1}\cdot\alpha^{(1)}\cdot\mathbf{T}_{1a}\cdot\vec{\mu}_a> + N_1(N_1 -$$
$$1)<\vec{\mu}_{a1}\cdot\alpha^{(1)}\cdot\mathbf{T}_{12}\cdot\alpha^{(2)}\cdot\mathbf{T}_{2a}\cdot\vec{\mu}_a> + \cdots) \quad (A\text{-}6)$$

Squaring (A-6), and introducing the value of m^2 thereby obtained into the leading term of (A-4), one may reach the result, valid for dilute solutions,

$$<M_0^2> = N_2m^2 + N_2N_1((N_1 - 1)<\vec{\mu}_a\cdot\mathbf{T}_{a1}\cdot\alpha^{(1)}\cdot\alpha^{(2)}\cdot\mathbf{T}_{2a}\cdot\vec{\mu}_a> +$$
$$<\vec{\mu}_a\cdot\mathbf{T}_{a1}\cdot\alpha^{(1)}\cdot\alpha^{(1)}\cdot\mathbf{T}_{1a}\cdot\vec{\mu}_a> - N_1<\vec{\mu}_a\cdot\mathbf{T}_{a1}\cdot\alpha^{(1)}\frac{\vec{\mu}_a}{\mu} >$$
$$< \frac{\vec{\mu}_a}{\mu}\alpha^{(1)}\cdot\mathbf{T}_{1a}\cdot\vec{\mu}_a>) + \cdots \quad (A\text{-}7)$$

All but the first term on the right-hand side of eq. (A-7) are fluctuations, the largest of which, explicitly exhibited there, are of second order in $(\alpha\cdot\mathbf{T})$. Since $|\alpha\cdot\mathbf{T}|$ is usually considerably less than unity for most configurations of a pair of neighboring molecules, the leading term should be a good approximation to $<M_0^2>$.

The distortion polarization term (A-2) can be treated by the methods originally introduced by Kirkwood.[10] Expanding (A-2) in powers of α, one obtains as the leading term the Clausius–Mossotti result (13), with higher terms accounting for fluctuations and anisotropy. Since (A-2) deals with a spherical sample rather than the cylindrical sample chosen by Kirkwood, the averages involved here have different values than those of his paper, and should not be compared directly.

Appendix 2. The Total Moment of a Dielectric Containing a Polarized Ellipsoid

In Section III of the paper we require the total moment of an ellipsoid and surrounding dielectric when the ellipsoid is homogeneously polarized with a given total moment. The most direct way of making this calculation is to obtain the potential, ψ, at all points in space, and to integrate the polarization $\vec{P} = -((\epsilon - 1)/4\pi)\nabla\psi$ over the region external to the ellipsoid. However, this integration requires manipulation of multiple elliptic integrals, so that a more indirect method which involves but one elliptic integral was actually employed.

We shall first evaluate the total moment of a large sphere of dielectric containing the polarized ellipsoid and surrounded by vacuum. We then relate the moment of the spherical specimen to the moment of a similar specimen not possessing the spherical boundary. This procedure will enable us to deduce the total moment of an unbounded specimen from the coefficient of the dipole term in the potential outside a spherical specimen, thus avoiding an integration of the polarization. Accordingly, consider the following boundary value problem. A shell of dielectric of permittivity ϵ is bounded by an ellipsoid of principal semi-axes a, b and c, and by a larger ellipsoid confocal with the smaller ellipsoid

and of sufficient size that it may be regarded as spherical. Introducing elliptical coordinates with the smaller ellipsoid as the reference surface for which the coordinate $\xi = 0$, the larger ellipsoid will be the surface $\xi = \Xi$, $\Xi \gg 1$. The remainder of space will be of permittivity unity, and the inner ellipsoid will contain a uniform fixed polarization of magnitude $\vec{p}$ per unit volume, directed along the principal semi-axis of length a. A boundary condition at $\xi = 0$, then, is that $\epsilon(\partial\psi/\partial n)$ will suffer a discontinuity of magnitude $-\vec{p}\cdot n$, where $\hat{n}$ is a unit vector normal to the bounding surface. The remaining boundary conditions result from the continuity everywhere of ψ and its regularity at infinity, and continuity of $\epsilon(\partial\psi/\partial\hat{n})$ at the outer boundary surface.

The boundary value problem just described may be solved by standard methods.[20] It is found that the potential outside the specimen assumes the form, in the limit of large Ξ

$$\psi = \left(\frac{3}{\epsilon + 2}\right)\left(\frac{\epsilon}{\epsilon + (1 - \epsilon)A}\right)(-2\pi p abc)x$$
$$\int_{\xi}^{\infty} \frac{ds}{(s + a^2)^{3/2}(s + b^2)^{1/2}(s + c^2)^{1/2}} \quad \text{(A-8)}$$

where the cartesian coördinate x has been introduced in place of an equivalent expression in terms of the elliptical coördinates. The quantity A is the

(20) See, for example, J. A. Stratton. "Electromagnetic Theory," McGraw-Hill Book Co., New York, N. Y., 1941. pp. 207ff.

integral defined by eq. 6 of the main text. The integral appearing in (A-8) can be shown to approach, for large ξ, the limiting value $^2/_3 r^3$, where r is the distance to the center of the ellipsoidal system, so that (A-8) shows that the potential is that of a dipole of total moment

$$m'' = \left(\frac{3}{\epsilon + 2}\right)\left(\frac{\epsilon}{\epsilon + (1 - \epsilon)A}\right)\left(\frac{4\pi abc}{3} p\right) \quad \text{(A-9)}$$

Since the volume of the small ellipsoid is $4\pi\, abc/3$, the last parenthesis of (A-9) is just the total moment m' of the ellipsoid of fixed polarization.

Finally, we relate the moment m'' of a macroscopic sphere, containing at its center a specified ellipsoid, to the moment m of a boundless dielectric containing the same ellipsoid. These quantities are connected by an equation first used by Kirkwood,[2] and discussed subsequently by Harris and Alder.[21] The result is

$$m = \left(\frac{\epsilon + 2}{3}\right)\left(\frac{2\epsilon + 1}{3\epsilon}\right) m'' \quad \text{(A-10)}$$

Combining (A-10) with (A-9), and introducing m' as discussed already, one may find

$$m = m'\left(\frac{2\epsilon + 1}{3}\right)\left(\frac{1}{\epsilon + A(1 - \epsilon)}\right) \quad \text{(A-11)}$$

Reviewing the definitions of m, m' and A, we see that (A-11) has the same meaning as eq. 9 of the main text.

(21) See appendix 1 of reference 3.

CAMBRIDGE 38, MASSACHUSETTS

The Reaction of Methyl Radicals with Deuterium

BY JAMES R. MCNESBY, ALVIN S. GORDON AND S. RUVEN SMITH

The photolysis of acetone in the presence of deuterium has been investigated with a mercury resonance lamp and a medium pressure mercury arc with self reversed resonance line. The system has been studied from 140–450°, including the effect of surface, incident light intensity, helium and pressure. The activation energy for the abstraction of D from D_2 by a methyl radical was found to be 11.9 kcal. The experiments with 2537 Å. radiation showed greatly increased relative amounts of CH_3D formed from mercury sensitized production of D atoms, followed by a reaction taking place at least partly on the wall between CH_3 and D atoms to form CH_3D.

Introduction

The activation energy for the reaction

$$CH_3 + H_2 \longrightarrow CH_4 + H \quad \text{(1)}$$
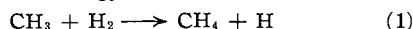
has been the subject of some disagreement. Anderson and Taylor[1] studied the photolysis of cadmium dimethyl in the presence of H_2 and reported the activation energy for reaction (1) is 13 ± 2 kcal. Since that time Davison and Burton[2] have reported that $E_1 \approx 13$ in agreement with Anderson and Taylor, while Steacie and his co-workers[3–5] have differed sharply, and contend that $E_1 \approx 10$–11

(1) R. D. Anderson and H. A. Taylor, J. Phys. Chem., 56, 498 (1952).

(2) S. Davison and M. Burton, THIS JOURNAL, 74, 2307 (1952).

(3) T. G. Marjury and E. W. R. Steacie, Can. J. Chem., 30. 800 (1952).

(4) E. Whittle and E. W. R. Steacie, J. Chem. Phys., 21, 993 (1953).

(5) R. E. Rebbert and E. W. R. Steacie, Can. J. Chem., 32, 113 (1954).

kcal. The extent of the disagreement is illustrated in Table I, which summarizes the findings of various workers on the reactions of methyl and deutero methyl radicals with H_2 and D_2.

Davison and Burton studied the reaction

$$CH_3 + D_2 \longrightarrow CH_3D + D \quad \text{(2)}$$
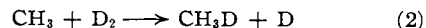
by photolysis of acetone in the presence of D_2 in the temperature range 150–450°. The Arrhenius plot of the CH_4/CH_3D ratio gives two straight lines which intersect at about 350°. The slope of the 150–350° line gives an E_2 in good agreement with both Whittle and Steacie's[4] and with Marjury and Steacie's[3] values, while the slope of the 350–450° curve gives an E of 14 kcal. They accepted the higher value, suggesting that the lower value resulted from hot radical effects. They pointed out that reaction (1) has an activation energy about 1 kcal. lower than reaction (2), and therefore $E_1 \approx$