THE DIELECTRIC CONSTANTS OF POLAR LIQUIDS[1]

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A solution to the problem of interpreting the dielectric constants of polar liquids (i.e., liquids whose molecules possess permanent dipole moments) in terms of molecular properties has been sought for a long time. Until recently very little progress had been made; Debye (6) and Fowler (9) had suggested their theory of hindered rotation, but this theory, though it accounts for some of the experimental facts, is not entirely satisfactory. A few years ago, however, a brilliant attack on the problem was made by Onsager (24), who succeeded in developing a theory which appears to account for the dielectric properties of polar liquids in general in a very satisfactory manner. More recently Kirkwood (16) has developed an elegant extension of Onsager's theory.

The major portion of the present review will be devoted to a discussion of Onsager's theory and its application to experiment. This will be preceded, however, by an account of the manner in which Debye's theory of gaseous dielectrics fails when it is applied to polar liquids and solutions. A brief discussion will also be given of the theory of hindered rotation. The derivation of Onsager's equation will then be outlined and a modification suggested which takes the anisotropy of molecular polarizability into account. Following this a qualitative discussion will be given of the specific effects which prevent close agreement between Onsager's theory and experiment, and are to be interpreted as arising largely from the difference between the structures of actual molecules and the model used by Onsager. In this connection mention will be made of Kirkwood's extension of Onsager's theory. Finally, Onsager's equation will be used to calculate dipole moments from the dielectric constants of several polar liquids and solutions. The values obtained will be compared with those calculated from the dielectric constants of polar gases. It will be shown that the sign of the difference between the two values is consistent with the qualitative arguments given in the discussion of Onsager's theory, and

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provides some evidence regarding the nature of the association between polar molecules in liquids.

The dielectric properties of gases can be satisfactorily accounted for in terms of molecular constants by means of the Langevin–Debye equation (4):

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \sum_i N_i \left(\alpha_i + \frac{\mu_i^2}{3kT} \right) \tag{1}$$

where ϵ is the dielectric constant, N_i is the number of molecules of the i'th species present per cubic centimeter, and α_i, μ_i are the corresponding polarizabilities and permanent dipole moments, respectively.

The validity of this equation depends on the assumptions that the applied field E is small enough so that powers of E higher than the first may be neglected, and that in the interior of the gas the effective field acting on a molecule is the so-called Clausius–Mossotti internal field, $\frac{\epsilon + 2}{3}\mathbf{E}$. This value of the internal field has been derived rigorously, however, only for cubic crystals and for very dilute gases (20).

It is known experimentally that equation 1 holds quite accurately for non-polar liquids, and that dipole moment values which are fairly consistent with those calculated from the dielectric constants of polar gases can be obtained by the application of the same equation to the dielectric constants of very dilute solutions of polar molecules in non-polar solvents. It has been shown by the careful experiments of Müller (22), however, that the values of the permanent dipole moment obtained from solution measurements depend in a systematic way on the dielectric constant of the solvent; in order to obtain reliable values for the moment of a free polar molecule from studies of the dielectric constant of solutions it is necessary to make measurements using a variety of solvents and to extrapolate to dielectric constant unity. A convenient method for performing this extrapolation has been suggested by Sugden (35).

In concentrated solutions and especially in pure polar liquids equation 1 becomes entirely inapplicable, as may be seen by solving for the dielectric constant ϵ. The expression obtained has as denominator

$$1 - \frac{4\pi}{3} N \left(\alpha + \frac{\mu^2}{3kT} \right)$$

a quantity which for most polar liquids has a zero in the vicinity of room temperature. In other words, equation 1 predicts for polar liquids a critical temperature analogous to the Curie point, contrary to fact.

A number of empirical equations have been suggested (17, 44, 36) for the correlation of molecular constants with the dielectric properties of polar liquids and solutions. Of these the most successful is the semi-empirical equation of van Arkel and Snoek (36):

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi N}{3}\left(\alpha + \frac{\mu^2}{3kT + CN\mu^2}\right) \tag{2}$$

This equation differs from equation 1 only in the term $CN\mu^2$, which was deliberately introduced to reduce the importance of the dipole orientation term $\mu^2/3kT$. The empirical constant C does not vary greatly from one polar liquid to another (hydrogen-bonding liquids excepted) and is only slightly dependent on temperature; for concentrated solutions of a given polar substance in non-polar solvents it varies little with the nature of solvent. The equation has been discussed at some length by Smyth (30) and by Müller (23), who has also pointed out that the numbers given by van Arkel and Snoek as values of C are in reality values of $3C/4\pi$.

THE THEORY OF RESTRICTED ROTATION

Debye (6) and Fowler (9) have attempted to account for the dielectric properties of polar liquids on the basis of the assumption that a dipole molecule in a liquid is not free to rotate, but rather carries out oscillations about an axis whose direction changes slowly but over short periods of time is fixed by the arrangement of neighboring molecules. When the axis of the dipole is rotated through an angle θ, measured from the momentary axis about which it oscillates, the dipole molecule is assumed to acquire a potential energy $-W \cos \theta$. On the basis of these assumptions and the assumption that the Clausius–Mossotti expression for the internal field will hold in a polar liquid, it is shown that the term $\mu^2/3kT$ in equation 1 must be multiplied by a correction factor $1 - L^2(y)$, where $L(y)$ is the Langevin function $\coth(y) - \frac{1}{y}$ and $y = \frac{W}{kT}$. Using a constant value of W, Debye has been able to account for the differences between gaseous and liquid water with respect to the Kerr effect, molar polarization, and dielectric saturation. No method is known, however, for calculating the energy W theoretically.

If the theory of restricted rotation is to be valid, it appears that the time required for the momentary axis of oscillation of the dipole to become oriented in the applied field should be long compared with the period of the field, which for usual dielectric constant measurements is of the order of 10^{-6} seconds. It has not been shown theoretically that the time required to orient the momentary axis of oscillation is of this order of magnitude; it may well be of the order of the relaxation time of the dielectric, which is known to be about 10^{-12} seconds (7) for most polar liquids.

The theory has been discussed by Van Vleck (39). In his opinion the discontinuities which occur in the dielectric constants and other properties of certain crystals (e.g., hydrogen chloride and hydrogen bromide in the vicinity of 100°K.) may be reasonably explained as due to the cessation of free rotation, but the hindering of free rotation cannot consistently be used to account also for the dielectric properties of these substances at higher temperatures.

A discussion of the theory of free rotation has also been given by Müller (23), who has shown that the energy W may be approximately identified with $\frac{2}{3} CN\mu^2$, where C is the van Arkel and Snoek constant. The theory of Onsager, which will be discussed in the following section, can also be correlated with the van Arkel and Snoek equation but has the advantage of leading to theoretical values of C which agree approximately with experiment.

The objections presented above to the Debye–Fowler theory of restricted rotation should not be considered as implying that hindered rotation does not exist in liquids. It has been pointed out by Kirkwood (16) that the principal difficulty with the theory lies in the assumption of the validity of the Clausius–Mossotti internal field. Kirkwood's extension (16) of Onsager's theory takes the effect of restricted rotation formally into account in a much more satisfactory way.

ONSAGER'S THEORY

It was long ago suggested and has recently been emphasized (24, 38, 39) that the fundamental reason for the failure of equation 1 when applied to polar liquids is the inapplicability of the Clausius–Mossotti internal field. The important advance made by Onsager (24) is the derivation of an alternative expression for the internal field; on this expression he has based the development of a new theory of the dielectric constants of polar liquids. The remaining sections of the present paper will be devoted to a discussion of Onsager's theory and its application.

Onsager represents a polar molecule in a liquid as a point-dipole at the center of a spherical cavity of dielectric constant unity in a homogeneous isotropic continuum of dielectric constant ϵ; the radius a of the cavity is of the order of the radius of the molecule. For this model it is found by the methods of classical electrostatics that the internal field acting on the dipole may be represented as the resultant of two fields $\mathbf{R}$ and $\mathbf{G}$: the reaction field $\mathbf{R}$ is caused by polarization of the surrounding medium by the field of the dipole, acts parallel to the instantaneous dipole $\mathbf{m}$, and exists even in the absence of an applied field; the cavity field $\mathbf{G}$ is caused by and acts parallel to the applied field **E**. These fields are found by straightforward calculation to have the following values[2]:

$$\mathbf{R} = \frac{2(\epsilon - 1)}{2\epsilon + 1} \frac{\mathbf{m}}{a^3} \tag{3}$$

$$\mathbf{G} = \frac{3\epsilon}{2\epsilon + 1} \mathbf{E} \tag{4}$$

where **m** is a vector representing the instantaneous magnitude and direction of the dipole and a is the radius of the cavity.

The derivation of the Clausius–Mossotti field (5) is formally similar to the foregoing: A spherical surface whose radius is *large* compared to molecular dimensions is imagined to exist in the polarized medium. The field acting on a molecule at the center of this sphere is then considered to be the resultant of two fields: E_1, the field at that point due to the applied field plus the polarization of the molecules outside the sphere[3], and E_2, the field at that point due to the molecules inside the sphere, except for the molecule under consideration. For a sufficiently dilute gas there will be no molecules except the central one within the sphere, and E_2 will have the value zero. It can also be shown that $E_2 = 0$ in case the dipoles within the sphere are arranged in a cubic lattice. Both these cases lead to the Clausius–Mossotti internal field. For any other case the calculation of E_2 is very difficult; the application of the Debye equation to dilute solutions of polar molecules in non-polar solvents is based on the assumption that E_2 is negligible. That this assumption is invalid is shown by the previously cited experimental work of Müller (22).

The difference between the derivations of the Clausius–Mossotti field and the Onsager field should now be clear: in deriving the former the polarization of the molecule (the material within the sphere) is assumed to have its average rather than its instantaneous value, whereas the Onsager field is derived for the instantaneous orientation of the central molecule. As Onsager pointed out, the value of the reaction field obtained from this calculation is not strictly applicable to any actual liquid because of the simplified molecular model which is used. A more detailed qualitative discussion of this point will be given later.

We may now continue with the development of Onsager's theory.

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[2] All quantities printed in bold-face type are to considered as vectors. The derivation of equations 3 and 4 is given in an appendix to this paper.

[3] Note that G is the field due to the applied field and material outside the sphere when the sphere is empty.

Under the influence of the fields **R** and **G** the molecule will be polarized so that its dipole moment will be, not the permanent moment μ, but

$$\mathbf{m} = \mu\mathbf{u} + \frac{3\epsilon}{2\epsilon + 1}\alpha\mathbf{E} + \frac{2(\epsilon - 1)}{2\epsilon + 1}\frac{\alpha}{a^3}\mathbf{m} \tag{5}$$

where $\mathbf{u}$ is a unit vector in the direction of the permanent dipole μ. After this equation is solved for $\mathbf{m}$, it is easy to calculate the potential energy of the dipole as a function of its orientation in the applied field, and by the use of Boltzmann statistics to evaluate $\bar{m}_E$, the average moment in the direction of the applied field. The details of this procedure are given in the appendix to the present paper. The equation for the dielectric constant of the liquid is then obtained by the use of a fundamental equation of electrostatics:

$$\bar{P} = \frac{\epsilon - 1}{4\pi}E = N\bar{m}_E \tag{6}$$

In order that the resulting equation shall reduce to the Debye equation for non-polar liquids it is necessary to define the radius a of the cavity by the equation

$$\frac{4\pi}{3}Na^3 = 1 \text{ cm.}^3 \tag{7}$$

It is also convenient to substitute for the polarizability α the index of refraction n, by means of the equation

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3}N\alpha = \frac{\rho}{M}(P_E + P_A) \tag{8}$$

where ρ is the density of the liquid, M is the molecular weight, and P_E and P_A are the so-called electronic and atomic molar polarizabilities, respectively.

Onsager's equation for the dielectric constant of polar liquids, with the usual approximation that powers of E higher than the first are neglected, then assumes its usual form

$$\frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)} = \frac{4\pi N}{3}\frac{\mu^2}{3kT} \tag{9}$$

DISCUSSION OF ONSAGER'S THEORY

When the preceding treatment is carried out in detail it is found, after the substitutions given in equations 7 and 8 have been made, that the value m of the dipole in the liquid in the absence of an applied field is greater than the permanent moment μ by the factor

$$\frac{(n^2 + 2)(2\epsilon + 1)}{3(2\epsilon + n^2)}$$

At 0°C. this factor has the following values[4]: for ethyl bromide, 1.40; ethyl ether, 1.23; chlorobenzene, 1.34. Evidence for the predicted increase in dipole moment is afforded by the influence of the dielectric constant of the solvent on the rate of some chemical reactions of polar solutes (40) and by the fact that the absorption of infrared radiation of the appropriate vibrational frequencies by HCl and HBr is much greater in the pure liquid or in solution than in the vapor (26, 42). The absorption coefficient depends to be sure not on μ but on $(\partial\mu/\partial r)$, where r is the coördinate involved in the vibration; nevertheless the large change in $\partial\mu/\partial r$ suggests that a considerable change has taken place in μ also. In solution, moreover, the Raman frequencies of hydrogen chloride, hydrogen bromide, ammonia, and sulfur dioxide are lower than in the gas phase; the frequency shift seems to depend in a systematic way on the dielectric constant of the solvent (41).

In the original development of Onsager's theory no account was taken of the optical anisotropy of the polar molecule. This is of some importance, since the reaction field **R** is directed along the axis of the instantaneous dipole of the molecule, and this in turn has its principal component along the axis of the permanent dipole. It is known from measurements of the Kerr effect and of the depolarization of scattered light in polar gases that the polarizability along the dipole axis is in general different from the polarizability averaged over all directions. We may take this fact into account in the following way: We assume that the forces acting on the dipole are given by equations 3 and 4 and take components A and B of the instantaneous dipole $\mathbf{m}$ in the directions of $\mathbf{E}$ and of the permanent dipole,

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[4] A similar increase in moment on solution of a polar molecule in a liquid has been predicted by Fairbrother (8) on the basis of the concept that the state of a polar molecule may be roughly described as the result of quantum-mechanical resonance between a pure covalent and a pure ionic state. The magnitude of the dipole moment is determined by the extent to which the ionic state contributes to the structure. The ionic state is stabilized in solution by the energy of solvation of a dipole and consequently makes a greater contribution to the state of the molecule in solution than in the vapor. This calculation is essentially the same as that made by Onsager, but is expressed in a different language; it predicts an increase in the dipole moment of the same order of magnitude as does Onsager's theory but may be no more accurate because of the necessarily approximate value of the solvation energy which was used and the approximate nature of the quantum-mechanical variation treatment which was adopted.

i.e., along the unit vector $\mathbf{u}$. Assume that the polarization produced by forces in the direction of $\mathbf{u}$ may be calculated by use of the polarizability α_1 along the dipole axis, while that produced by forces in the direction of $\mathbf{E}$ may be calculated by use of the average polarizability α. (This is a good approximation, since for fields far from saturation the orientation of the dipole in the field is nearly random.) Proceeding as in equation 5 we obtain

$$\mathbf{m} = A\mathbf{u} + B\mathbf{E} = \mu\mathbf{u} + \frac{3\epsilon}{2\epsilon + 1}\,\alpha\mathbf{E} + \frac{2(\epsilon - 1)}{(2\epsilon + 1)}\left(A\,\frac{\alpha_1}{a^3}\,\mathbf{u} + B\,\frac{\alpha}{a^3}\,\mathbf{E}\right) \qquad (10)$$

Equating coefficients of $\mathbf{u}$ and $\mathbf{E}$ separately we may solve for A and B, and, substituting for a^3 and α by means of equations 7 and 8, and for α_1 by means of an equation in n_1^2 similar to equation 8, we obtain

$$\mathbf{m} = \frac{(2\epsilon + 1)(n_1^2 + 2)}{3(2\epsilon + n_1^2)}\,\mu\mathbf{u} + \frac{\epsilon(n^2 + 2)}{2\epsilon + n^2}\,\alpha\mathbf{E} \qquad (11)$$

Proceeding from this point just as in Onsager's original treatment we obtain as our final result

$$\frac{\epsilon - 1}{\epsilon} - \frac{3(n^2 - 1)}{2\epsilon + n^2} = \frac{4\pi N}{9kT}\,\mu^2\,\frac{(2\epsilon + 1)(n_1^2 + 2)^2}{(2\epsilon + n_1^2)^2} \qquad (12)$$

A more tedious but more rigorous treatment in which it is assumed that the polarizability ellipsoid of the molecule has components α_1, α_2, α_3 to which correspond indices of refraction n_1, n_2, n_3, and that the permanent dipole μ is parallel to α_1 yields an equation identical with equation 12 except that the term

$$\frac{3(n^2 - 1)}{2\epsilon + n^2}$$

becomes

$$\frac{n_1^2 - 1}{2\epsilon + n_1^2} + \frac{n_2^2 - 1}{2\epsilon + n_2^2} + \frac{n_3^2 - 1}{2\epsilon + n_3^2} \qquad (13)$$

The correction 13 is not important for polar liquids at usual temperatures where ϵ is large.

It was realized by Onsager that for several reasons his method of calculation can give only a rough approximation to the value of the reaction field in actual liquids: the treatment of the molecule as a sphere containing a central dipole, the treatment of the environment of the molecule as a homogeneous continuum, the neglect of dielectric saturation in considering the effect of the strong fields in the vicinity of the central dipole, and the arbitrary choice of the value of a, the radius of the cavity, are all obviously approximations.

The reaction field arises chiefly from the polarization of those molecules which are close to the central dipole. At short distances it is certainly not permissible to consider the environment of the central dipole as a continuum, since the amount of polarizable matter contained in a continuum will be greater (by a factor which we shall call β) than the amount contained in the discontinuous medium. The reaction field calculated on the basis of a continuous environment of the central dipole will then be too large by approximately the factor β. The error may be corrected by using a value of a^3 which is greater by a factor β than the average of the cube of the molecular radius. This correction is in fact achieved by the use of the definition of a given in equation 7, since if the molecule is considered to be a rigid body the volume of the cavity is greater than the volume of the molecule by precisely the factor β. We may consider then that the definition of a given in equation 7 brings Onsager's theory into agreement with the dielectric properties of non-polar liquids by correcting for the discontinuous nature of the environment of the molecule. It is not to be expected that this correction will work as well in polar liquids however.

It is difficult to estimate the magnitude and for many molecules even the sign of the error which is introduced into the calculation of the reaction field by the fact that the structure of actual molecules differs from Onsager's model. Departure of the structure of the molecule from agreement with Onsager's model may be expected in the majority of cases to make the true value of the reaction field greater than that calculated by Onsager, since the structure of most polar molecules is such that neighboring dipoles are able to approach the dipole of a given molecule to within distances smaller than $2a$. On the other hand, dielectric saturation effects in the strong fields surrounding a given dipole will, if they occur, be expected to make the true value of the reaction field less than that calculated by Onsager. It is evident that the estimation of the resultant effect of the various errors entering into the calculation of the reaction field is a very difficult matter; no attempt will be made in the present paper to carry out such an estimation. In making applications of Onsager's theory to experimental data it must be borne in mind that a reaction field error exists, and that the error will not be negligible even in very dilute solutions of polar solutes in non-polar solvents.

Disagreement between experiment and Onsager's theory will be expected to arise from still another cause, which we shall call the *association error.* It has been shown by Fuoss (11) that, in solutions of polar substances in non-polar solvents, the attractive forces existing between dipoles will be expected to lead to the formation of aggregates of polar molecules. These aggregates will not be oriented in the applied field in the same manner as simple dipoles, since each dipole exerts a field which influences the orientation of its neighbors. The result will be either an increase or a decrease in the effective mean value of μ^2, depending on the manner in which the dipoles associate. This effect will be expected to exist also in the pure liquid; it is not predicted by Onsager's theory because in that theory a polarizable continuum is used as a model for the environment of the polar molecule. Kirkwood (16) has recently devised a very elegant theoretical treatment which takes the effect of association formally into account and places the theory of liquid dielectrics on a firmer foundation. For a liquid made up of molecules of dipole moment μ and polarizability zero (i.e., $n^2 = 1$), Kirkwood has derived an equation of the same form as equation 9, but with n^2 replaced by unity and μ^2 replaced by $\boldsymbol{\mu} \cdot \bar{\boldsymbol{\mu}}$. The quantity $\bar{\boldsymbol{\mu}}$ is the average resultant of the moments of all molecules included within a spherical volume, of radius large compared with molecular dimensions, circumscribed about a given dipole as center, and the dot product $\boldsymbol{\mu} \cdot \bar{\boldsymbol{\mu}}$ is a vector notation for $\mu\bar{\mu} \cos \theta$, where θ is the angle between $\boldsymbol{\mu}$ and $\bar{\boldsymbol{\mu}}$. Since Kirkwood's equation was derived by a rigorous application of the methods of classical statistics and does not depend for its validity on a geometrical model, it will be expected that Onsager's equation should contain a quantity analogous to $\boldsymbol{\mu} \cdot \bar{\boldsymbol{\mu}}$ in place of μ^2.

The dipole association referred to here is not to be confused with chemical association; its effect on the thermodynamic properties of the liquid will be much smaller and more subtle than the effect of chemical association. The aggregates of molecules mentioned above are not to be considered as chemical polymers but rather as aggregates of the type which, because of the attraction between positive and negative ions, occurs in solutions of strong electrolytes. If chemical association does occur, as it does for instance in hydrogen-bonding liquids, it may be expected of course to have a pronounced effect on the average value of μ^2.

The effect of association is formally accounted for in Kirkwood's equation by the quantity $\boldsymbol{\mu} \cdot \bar{\boldsymbol{\mu}}$, which is to be calculated by statistical methods; the calculation of this quantity is unfortunately extremely difficult. If the dipole axis is also an axis of symmetry of the molecule, however, and only dipole–dipole interactions are involved, it can at least be predicted that $\bar{\boldsymbol{\mu}}$ will be parallel to $\boldsymbol{\mu}$. In the present paper an attempt will be made to predict, from a consideration of the structure of the molecules which make up the liquid, whether $\boldsymbol{\mu} \cdot \bar{\boldsymbol{\mu}}$ will be greater or less than μ^2.

We shall divide dipole association into two classes: *co-association*, in which the dipoles prefer to orient head to tail, so that their moments reinforce one another, and *contra-association*, in which the dipoles tend to orient in an antiparallel configuration, so that their moments cancel.

Co-association will increase the value of $\boldsymbol{\mu}\cdot\bar{\boldsymbol{\mu}}$ relative to μ^2; contra-association will decrease it. It will be recalled that the potential energy of one dipole in the field of another is

$$V = \frac{\mu_1\mu_2}{r^3}\{\cos(\mu_1, \mu_2) - 3\cos(\mu_1, r)\cos(\mu_2, r)\}$$

where (μ_1, r) is the angle between the dipole μ_1 and the radius vector r from μ_1 to μ_2. On the basis of this formula and the structure of the molecule, we make the qualitative prediction that in liquid diethyl ether co-association will predominate, because configurations such as that shown in figure 1a are energetically much more favorable than those which contribute to contra-association. We shall therefore expect values of μ^2 calculated from the dielectric constant of diethyl ether by means of equation 9 or 12 to be too large. In liquid chlorobenzene, on the other hand, since configurations such as that shown in figure 1b are energetically favorable, contra-association will be expected to predominate; values of the dipole moment of chlorobenzene calculated by means of equation 9 or 12 will be too low. The association error will be expected to decrease as the temperature increases or as the concentration of polar solute in a nonpolar solvent approaches zero. It will be found later that the results of the application of Onsager's theory to the dielectric constants of polar liquids can be interpreted consistently on the basis of a consideration of the association error alone. The possibility is thereby suggested that in polar liquids the association error is considerably more important than is the reaction field error in causing Onsager's equation to deviate from agreement with experiment. Before considering the experimental applications in detail, it may be well to review briefly some critical discussions of Onsager's theory which have been carried out by Van Vleck and his associates.

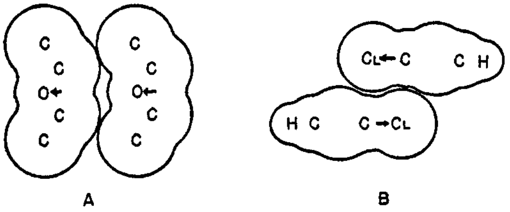


FIG. 1. (a) Co-association of ether molecules; (b) contra-association of chlorobenzene molecules.

Van Vleck (38, 39) has shown that the Onsager internal field is more consistent with a statistical-mechanical treatment of dipole–dipole coupling than is the Clausius–Mossotti field, and has shown that Onsager's theory will explain the fact that the marked dielectric saturation predicted by the Clausius–Mossotti theory for polar liquids in moderately strong fields does not occur. Van Vleck also mentions a possibility suggested by H. Mueller (39), namely, that since the period of free rotation of a molecule is much smaller than the relaxation time of a polar dielectric, the liquid surrounding a dipole may not have time to adjust its polarization to the changing field of the rotating dipole. This effect, if it existed, would result in a value of the reaction field much smaller than that calculated by Onsager. It is difficult to decide *a priori* how much weight should be given to Mueller's suggestion. It may be mentioned, however, that Kirkwood (15) has shown that in a gas at ordinary temperatures a dipole molecule has the same effective mean square moment whether interacting with the field of another freely rotating dipole or with an external electric field. It is, moreover, in better accord with modern ideas of the structure of liquids to consider a molecule in a liquid not as freely rotating but rather as oscillating about a changing position of equilibrium whose rate of change is slow compared with the rate of free rotation. In view of these considerations it should be possible for the reaction field to follow the changing position of the dipole fairly closely. It will be shown later that there are empirical reasons for believing that the effect suggested by Mueller is not important.

Mention should be made of the information which can be gained from the dielectric constants of polar liquids by the application of Kirkwood's theory (16) in the form which takes into account the polarizability of the molecules in the liquid. By means of this theory an accurate value of the quantity $\boldsymbol{\mu}_L \cdot \bar{\boldsymbol{\mu}}_L$ can be calculated from the dielectric constant of a polar liquid. The quantity μ_L is the dipole moment of a molecule in the liquid, and differs from the gas value μ_G by the extra polarization due to the reaction field; $\bar{\mu}_L$ is related to μ_L in the manner previously described, and is a measure of dipole association in the liquid. In calculating the quantity $\boldsymbol{\mu}_L \cdot \bar{\boldsymbol{\mu}}_L$ from the dielectric constant by means of Kirkwood's theory, one gains an accurate knowledge of the combined effects of the reaction field and of what we have called the association effect, but no knowledge of the effect of either one alone. This fact is not surprising, since the two effects are manifestations of intermolecular interaction and are interdependent. In the present discussion of the application of Onsager's theory we are really making an artificial separation of the effect of intermolecular interaction into two parts: the reaction field effect which results in an increase of the average moment of the polar molecules in the liquid, and the association effect which is a measure of the extent to which the orientation of a given dipole in the applied field is influenced on the average by the action of its neighbors.

APPLICATIONS OF ONSAGER'S THEORY TO POLAR LIQUIDS

The relation of Onsager's equation 9 to the empirical equations mentioned previously will first be discussed. Onsager showed (24) that for large values of the dielectric constant equation 9 approximates the empirical equation of Wyman (43). It has furthermore been shown by Böttcher (1) that equation 9 can be put in the form of the semi-empirical equation 2 of van Arkel and Snoek, and that the empirical constant C of the latter equation is then identified with the expression

$$\frac{4\pi}{3}\,\frac{2\epsilon-2}{2\epsilon+1}\,\frac{n^2+2}{3}$$

In table 1 values of $\frac{3}{4\pi}C$ for pure ethyl bromide, as calculated from the above expression, are compared with the experimental values calculated by Smyth (30). The values of ϵ have been taken from Smyth and Morgan (27) and the values of n^2 have been calculated from the value of $P_E + P_A = 21.5$ cc. (29).

TABLE 1

Comparison of values of $\frac{3}{4\pi}C$ *for ethyl bromide*

t, °C.	−90	−50	−10	+30
$\frac{3}{4\pi}C$ (experimental)	1.49	1.43	1.38	1.32
$\frac{3}{4\pi}C$ (theoretical)	1.36	1.30	1.24	1.18

The theoretical and experimental values show fair agreement in magnitude and change in a similar way with increasing temperature.

An extensive comparison of equation 9 with experimental data on pure polar liquids has been undertaken by Böttcher (2) in a paper which contains a very complete compilation of dielectric constants and densities of polar liquids at various temperatures. The procedure was to compute values of n^2 using the electronic polarizability P_E alone; the latter quantity was obtained by extrapolating the mole refractivity to infinite wave length. Values of μ were then calculated from equation 9. The dipole moments calculated in this way depend to only a slight extent on the temperature and agree fairly well with those calculated from dielectric constant measurements on gases; in many cases they agree better with the gas values than do those obtained by the application of equation 1 to the dielectric constants of dilute solutions of polar substances in non-polar solvents. Some of the results of Böttcher's computations are shown in table 2.

The excellence of this agreement is empirically useful but theoretically surprising and in the opinion of the present author is probably due to a fortuitous cancellation of errors. In view of the association error, the reaction field error, and the error involved in the neglect of optical anisotropy, equation 9 would hardly be expected to lead to correct values of the dipole moment; the results obtained by Böttcher indicate that approximate compensation for these errors can be made by using a value of n^2 smaller than the correct one.

TABLE 2

Böttcher's dipole moment values

Calculated from dielectric constants of liquids

LIQUID	μ CALCULATED	μ GAS VALUE	μ SOLUTION VALUE
Nitrobenzene	4.2	4.2	3.9–4.1
Nitromethane	3.7	3.4	3.0–3.1
o-Nitrotoluene	3.9	3.6	3.7
Acetone	3.0–3.1	2.8	2.7–2.8
Aniline	1.5	1.5	1.5–1.6
Acetonitrile	3.6	3.9	3.1–3.5
Benzonitrile	3.6–3.7	4.4	3.9
Anisole	1.5	1.2	1.2–1.3
Methyl chloride	1.8	1.8	1.6–1.8
Methyl bromide	1.6	1.8	1.5
Methyl iodide	1.3–1.4	1.6	1.4
Ethyl bromide	1.8–1.9	2.0	1.8–1.9
Bromobenzene	1.5–1.6	1.7	1.5–1.6
Acetic acid	1.3–1.7	1.7	
Water	3.0–3.1	1.8	1.7–2.0
Ethyl alcohol	2.8–3.1	1.7	1.7

The mole electronic polarizability P_E, and the molecular electronic polarizability α_E connected with it, may be defined for the low-frequency radiation used in measuring dielectric constants by the equation

$$P_E \rho/M = \frac{4}{3}\pi N\alpha_E = \frac{n_\infty^2 - 1}{n_\infty^2 + 2} \tag{14}$$

where n_∞ is a quantity obtained by extrapolating the optical index of refraction to infinite wave length. In order to calculate the temperature-independent term $\frac{4}{3}\pi N\alpha$, experimentally obtained from the study of the dielectric constant of a polar gas over a range of temperatures, however, it is found that a correction must be added to P_E. This correction is called the atomic polarizability, P_A, and may be defined by the following equation in conjunction with equation 14:

$$(P_E + P_A)\,\rho/M = \frac{4}{3}\pi N\alpha\ (\text{experimental}) = \frac{n_{\text{eff.}}^2 - 1}{n_{\text{eff.}}^2 + 2} \qquad (15)$$

Neither the effective index of refraction, $n_{\text{eff.}}$, nor the quantity n_∞ is a true index of refraction, since the dielectric constant for radiation of any frequency is equal to the square of the index of refraction for that frequency (provided of course that the magnetic permeability is close to unity). The quantity $n_{\text{eff.}}$ is to be regarded as a derived quantity related to that part of the polarizability of a polar gas which does not depend on the orientation of permanent dipoles; it is this quantity which in our opinion should be used as the n of equation 9.

TABLE 3

Table of data

LIQUID	ϵ AT 0°C.	REFERENCE	$P_E + P_A$	REFERENCE	μ_G	REFERENCE
Ethyl iodide..........	8.38	(19, 28)	25.7	(29)	1.90	(29)
Ethyl bromide........	10.23	(19, 27)	21.5	(29)	2.02	(29)
Ethyl ether...........	4.80	(19)	25.8	(10)	1.14	(10)
Chloroform............	5.17	(19, 27)	23.0	(10)	1.15	(10)
Chlorobenzene........	6.04	(19, 27)	33.2	(10)	1.69	(12)
Benzonitrile...........	27.6	(19)	31.6	(12)	4.39	(12)
Nitrobenzene..........	39.8	(19)	36.2	(12)	4.23	(12)
Acetone...............	21.58	(19)	18.4	(10)	2.84	(46, 32)
Methyl chloride.......	12.61*	(21)	13.6	(29)	1.86	(29)
Methyl bromide.......	9.97	(21)	15.4	(29)	1.78	(29, 14)
Methyl alcohol........	35.8	(19)	8.6	(30)	1.69	(30)
Ethyl alcohol.........	27.9	(19)	13.6	(30)	1.70	(30)
Acetic acid............	6.17†	(19)	12.9‡	(44)	1.73	(44)
Water.................	83.2	(18)	3.9	(13)	1.84	(13)

* At 20°C.

† At 20°C.

‡ Estimated from optical data.

The physical significance of the atomic polarizability P_A has been discussed in detail by Van Vleck (37); the quantity is interpreted as being that part of the polarizability which arises from vibrations of the nuclei. In Böttcher's treatment it is implicitly assumed that P_A is negligible in liquids, whereas it is probable that in many liquids its value is slightly greater than in the gas.

There will now be presented the results of some calculations which were carried out in order to ascertain the extent to which dipole moments calculated by means of equation 9 from the dielectric constants of polar liquids differ from the accepted values. The data which were used are shown in table 3.

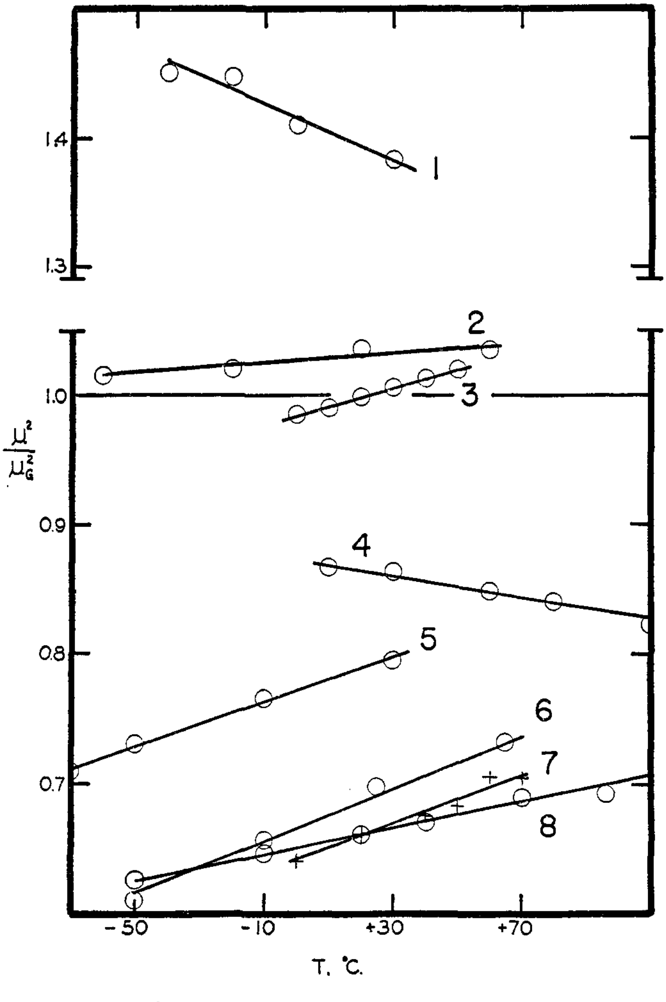


FIG. 2. Values of μ^2/μ_G^2 calculated by means of the unmodified Onsager equation (equation 9) from the dielectric constants of the following pure liquids: 1, diethyl ether; 2, chloroform; 3, acetone; 4, nitrobenzene; 5, ethyl bromide; 6, ethyl iodide; 7, benzonitrile; 8, chlorobenzene.

The values of $P_E + P_A$ and of μ_G, the permanent dipole moment of the free molecule, have been taken from the results of recent measurements of the dielectric constants of gases. The dielectric constant at 0°C. is listed for each liquid, together with the reference from which the dielectric constant measurements were taken. At each temperature for which a calculation has been made, a value of n^2 was computed by means of equation 15 from the density of the liquid at that temperature and was used, together with the experimental dielectric constant, to calculate a value of μ^2 from equation 9. The results are shown in figure 2, in which the ratio of μ^2 to the accepted value μ_G^2 is plotted as a function of temperature.

A qualitative estimate of the association error to be expected can be made by a consideration of the molecular models shown in figure 3; these

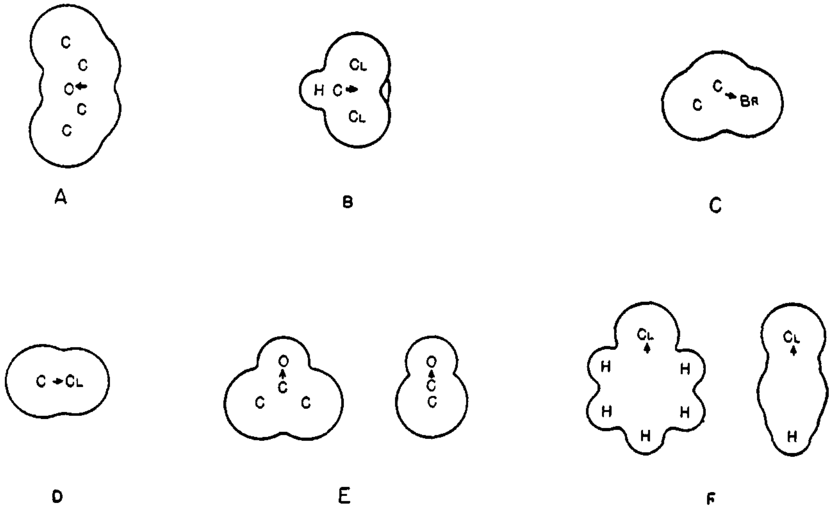


FIG. 3. Molecular models drawn to scale according to the bond distances and van der Waals' radii given by Pauling (25): A, diethyl ether; B, chloroform; C, ethyl bromide; D, methyl chloride; E, acetone; F, chlorobenzene. For each of the last two compounds two views are given: one from a direction perpendicular to the plane of the molecule, the other from a direction lying in the plane.

models have been drawn approximately to scale with the aid of the bond distances and van der Waals' radii given by Pauling (25). The estimated position of the effective dipole is indicated by a short heavy arrow.

It is evident that Onsager's molecular model is approximated more closely by the structures of chloroform and acetone than by the others. We shall therefore expect the dipole moment values calculated for these substances to show relatively close agreement with the accepted values. We shall, however, expect a small co-association error (too high a value of μ) for chloroform, and a small contra-association error (too low a value of μ) for acetone. Ether, on the other hand, should show a relatively large co-association error; the halides should show contra-association errors which increase in the order methyl halide, ethyl halide, phenyl halide. The values of μ^2/μ_G^2 should moreover approach but not cross the value unity as the temperature increases. It is seen from the curves shown in figure 2 that the results obtained by the use of equation 9 are not altogether satisfactory.

A similar calculation in which the optical anisotropy was taken into account has been carried out by means of equation 12 with more satisfactory results. The calculation of n_1^2 was made by use of the equation

$$\frac{n_1^2 - 1}{n_1^2 + 2} M/\rho = (P_E + P_A)_1 \tag{16}$$

Assuming

$$(P_E + P_A)_1 = \frac{\alpha_1}{\alpha} (P_E + P_A) \tag{17}$$

where α_1 and α are, respectively, the molecular polarizability along the axis of the permanent dipole and the polarizability averaged over all directions. The value of α_1/α for ethyl bromide was estimated from data on the depolarization of light by the gas (33); for all other substances which were considered, values were taken from the table compiled by Stuart and Volkmann (34). All these values are for visible light. The assumption 17 is, of course, an approximation but should not cause serious error. The values of $(P_E + P_A)_1$ which were used are as follows: ethyl bromide, 27.5 cc.; acetone, 20.6 cc.; ethyl ether, 23.2 cc.; chloroform, 18.65 cc.; chlorobenzene, 43.2 cc.; nitrobenzene, 49.7 cc.

The results are shown in figure 4. The sign of the error in μ^2 appears in all cases to be consistent with the qualitative predictions which would be made on the basis of a knowledge of molecular structure, and in no case is there a trend of the ratio μ^2/μ_G^2 away from unity with increasing temperature. It is evident that much better qualitative agreement between Onsager's theory and the results of experiment is obtained if the optical anisotropy of the polar molecule is taken into account. The results may be considered as furnishing a rough measure of the magnitude of the association error, and as providing some information regarding the average environment of molecules in polar liquids.

The effects of association will be expected to be especially pronounced in hydrogen-bonding liquids such as water, alcohols, and organic acids. Values of the ratio μ^2/μ_G^2 have been calculated by means of equation 9 for several of these liquids and have been found to vary as follows: for water, from 2.76 at 12.5°C. to 2.54 at 100°C.; for methyl alcohol, almost constant at 3.0 from 0°C. to 60°C.; for ethyl alcohol, from 3.1 at 0°C. to 3.0 at 55°C.; for acetic acid, from 0.55 at 10°C. to 0.91 at 80°C. Equation 12 was not used in this calculation because the orientation of the polarizability ellipsoid is not known for any of these molecules except water. The results of the calculation indicate that for water and the alcohols $\bar{\mu}$ as defined by Kirkwood is several times larger than μ. No very detailed evidence regarding the nature of the association in the liquid is thereby obtained, since the angle between $\bar{\boldsymbol{\mu}}$ and $\boldsymbol{\mu}$ is not known. Moreover, the associating molecules reinforce one another; in acetic acid, that form of application of equation 9 gives only approximate average values of the effective value of μ^2, since the reaction field error in strongly associated liquids is probably large. It is clear, however, that in water and the alcohols association occurs largely in such a way that the moments of

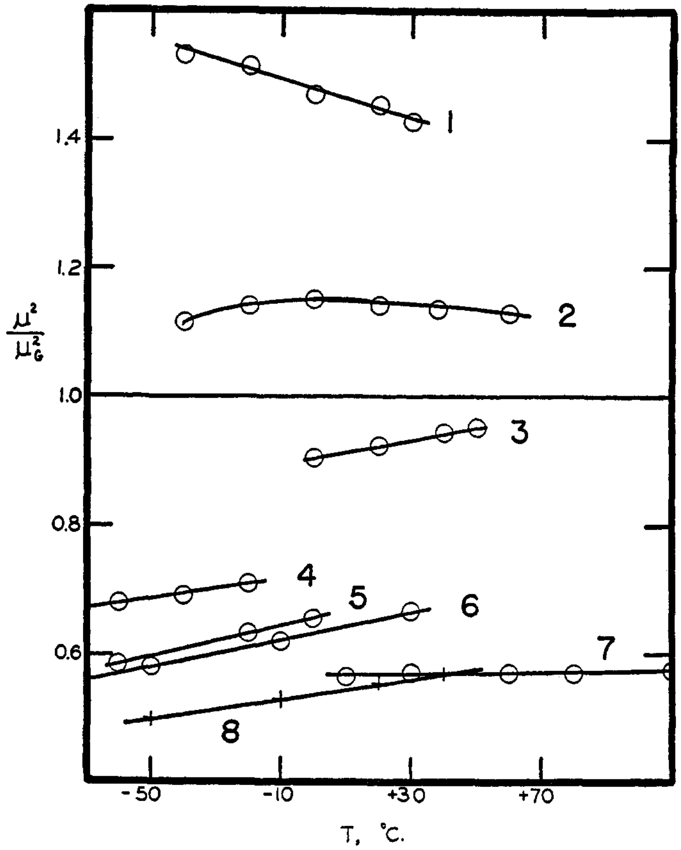


FIG. 4. Values of μ^2/μ_G^2 calculated by means of the modified Onsager equation from the dielectric constants of the following pure liquids: 1, diethyl ether; 2, chloroform; 3, acetone; 4, methyl chloride; 5, methyl bromide; 6, ethyl bromide; 7, nitrobenzene; 8, chlorobenzene.

association predominates in which the moments of associating molecules are opposed. These results are in accordance with Pauling's discussion (25) of hydrogen-bond formation in alcohols and organic acids, and with the experimental evidence compiled by him.

In the discussion of the criticisms which have been directed at Onsager's theory it was mentioned that Mueller (39) had suggested that the value of the reaction field calculated by Onsager might be too large, because of the inability of neighboring polar molecules to follow the motion of a given dipole. It is possible to carry out an empirical test of Mueller's suggestion by deriving an equation similar to equation 12 but using n^2 instead of ϵ in the expression for the reaction field. This is equivalent to assuming that the dipoles surrounding a given dipole are unable to follow the motion of the latter at all, and thus represents the most extreme possible application of Mueller's criticism. By means of the equation so derived, values of μ^2/μ_G^2 have been calculated and examined as before for consistency with the predicted effects of the association error. The values obtained in this way, over the same range of temperatures as given in figure 4, are about 0.75 for chlorobenzene, 0.9 to 1.0 for ethyl bromide, 1.1 to 1.0 for nitrobenzene, 1.3 for acetone, 1.45 to 1.39 for chloroform, and 1.9 to 1.8 for ether. These values do not appear reasonable in view of our previous considerations. We conclude that, empirically at least, the effects suggested by Mueller do not occur in an important way, though the possibility has not been eliminated that they may occur to a small extent.

APPLICATION OF ONSAGER'S THEORY TO POLAR SOLUTIONS

In his original paper Onsager (24) developed an extension of equation 9 to account for the dielectric constants of polar solutions. By means of the same procedure as he used, an equation may be derived which is an extension of equation 12 and takes into account the optical anisotropy of the polar molecule; for a solution of a single polar solute in a non-polar solvent this equation is

$$\frac{\epsilon - 1}{\epsilon} = \frac{4\pi N_2}{9kT}\mu_2^2\frac{(n_{21}^2 + 2)^2(2\epsilon + 1)}{(2\epsilon + n_{21}^2)^2} + \frac{3\theta_2(n_2^2 - 1)}{(2\epsilon + n_2^2)} + \frac{3\theta_1(n_1^2 - 1)}{2\epsilon + n_1^2} \qquad (18)$$

Here ϵ is the dielectric constant of the solution, N_2 is the number of polar molecules per cubic centimeter of solution, and θ_2, θ_1 are the fractions of the total volume occupied by polar solute and non-polar solvent, respectively. The average index of refraction n_2 of the polar molecule and the index of refraction n_{21} corresponding to polarization along the axis of the permanent dipole, are calculated as before from equations 15 and 16 with the use of values of M and ρ for the pure polar liquid at the temperature T. The value of n_1^2, the square of the index of refraction of the solvent, has been taken as equal to the dielectric constant of the solvent at the given temperature T. In the calculations whose results are presented here the following expressions have been assumed for N_2, θ_2, and θ_1:

$$N_2 = \frac{N_A \rho}{M_2 + \frac{1-X}{X} M_1}$$

$$\theta_2 = \left(1 + \frac{M_1}{M_2}\frac{\rho_2}{\rho_1}\frac{1-X}{X}\right)^{-1} \tag{19}$$

$$\theta_1 = \left(1 + \frac{M_2}{M_1}\frac{\rho_1}{\rho_2}\frac{X}{1-X}\right)^{-1}$$

where X is the mole-fraction of polar solute, ρ is the density of the solution; M_2, M_1 are the molecular weights of solute and solvent, respectively; ρ_2, ρ_1 are the densities of the corresponding pure liquids; and N_A is Avogadro's number.

No detailed derivation of equation 18 will be given here; the principal new assumption involved in its development is

$$\frac{4\pi}{3}(N_1 a_1^3 + N_2 a_2^3) = 1 = \theta_1 + \theta_2 \tag{20}$$

where a_1 and a_2 are the cavity radii for molecules of solvent and solute, respectively.

The measured dielectric constants and densities of polar solutions have been used to calculate values of μ^2 for the polar solute by means of equation 18. The results are expressed as before in the form of the ratio μ^2/μ_G^2, which is plotted in figure 5 as a function of the concentration c of polar solute. In accordance with our expectations the curves for ethyl bromide and chlorobenzene are seen to approach the value unity as the concentration decreases. The behavior shown by the curve for chloroform is difficult to understand but may be due to small errors in the dielectric constant measurements, or to an error in the choice of the value of n^2, or to a large reaction field error. The curve calculated from dielectric constants of very dilute solutions of acetone in benzene, and shown in figure 6, is quite satisfactory, however. The association error in this case is small, as would be expected. It is possible to extrapolate this curve to infinite dilution; the fact that the extrapolated value of μ^2/μ_G^2 (0.96) is not exactly equal to unity is not surprising, inasmuch as the reaction field error will be expected to exist even at infinite dilution.

Some years ago a calculation was made by Fuoss (11) which showed that in dilute polar solutions the effective value of μ^2 for a polar solute

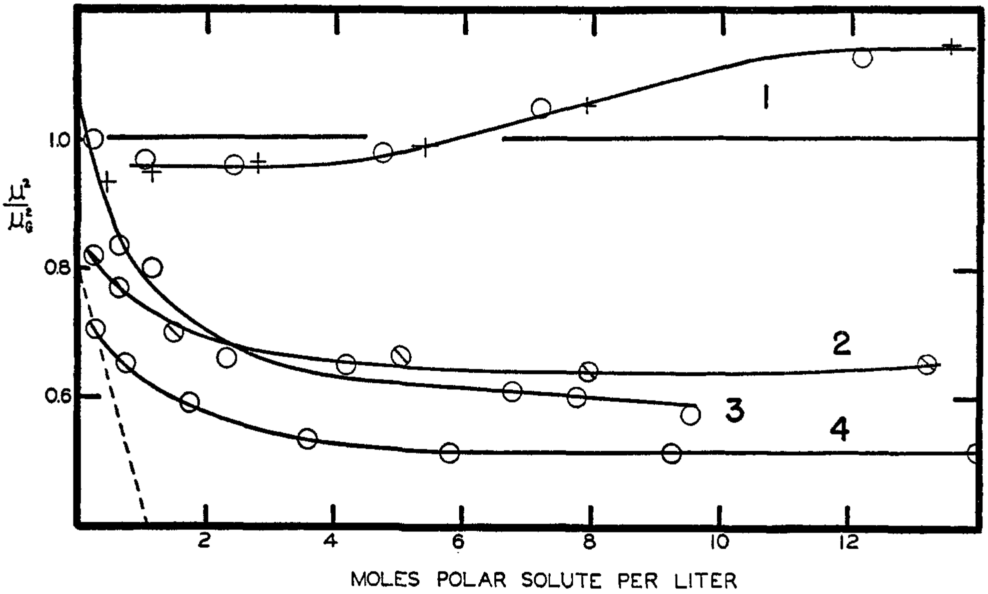


FIG. 5. Values of μ^2/μ_G^2 for the polar solute, calculated from the dielectric constants of hexane solutions of the following: 1, chloroform (circles refer to measurements at 40°C.; crosses to measurements at −50°C.); 2, ethyl bromide at 40°C.; 3, chlorobenzene at 50°C.; 4, ethyl bromide at −90°C. Experimental data in all cases were taken from Smyth and Morgan (27). The limiting slope calculated for ethyl bromide at 40°C. by means of the theory of Fuoss is shown by the dotted line.

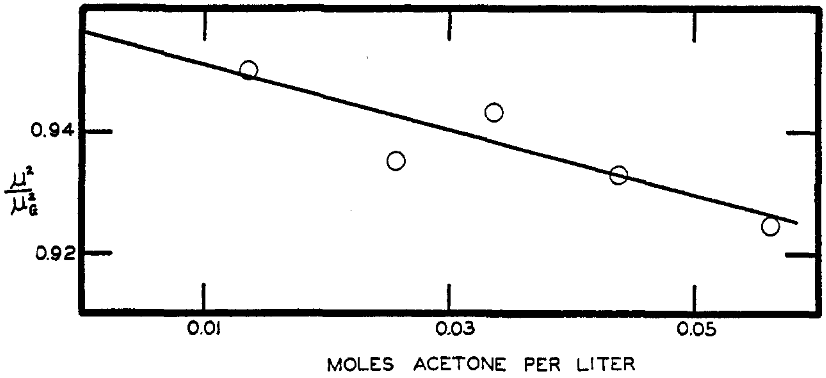


FIG. 6. Values of μ^2/μ_G^2 calculated from the dielectric constants of dilute solutions of acetone in benzene at 22°C. Measurements by Wolf and Gross (43).

would be expected to change rapidly with concentration because of the formation of dipole pairs which would not be oriented in the applied field as would be a free dipole. Fuoss found that, because of this effect, the effective value of μ^2 in dilute polar solutions is

$$\mu^2_{\text{eff.}} = \mu_0^2\left\{1 + \frac{N}{4\pi}\int\int\int e^{\frac{-u_m}{kT}} r^2\, dr\, dw'\, dw''\right\} \tag{21}$$

where μ_0 is the moment of a free dipole in the liquid, r is the distance between two interacting dipoles, dw' and dw'' are elements of solid angle which determine their relative orientation, and u_m is the interaction energy of two dipoles in the liquid, expressed as a function of r, w', and w''. The right-hand side of equation 21 is essentially equal to Kirkwood's quantity $\boldsymbol{\mu}\cdot\bar{\boldsymbol{\mu}}$ for the special case of a solution sufficiently dilute that only interactions between pairs of dipoles need be considered. For an idealized molecular model, namely, an ellipsoid of revolution containing at its center a dipole of moment μ_0 oriented parallel to the major axis, it has been shown by Fuoss that the integral in equation 21 is approximately equal to

$$-4\pi\left(\frac{\pi}{3}\right)^{3/2}\frac{\mu_0^2}{\epsilon kT}\,\frac{Ze^y}{y^{7/2}} \tag{22}$$

where a is the major axis of the ellipsoid, b is the minor axis, $\lambda = b/a$,

$$Z = \left(\frac{1}{2\lambda^2} - 1\right)^{-1/2}, \quad y = \frac{\mu_0^2}{b^3 \epsilon kT}$$

and ϵ is the dielectric constant of the solution. Reference to figure 3 shows that the structure of ethyl bromide corresponds roughly to Fuoss' model; the expression 22 has accordingly been computed for a dilute solution of ethyl bromide in hexane at 40°C., and used to calculate

$$\frac{\partial}{\partial c}\left(\frac{\mu^2}{\mu_G^2}\right)_{c\to 0}$$

where c is the concentration of ethyl bromide in moles per liter. In this calculation the axes of the ellipsoid were assigned the values 7.0 and 4.3 Å.; the dipole moment μ_0 in expression 22 was corrected for the extra polarization produced by the reaction field, and ϵ was given the value 1.88, the dielectric constant of hexane at 40°C. The calculated value of the limiting slope was -0.36; a straight line of this slope is drawn in figure 5. The calculated slope is evidently of a reasonable order of magnitude, since it is possible that the curve for ethyl bromide should be extrapolated to a value of μ^2/μ_G^2 somewhat lower than unity because of the persistence of the reaction field error at infinite dilution. Too much significance should not be attached to the value -0.36 calculated for the slope, since there is considerable uncertainty regarding the appropriate choice of values of ϵ

and μ_0 to be applied in expression 22, and the structure of ethyl bromide is only a rough approximation to Fuoss' model.

In figure 7 is shown a curve in which values of μ^2/μ_G^2 for ethanol in benzene at 20°C. are plotted against the concentration of ethanol. In making this calculation n_{21}^2 was put equal to n_2^2, since the orientation of the polarizability ellipsoid in ethanol is not known. The curve can be interpreted in the following way: In a concentrated solution high-order polymers will be expected to predominate, many of which will have flexible chain structures of the following sort[5] (25, pages 285–95):

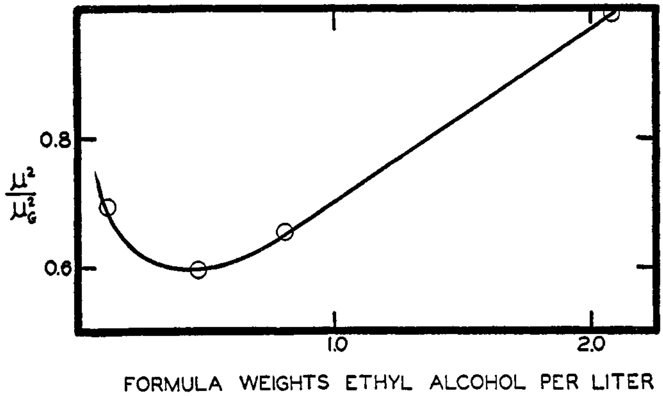
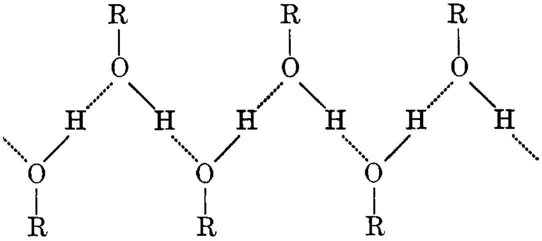


FIG. 7. Values of μ^2/μ_G^2 calculated for dilute solutions of ethanol in benzene at 20°C. Dielectric constant measurements by Smyth and Stoops (28).



These chains will have a large moment; their presence will cause a large increase in the mean value of μ^2. The chains will have some tendency to form rings, however, since on ring closure the polymer is stabilized by the formation of an extra hydrogen bond; this tendency will be opposed by the decrease in entropy involved. In more dilute solutions polymers of lower order will predominate, and will have a greater tendency to form rings

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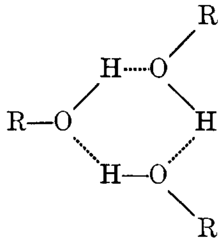
[5] The dotted lines indicate hydrogen bonds.

because the entropy decrease on ring closure is less for a short chain than for a long chain. The dipole moment of these rings will be small, as may be seen from the following possible structure for a trimer with zero moment:



The predominance of such ring structures may account for the minimum in the curve shown in figure 6. At still lower concentrations the monomer predominates, and the ratio μ^2/μ_G^2 approaches unity.

It is possible that in order to account for the ethanol curve it will be necessary to assume that the stable configuration of the dimer in dilute hexane solution is cyclic with zero moment. A further investigation of this possibility would be of interest, since there is at present no evidence for the existence of cyclic dimers of monobasic alcohols. At first glance a cyclic dimer, which would bring positively charged hydroxyl hydrogens close together and would make the R—O moments collinear and antiparallel, would appear to be unstable relative to a chain dimer.

SUMMARY

A discussion has been given of Onsager's theory of liquid dielectrics and of its application to experiment. It has been shown that if Onsager's theory is modified to include the effect of optical anisotropy, the deviations of the modified theory from agreement with experiment can be consistently correlated with a qualitative discussion of the influence of molecular structure on intermolecular association in polar liquids. This result is somewhat surprising in view of the possibility that the value of the reaction field calculated by Onsager is for actual liquids seriously in error. It is difficult to believe that the observed consistency between the experimental data and the interpretation given here is the result of coincidence; this possibility must nevertheless be kept in mind. If, however, the interpretation given here is correct, the application of Onsager's theory to dielectric constant data can be used to obtain qualitative or perhaps even semi-quantitative information regarding the nature of intermolecular association in polar liquids and solutions; for example, the results given in the present paper indicate that in liquid diethyl ether, ethyl alcohol, and water the molecules are associated in such a way that the effective mean square

dipole moment is greater than that of a free molecule; in liquid aryl and alkyl monohalides, on the other hand, the effective mean square moment is less than that of a free molecule.

I am grateful to Professor J. G. Kirkwood for his kindness in making available to me, prior to publication, the results of his elegant theoretical treatment of the dielectric properties of polar liquids. I am also indebted to Dr. Lloyd Zumwalt, Dr. Saul Winstein, and especially to Professor Linus Pauling and Dr. Verner Schomaker for many helpful suggestions.

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APPENDIX A

Derivation of equations 3 and 4

It is known from the theory of electrostatics that the potential ψ in a region where there are no free charges must satisfy Laplace's equation $\nabla^2 = 0$. The field in any direction x is

$$E_x = -\frac{\partial\psi}{\partial x}$$

The following boundary conditions must also be satisfied: the potential must be a continuous function, and across any interface the normal component of the displacement vector $\mathbf{D} = \epsilon\mathbf{E}$ must be continuous. It is also required that the potential produced by the presence of polarizable bodies in the region must vanish at least as fast as $1/r$ at large distances. It can be shown that a solution of Laplace's equation which satisfies the conditions outlined above is a unique solution except for an additive constant.

Since we are interested in finding the field in a spherical cavity it will be convenient to use spherical polar coördinates r, θ, φ with origin at the center of the cavity. It is known that the general solution of Laplace's equation in these coördinates is a sum of spherical harmonics of the form

$$r^n P_n^m(\cos\theta)(A_{nm}\sin m\varphi + B_{nm}\cos m\varphi) \tag{1a}$$

and

$$r^{-(n+1)} P_n^m(\cos\theta)(A_{nm}\sin m\varphi + B_{nm}\cos m\varphi) \tag{2a}$$

where the A_{nm} and B_{nm} are constants, n is integral, and P_n^m $(\cos\theta)$ is an associated Legendre function of order m and degree n. In the cases we wish to consider it will be evident that the solutions must be cylindrically symmetric: i.e., with the proper choice for the orientation of the polar axis of the coördinate system, the solution of Laplace's equation will not depend on φ. Since this is the case, $m = 0$, and we need only consider the simple Legendre functions P_n^0 $(\cos\theta)$ for the formation of possible solutions, e.g., P_0^0 $(\cos\theta) = 1$; P_1^0 $(\cos\theta) = \cos\theta$; P_2^0 $(\cos\theta) = (3\cos^2\theta - 1)$; etc. In simple cases it can be decided by inspection which of these functions is likely to fit the boundary conditions.

Derivation of equation 4

We wish to discuss the modification of a homogeneous field E in an isotropic homogeneous medium of dielectric constant ϵ by the introduction of a cavity of radius a and dielectric constant unity. Let the unperturbed potential in the absence of the cavity be

$$\psi_0 = -Er \cos \theta$$

(i.e., the field E is directed along the polar axis). Let the potential after the introduction of the cavity be $\psi_0 + \psi_p$ outside the cavity, and ψ_i inside the cavity. The perturbation potential ψ_p must decrease at large distances from the cavity at least as fast as $1/r$. Each of these potentials must satisfy Laplace's equation, since outside the cavity

$$\nabla^2(\psi_0 + \psi_p) = 0 = \nabla^2\psi_0 + \nabla^2\psi_p = 0 + \nabla^2\psi_p$$

The boundary conditions are

$$(\psi_0 + \psi_p) = \psi_i \quad (r = a) \tag{3a}$$

$$\epsilon \frac{\partial}{\partial r} (\psi_0 + \psi_p) = \frac{\partial \psi_i}{\partial r} \quad (r = a) \tag{4a}$$

In view of these boundary conditions and the form of ψ_0, an obvious solution to try is

$$\psi_i = -Br \cos \theta \tag{5a}$$

$$\psi_p = -\frac{A}{r^2} \cos \theta \tag{6a}$$

where A and B are undetermined constants. Substitute 5a, 6a, and the value of ψ_0 in equations 3a and 4a and solve with $r = a$. It is found that the boundary conditions are satisfied if

$$A = \frac{\epsilon - 1}{2\epsilon + 1} a^3 E$$

$$B = \frac{3\epsilon}{2\epsilon + 1} E$$

Then the field inside the cavity is

$$(3\epsilon/2\epsilon + 1)\mathbf{E} = \mathbf{G} \qquad \text{(equation 4)}$$

Derivation of equation 3

To find the field produced when a point-dipole of moment m is introduced at the center of a spherical cavity of radius a in a homogeneous isotropic medium of dielectric constant ϵ, in the absence of an applied field. Let the moment m be directed along the polar axis. Let the potential outside the cavity be ψ_e, and that inside the cavity be $\psi_0 + \psi_p$, where ψ_0 is the potential which would describe the field of the dipole in free space:

$$\psi_0 = \frac{m}{r^2} \cos \theta \tag{7a}$$

The boundary conditions are

$$\psi_0 + \psi_p = \psi_e \quad (r = a)$$

$$\frac{\partial}{\partial r}(\psi_0 + \psi_p) = \epsilon \frac{\partial \psi_e}{\partial r} \quad (r = a)$$

In view of the form of ψ_0, and of the fact that the potential of the dipole will be expected to fall off outside the cavity as $1/r^2$, we try the solution

$$\psi_p = Rr \cos\theta$$

$$\psi_e = \frac{C}{r^2}\cos\theta$$

The boundary conditions are satisfied by

$$R = -\frac{2(\epsilon - 1)}{2\epsilon + 1}\frac{m}{a^3}$$

$$C = \frac{3m}{2\epsilon + 1}$$

Within the cavity the field in the direction of the axis m, i.e., in the direction $\cos\theta = 1$, is

$$-\frac{\partial}{\partial r}(\psi_0 + \psi_p)_{\cos\theta = 1} = \frac{2m}{r^3} + \frac{2(\epsilon - 1)}{2\epsilon + 1}\frac{m}{a^3}$$

The second term is the reaction field R, which will tend to increase the moment of the dipole in the cavity and acts parallel to the axis of the dipole. In vector notation its value is

$$\mathbf{R} = \frac{2(\epsilon - 1)}{2\epsilon + 1}\frac{\mathbf{m}}{a^3} \qquad \text{(equation 3)}$$

APPENDIX B

Derivation of Onsager's equation

Solving equation 5 for $\mathbf{m}$, one obtains

$$\mathbf{m} = \mu\mathbf{u} + \left(\frac{3\epsilon}{2\epsilon + 1}\alpha\right)\mathbf{E} \bigg/ \left\{1 - \frac{2(\epsilon - 1)}{2\epsilon + 1}\frac{\alpha}{a^3}\right\} \qquad (1b)$$

Substitute

$$\frac{n^2 - 1}{n^2 + 2} = \frac{\alpha}{a^3}$$

from equations 7 and 8, and simplify. The equation becomes

$$\mathbf{m} = \frac{(n^2 + 2)(2\epsilon + 1)}{3(2\epsilon + n^2)}\mu\mathbf{u} + \frac{\epsilon(n^2 + 2)}{2\epsilon + n^2}\alpha\mathbf{E} \qquad (2b)$$

$$= \mu'\mathbf{u} + \beta\mathbf{E} \qquad (3b)$$

The torque acting on the dipole is $(\mathbf{R} + \mathbf{G})\mathbf{x}\mathbf{m} = \mathbf{T}$. Since $\mathbf{R}$ is parallel to $\mathbf{m}$, $\mathbf{Rxm} = 0$, and

$$\mathbf{T} = \mathbf{Gxm} = \frac{3\epsilon}{2\epsilon + 1}\mathbf{E}\mathbf{x}(\mu'\mathbf{u} + \beta\mathbf{E}) = \frac{3\epsilon}{2\epsilon + 1}\mu'\mathbf{Exu} = \frac{\epsilon(n^2 + 2)}{2\epsilon + n^2}\mu E \sin\theta = \mu^* E \sin\theta$$

where θ is the angle between $\mathbf{E}$ and $\mathbf{u}$. The potential energy is then equal to

$$U = -\mu^* E \cos\theta \tag{4b}$$

The component of $\mathbf{m}$ in the direction of $\mathbf{E}$ is

$$m_E = \mu' \cos\theta + \beta E$$

In order to determine $\bar{m}_E$, the average value of m_E, it is necessary to find the average value of $\cos\theta$.

Using Boltzmann statistics, we obtain

$$\overline{\cos\theta} = \frac{\int_0^{2\pi}\int_0^{\pi} e^{-\frac{U}{kT}} \cos\theta \sin d\theta \, d\varphi}{\int_0^{2\pi}\int_0^{\pi} e^{-\frac{U}{kT}} \sin\theta \, d\theta \, d\varphi}$$

For fields sufficiently small that powers of μ^*E/kT higher than the first are negligible, the above expression becomes

$$\overline{\cos\theta} = \frac{\mu^* E}{3kT}$$

Whence

$$\bar{m}_E = \frac{\mu'\mu^*}{3kT}E + \beta E = \left\{\frac{(n^2 + 2)^2(2\epsilon + 1)}{3(2\epsilon + n^2)^2}\frac{\mu^2}{3kT} + \frac{\epsilon(n^2 + 2)}{2\epsilon + n^2}\alpha\right\}E$$

To eliminate α and $\bar{m}_E$ substitute

$$\alpha = \frac{3}{4\pi N}\frac{n^2 - 1}{n^2 + 2}$$

$$\bar{m}_E = \frac{\bar{P}}{N} = \frac{\epsilon - 1}{4\pi N}E$$

After simplification, equation 9 is obtained:

$$\frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)^2} = \frac{4\pi N}{9kT}\mu^2$$