which is general.[8]

It is of interest also to consider the moment of glycine calculated from the relation given above. On the basis of the observations in water at 25° the polarization is 3060 cc. and the moment 12.2 $\times$ 10^{-18} e. s. u. This would correspond to a dipole distance of 2.55 Å. Recent calculations

(8) It may also be worth mentioning the implication of *any* linear relation between polarization and dielectric constant in the case of anomalous dispersion. According to the Debye treatment, based on the Clausius–Mosotti equation, the absorption index reaches a maximum at a frequency given by

$$2\pi\nu = \frac{1}{\tau}\frac{\epsilon_0 + 2}{\epsilon_1 + 2}\sqrt{\frac{\epsilon_1}{\epsilon_0}}$$

where τ is the relaxation time, ϵ_0 the dielectric constant at low frequencies and ϵ_1 the dielectric constant at frequencies above the region of dispersion. On the other hand, if the Clausius–Mosotti relation be replaced by any linear relation, the same for both ϵ_0 and ϵ_1, this expression reduces to

$$2\pi\nu = \frac{1}{\tau}\sqrt{\frac{\epsilon_1}{\epsilon_0}}$$

(see Debye, "Polar Molecules," Chemical Catalog Co., New York City, 1929).

based on a model proposed by Kirkwood[9] give a value of 3.17 Å. for this distance, or a moment of 15.2 $\times$ 10^{-18} e. s. u.

Summary

A correlation of the dielectric constant of a large number of polar liquids with assumed values of the polarization per cc. calculated by ascribing to the molecules in the liquid state the electric moments obtained from measurements on the vapor and on dilute solutions in non-polar solvents suggests an empirical relation between polarization and dielectric constant: $p = (\epsilon + 1)/8.5$. This relation is fairly satisfactory when applied to the variation of dielectric constant with temperature and with pressure in the case of a number of polar liquids for which data are available. The meaning of such a relation in terms of the internal field in the liquid is discussed.

(9) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

Electric Moments of Molecules in Liquids

BY LARS ONSAGER

In its original, still generally accepted, form Debye's dipole theory[1] accounts quantitatively for the dielectric properties of gases, and qualitatively for those of liquids. In view of the extensive and consistent evidence the fundamental hypothesis of molecules possessing permanent electric moments is not in doubt.

When the theory is applied to liquids (and solids), the interaction of a molecule with its environment must be taken into account. For this purpose, Debye borrowed the theory of "internal field" which was developed by Clausius and Mosotti, one that has been applied universally and with remarkable success to aggregates of polarizable molecules. According to this theory, the "internal field" which polarizes a molecule in the dielectric equals the external field, augmented by $(4\pi/3)$ times the electric moment induced in a unit volume of the dielectric. Debye's implicit assumption is that the force-couple which tends to orient an electrically asymmetric molecule in a polarized dielectric is proportional to the same "internal field." This assumption leads to

(1) P. Debye, *Physik. Z.*, **13**, 97 (1912).

Debye's well-known formula for the dielectric constant (ϵ)

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

where α denotes the polarizability of the molecule, μ its permanent electric moment, kT the energy of thermal agitation, and N the concentration (molecules/cc.), and the summation is extended over all species of molecules present.

Formula (1) can be tested in a number of ways. When only a single species of molecules is present, one can compute the dipole moment μ, with the aid of Eq. 1, from the observed dielectric constant, and the test is whether the dipole moments computed for the liquid state or in liquid mixtures with a non-polar component remain the same as that observed in the vapor state. A more thorough analysis of the problem shows that one should not expect the dipole moment to remain quite constant, because all real molecules have a positive polarizability α. The polarization of the dielectric in the electric field of the molecule itself gives rise to a *reaction field*, which tends to enhance the electrical asymmetry.

When Eq. 1 is compared with experience, one finds in general that for dilute solutions of polar substances in non-polar liquids the moments inferred with the aid of the formula come out approximately the same as in the vapor state, although with a systematic tendency for μ to decrease with increasing dielectric constant of the environment.[2] For pure polar liquids one computes very small moments; the discrepancy is more pronounced the higher the dielectric constant of the liquid. The reason for this remarkable result is the nature of the function $(\epsilon - 1)/(\epsilon + 2)$, which cannot exceed unity. Accordingly, Eq. 1 requires for any dielectric

$$(4\pi/3) \left(\alpha + \frac{\mu^2}{3kT} \right) \leqq \text{molecular volume}$$

The point of equality is known as the "Curie point"; it is characterized by an infinite dielectric constant. Beyond the Curie point, the theory predicts a stable state of permanent electric polarization, like the familiar permanent magnetic polarization of iron. Some bodies are actually capable of existing in such a "ferroelectric" state; the best known example is perhaps that of Rochelle salt, a solid. Nevertheless, the phenomenon is quite rare and certainly not, as one should expect from Eq. 1, a common occurrence with polar substances.

According to Eq. 1, a polar liquid with a high dielectric constant should necessarily be close to its Curie point, and, in this region its dielectric constant should be very sensitive to variations of all pertinent factors (temperature, pressure, field intensity), as seen from the formula

$$\Delta\epsilon = \frac{(\epsilon + 2)^2}{3} \Delta \left(\frac{\epsilon - 1}{\epsilon + 2} \right)$$

Like the Curie point, this predicted instability always fails to materialize; the observed variations of the electric susceptibility with temperature, pressure, volume and field intensity are of a smaller order of magnitude than those predicted by the theory.

This rather brief outline may suffice for a perspective of the difficulties which the original theory has encountered. Many authors have resigned themselves to the view that the consistent discrepancies were due to "association"; in other words, the forces between the polar molecules were so strong that their effects would not admit of any simple description.

J. Wyman[3] has shown that certain simple, general relations are approximately fulfilled by a large class of polar liquids, for example

$$(\epsilon - 1) \, T \sim \text{constant} \tag{2}$$

Such a discovery belies the pessimistic expectations of the "association theory," and indicates that our theoretical understanding of polar liquids is capable of great advancement.

Without reference to any particular theory, by straightforward thermodynamic reasoning, Wyman's relation (2) implies quite simply that the polarization of the dielectric (by orientation) involves practically no change of the internal energy. According to Debye's theory, the polarization should be greatly enhanced by the internal field, and the consequent reduction of the energy should often be much greater than the work required to accomplish the polarization.

Analysis of the Internal Field

We shall show presently that the original Mosotti theory of the internal field is not applicable to permanent dipoles, in that only a certain part of it, which we might call the *cavity field*, contributes to the orienting force-couple. The remaining part of the internal field, the *reaction field*, is parallel to the dipole moment; it has therefore the very different effect of enhancing both the permanent and the induced dipole moments, in a ratio given by the polarizability of the molecule.

For cases where the electric polarization by orientation is but a small fraction of the whole, the modification of the theory involves the underlying picture more than the predicted results. For cases where the polarization is mainly due to orientation, the predictions of the new theory are very different; for example, no Curie point is expected.

Our molecular model will be the same as that of the Debye theory. While the shape of the molecules will affect the result, in the present article our concern shall be limited to spheres, whose radius will be denoted by a. Further pertinent characteristics of a molecule are its polarizability, α, related to an "internal refractive index" n as follows

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

and a permanent electric moment μ_0 (*in vacuo*). In an electric field, $\mathbf{F}$, the total electric moment,

(2) H. Mueller, *Physik. Z.*, **34,** 689 (1933).

(3) Wyman, THIS JOURNAL, **58,** 1482 (1936).

is the vector sum of the permanent and the induced dipole moments

$$\mathbf{m} = \mu_0 \mathbf{u} + \alpha \mathbf{F} \qquad (4)$$

where $\mathbf{u}$ denotes a unit vector in the direction of the dipole axis. The statistical a priori expectation of $\mathbf{u}$ is isotropic.

First, let us consider an unpolarized medium of dielectric constant, ϵ, and introduce a rigid dipole of moment m into a cavity of radius a. For simplicity, let the dipole be a point singularity of the electric field, situated in the center of the spherical cavity. The potential ψ has to satisfy Laplace's equation

$$\Delta \psi = 0 \qquad (5a)$$

and the formulation of the boundary conditions in polar coördinates is

$$\psi(r,\theta) - \frac{m \cos \theta}{r^2} = \text{continuous} < \infty \qquad (5b)$$

$$\left(\frac{\partial \psi}{\partial r}\right)_{r = a - 0} = \epsilon \left(\frac{\partial \psi}{\partial r}\right)_{r = a + 0} \qquad (5c)$$

The solution of this problem is

$$\psi = \frac{m \cos \theta}{r^2} - Rr \cos \theta, \, (r < a)$$

$$\psi = \frac{m^* \cos \theta}{\epsilon r^2}, \, (r > a) \qquad (6)$$

whereby the coefficients m^* and R must equal

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

$$R = \frac{2(\epsilon - 1)}{2\epsilon + 1} \frac{m}{a^3} \qquad (7)$$

The former may be called the *external moment* of the immersed dipole; it determines the force (modified by the intervening medium), which the dipole will exert upon a distant charge in the dielectric. The coefficient R measures the electric field which acts upon the dipole as a result of electric displacements induced by its own presence, we shall refer to it as the *reaction field*.

For a neutral, spherical molecule with an arbitrary distribution of charges the above relations between m, m^* and R still maintain. In this more general case m is the actual dipole moment of the molecule, while m^* measures the dipole part of its external field, and R the homogeneous part of the reaction field. This important rule, that m^* and R are determined by m alone, independently of higher electric moments, admits of generalization to ellipsoidal molecules, whereby the coefficients naturally depend on the axes $(2a, 2b, 2c)$ of the ellipsoid.

As a complement to this consideration of an immersed dipole in the absence of an external

field, let us recall the familiar results for the modification of a homogeneous field E by an empty spherical cavity. The mathematical problem is the same as before, except that (5b) is replaced by

$$\psi(r, \theta) + Er \cos \theta = \text{continuous} < \infty \qquad (8b)$$

and the solution is

$$\psi = -Er \cos \theta - (M/r^2) \cos \theta, \, (r > a) \qquad (9)$$
$$\psi = -Gr \cos \theta \qquad \qquad , (r < a)$$

with the coefficients

$$M = \frac{\epsilon - 1}{2\epsilon + 1} Ea^3$$

$$G = \frac{3\epsilon}{2\epsilon + 1} E \qquad (10)$$

In passing, we observe a reciprocal relation between this case and Eq. 7, namely

$$G/E = m^*/m = 3\epsilon/(2\epsilon + 1) \qquad (11)$$

By combining the results (7) and (10) we now find the total field F which acts upon a spherical molecule in a polarized dielectric

$$\mathbf{F} = \mathbf{G} + \mathbf{R} = \frac{3\epsilon}{2\epsilon + 1} \mathbf{E} + \frac{2(\epsilon - 1)}{(2\epsilon + 1)a^3} \mathbf{m} \qquad (12)$$

This equation formulates the conditions for equilibrium *in the environment of the molecule*. The condition for internal equilibrium of the molecule is given by our model

$$\mathbf{m} = \mu_0 \mathbf{u} + \alpha \mathbf{F} \qquad (4)$$

Accordingly, for a given instantaneous direction $\mathbf{u}$ of the "permanent dipole" axis the total electric moment of the molecule is given by the formula

$$\left(1 - \frac{2(\epsilon - 1)}{(2\epsilon + 1)} \frac{\alpha}{a^3}\right) \mathbf{m} = \mu_0 \mathbf{u} + \frac{3\epsilon}{(2\epsilon + 1)} \alpha \mathbf{E} \qquad (13)$$

When we introduce the "internal dielectric constant" n^2 according to Eq. 3, we obtain a convenient explicit formula as follows

$$\mathbf{m} = \frac{(n^2 + 2)(2\epsilon + 1)}{3(2\epsilon + n^2)} \mu_0 \mathbf{u} + \frac{\epsilon(n^2 - 1)}{(2\epsilon + n^2)} a^3 \mathbf{E}$$
$$= \mu \mathbf{u} + \frac{\epsilon(n^2 + 2)}{(2\epsilon + n^2)} \alpha \mathbf{E} \qquad (14)$$

In the same notation, the explicit formula for the internal field becomes

$$\mathbf{E} + \mathbf{I} = \mathbf{F} = \left(1 + \frac{n^2(\epsilon - 1)}{(2\epsilon + n^2)}\right) \mathbf{E} + \frac{2(\epsilon - 1)}{(2\epsilon + 1)} \frac{\mu}{a^3} \mathbf{u} \qquad (15)$$

As regards the induced moment in the $\mathbf{E}$ direction, this formula does not differ greatly from that of Clausius and Mosotti, which is

$$\mathbf{I} = \mathbf{E}(\epsilon - 1)/3$$

while with $\mu = 0$, Eq. 15 gives

$$\mathbf{I} = \mathbf{E}n^2(\epsilon - 1)/(2\epsilon + n^2)$$

For a non-polar liquid we have $\epsilon = n^2$, and the two formulas are identical. In application to mix-

tures of non-polar liquids, Eq. 15 yields slightly higher values of ϵ.

Nevertheless, in applying the same formulas to polar liquids we shall presently derive results which are very different from those previously accepted. The problem before us is to compute the effective energy of interaction between the molecule and the field, and the consequent average orientation of the molecule.

For this purpose it is not admissible, as Debye did, to assume that the orienting force is proportional to the time average of $\mathbf{F}$. Since $\mathbf{F}$ depends on the orientation, we must compute the orienting force-couple for each individual direction of $\mathbf{u}$; the *work* involved in the process of orientation is then the potential of this orienting force.[4] The force-couple equals the vector product of $\mathbf{F}$ and $\mathbf{m}$. We can use either of the expressions for $\mathbf{F}$ given by Eqs. 12 and 15; the former represents a more instructive decomposition of the vector

$$\mathbf{F} = \mathbf{G} + \mathbf{R}$$
$$\mathbf{G} = \mathbf{E} \times 3\epsilon/(2\epsilon + 1)$$
$$a^3\mathbf{R} = \mathbf{m} \times 2(\epsilon - 1)(2\epsilon + 1)$$

The force-couple equals

$$\mathbf{M} = \mathbf{F} \times \mathbf{m} = \mathbf{G} \times \mathbf{m} = (3\epsilon/(2\epsilon + 1))\,\mathbf{E} \times \mathbf{m} \quad (16)$$

We observe that *the reaction-field $\mathbf{R}$, being parallel to the dipole $\mathbf{m}$, does not contribute to the orienting force-couple*. The calculation is easily completed with the aid of Eq. 14; this time only the part parallel to $\mathbf{u}$ matters, because $\mathbf{G} \times \mathbf{E}$ vanishes

$$\mathbf{M} = \mu\,\mathbf{G} \times \mathbf{u} = \mu^*\,\mathbf{E} \times \mathbf{u} \quad (17)$$

Here, in accord with the notation of Eq. 7

$$\mu^* = \mu\,3\epsilon/(2\epsilon + 1) \quad (18)$$

stands for the "external" characteristic moment of the molecule, while the actual electric moment μ will depend on the dielectric constant of the environment according to Eq. 14

$$\mu = \frac{(n^2 + 2)(2\epsilon + 1)}{3(2\epsilon + n^2)}\,\mu_0$$
$$\mu^* = \frac{\epsilon(n^2 + 2)}{(2\epsilon + n^2)}\,\mu_0 \quad (19)$$

Dropping the vector notation, Eq. 17 may be written

$$M = \mu^* E \sin \theta$$

then the work of orientation, w, is given by

$$\partial w/\partial\theta = M;$$
$$w = -\mu^* E \cos \theta \quad (20)$$

This extremely simple result suggests the possibility of an equally simple derivation; for this purpose, it is convenient to invert the problem. Let us keep the orientation of the molecule fixed, and find out how the work of creating a field of a certain intensity E in a given direction depends on the angle θ between this direction and the dipole axis of the molecule. The most elementary derivation is obtained if we assume that the external field is due to a charge of the magnitude $-r_1^2 E$ at some point (r_1, θ, φ) on a large sphere of radius r_1. In order to change the direction of the field at constant intensity, we move the charge to another point on the sphere. The work involved is given by the potential

$$\psi = \mu^* \cos \theta/\epsilon r^2$$

(*cf.* Eq. 6), of the field due to the molecule, and Eq. 20 obviously results. This alternative computation of w exhibits the reciprocal character of Eq. 11.

The mean orientation of the molecules in the field is given by Boltzmann's formula

$$\overline{\cos \theta} = \int \cos \theta\, e^{-w/kT} \sin \theta\, d\theta\, d\varphi \Big/ \int e^{-w/kT}$$
$$\sin \theta\, d\theta\, d\varphi = L(\mu^* E/kT) = \coth(\mu^* E/kT) -$$
$$(kT/\mu^* E) = (\mu^* E/3kT) - O(E^3)$$

Thus, for low field intensities E, we have[5]

$$\overline{\cos \theta} = \mu^* E/3kT \quad (21)$$

and we can compute the polarization per unit volume from Eq. 14, as follows

$$\mathbf{P} = N\overline{\mathbf{m}} = N\left(\frac{\mu\mu^*}{3kT} + \frac{\epsilon(n^2 + 2)}{(2\epsilon + n^2)}\,\alpha\right)\mathbf{E} \quad (22)$$

Dielectric Constants of Pure Polar Liquids

In computing the dielectric constant, we shall assume that the volume of the liquid equals the sum of the volumes of the molecules; accordingly

$$N \times 4\pi a^3/3 = 1 \quad (23)$$

With the notation expressed by Eq. 3, we then obtain

$$4\pi N(n^2 + 2)\,\alpha = 4\pi N(n^2 - 1)a^3 = 3(n^2 - 1) \quad (24)$$

Now the fundamental electrostatic formula

$$(\epsilon - 1)\,\mathbf{E} = 4\pi\mathbf{P} \quad (25)$$

yields in combination with Eqs. 22 and 24 the following implicit formula for the dielectric constant

$$\epsilon - 1 = 4\pi N\frac{\mu\mu^*}{3kT} + \frac{3\epsilon(n^2 - 1)}{2\epsilon + n^2}$$

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(4) In a polar medium, the field fluctuates with the rotation of the neighboring molecules. In such a case, the *average force* is the important quantity [(L. Onsager, *Chem. Rev.*, **13**, 73 (1933))]. An alternative procedure is to compute the work of charging a dipole in a given direction **u**.

(5) The given formula is not in general applicable to strong fields, *i. e.*, saturation; because its derivation involves the assumption of an isotropic environment.

which may be written more compactly

$$\frac{(2\epsilon + 1)(\epsilon - n^2)}{(2\epsilon + n^2)} = 4\pi N \frac{\mu\mu^*}{3kT} \qquad (26)$$

or in view of Eq. 18

$$3\epsilon(\epsilon - n^2)/(2\epsilon + n^2) = 4\pi N(\mu^*)^2/3kT \qquad (27)$$

Here, μ and μ^* still depend on ϵ according to Eq. 19. We obtain after elimination

$$(\epsilon - n^2)(2\epsilon + n^2)/\epsilon(n^2 + 2)^2 = 4\pi N\mu_0^2/9kT \qquad (28)$$

When ϵ is large, the left member is very nearly equal to

$$2\epsilon/(n^2 + 2)^2 \sim 4\pi N\mu_0^2/9kT \qquad (29)$$

One of the reasons for this simple limiting law is that μ and μ^* approach limits as ϵ increases. With the notation

$$\mu_\infty = \mu_0(n^2 + 2)/3 \qquad (30)$$

(cf. Eq. 19), we can write Eq. 28 in the alternative form

$$(2\epsilon + n^2)(\epsilon - n^2)/\epsilon = 4\pi N\mu_\infty^2/kT \qquad (31)$$

On the other hand, when only a small fraction of the electric susceptibility is due to orientation of the molecules, that is, whenever

$$\epsilon - n^2 \ll n^2$$

Eq. 27 agrees in the first approximation with the formula of Clausius and Mosotti. We readily derive from Eq. 27

$$\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} = \frac{3\epsilon(n^2 + 2)}{(2\epsilon + n^2)(\epsilon + 2)} \frac{4\pi N\mu_0^2}{9kT} = $$
$$\frac{4\pi N\mu_0^2}{9kT} f(\epsilon, n^2) \qquad (32)$$

Fig. 1 indicates the range where the approximation of Clausius and Mosotti is good.
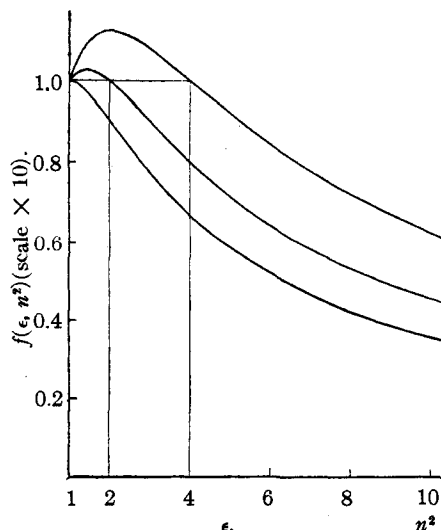

Fig. 1.

Dielectric Constants of Solutions

We shall consider a solution which contains in a unit volume $N_1, \ldots N_i, \ldots$ spherical molecules of different species, with radii $a_1, \ldots a_i, \ldots$, polarizabilities $\alpha_1, \ldots \alpha_i, \ldots$ and dipole moments $\mu_1, \ldots \mu_i, \ldots$, respectively. We introduce the individual refractive indices $n_1, \ldots n_i, \ldots$ by the relation

$$\alpha_i = a_i^3(n_i^2 - 1)/(n_i^2 + 2) \qquad (33)$$

and we shall denote the volume fractions by

$$\vartheta_i = N_i \times 4\pi a_i^3/3 \qquad (34)$$

The dipole moments will depend on the dielectric constant of the environment according to Eq. 19; the moments in vacuo will be denoted by μ_{0i}.

The fundamental electrostatic relation

$$(\epsilon - 1)\mathbf{E} = 4\pi \mathbf{P} \qquad (25)$$

yields in conjunction with Eqs. 22, 24 and 34

$$\epsilon - 1 = 4\pi \sum N_i \left(\frac{\epsilon(n_i^2 + 2)}{\epsilon + n_i^2} \alpha_i + \frac{\mu_i\mu_i^*}{3kT} \right) = $$
$$\sum \vartheta_i \frac{3\epsilon(n_i^2 - 1)}{n_i^2 + 2\epsilon} + 4\pi \sum N_i \frac{\mu_i\mu_i^*}{3kT} \qquad (35)$$

Making use of the identity

$$3\epsilon(n_i^2 - 1) = (2\epsilon + n_i^2)(\epsilon - 1) - (2\epsilon + 1)(\epsilon - n_i^2)$$

we can rearrange Eq. 35 in the form

$$(1 - \Sigma\vartheta_i)(\epsilon - 1) + (2\epsilon + 1)\Sigma\vartheta_i(\epsilon - n_i^2)/ $$
$$(2\epsilon + n_i^2) = 4\pi\Sigma N_i\mu_i\mu_i^*/3kT \qquad (36)$$

Now if we assume that the entire space is occupied by the molecules

$$\Sigma\vartheta_i = 1 \qquad (37)$$

the first term in the member of Eq. 36 vanishes. Then in view of Eq. 18, Eq. 36 may be written

$$\Sigma\vartheta_i(\epsilon - n_i^2)3\epsilon/(2\epsilon + n_i^2) = 4\pi\Sigma N_i(\mu_i^*)^2/3kT \qquad (38)$$

which furnishes the generalization of Eq. 27 to the case of several molecular species. The right member of Eq. 38 depends on the dielectric constant according to Eq. 19:

$$\mu_i^* = \frac{\epsilon(n_i^2 + 2)}{(2\epsilon + n_i^2)} \mu_{0i} = \frac{2\epsilon}{(2\epsilon + n_i^2)} \mu^*_{\infty i} = $$
$$\frac{3\epsilon}{(2\epsilon + n_i^2)} \mu_{\infty i} \qquad (39)$$

In the limit of high dielectric constants

$$\epsilon \gg n_i^2, (i = 1, 2, \ldots)$$

Eq. 38 becomes

$$\epsilon = O(n^2) + 4\pi\Sigma N_i\mu_{i\infty}\mu^*_{i\infty}/3kT = $$
$$O(n^2) + \sum \frac{(n_i^2 + 2)^2}{2} \frac{4\pi}{3} N_i \frac{\mu_{0i}^2}{3kT} \qquad (40)$$

We observe that in this limit, the dielectric constants of solutions are nearly additive.

The opposite extreme is a dilute solution of polar molecules in a non-polar medium. In the follow-

ing, the index m will refer to the non-polar solvent, the index s to a polar solute present in small concentration, so that

$$\epsilon_m = n_m{}^2 \gg \epsilon - \epsilon_m$$
$$\vartheta_m \gg 1 - \vartheta_m = \vartheta_s \qquad (41)$$

Neglecting terms of higher order in the concentration (N_s), we obtain for the dielectric constant of the solution

$$\epsilon = n^2 + \frac{4\pi(\mu^*)^2}{3kT} N_s \qquad (42)$$

here the "refractive index" of the solution differs from that of the solvent by the amount

$$n^2 - n_m{}^2 = \vartheta_s \frac{3n_m{}^2}{2n_m{}^2 + n_s{}^2} (n_s{}^2 - n_m{}^2) \qquad (43)$$

and the (external) dipole moment depends on the dielectric constant of the non-polar solvent according to Eq. 19

$$\mu^* = \frac{3n_m{}^2}{2n_m{}^2 + 1} \mu = \frac{n_m{}^2(n_s{}^2 + 2)}{2n_m{}^2 + n_s{}^2} \mu_0 \qquad (44)$$

For comparison, the Clausius–Mosotti formula yields (on our restrictive assumption of additive volumes)

$$\frac{\epsilon - 1}{\epsilon + 2} = \vartheta_m \frac{\epsilon_m - 1}{\epsilon_m + 2} + \vartheta_s \frac{n_s{}^2 - 1}{n_s{}^2 + 2} + \frac{4\pi}{3} N_s \frac{\mu_0{}^2}{3kT} \qquad (45)$$

and by neglecting terms of higher order we obtain the analogs of Eqs. 42 and 43

$$\epsilon = n^2 + 4\pi N_s((n_m{}^2 + 2)\mu_0/3)^2/3kT \qquad (46)$$

$$n^2 = n_m{}^2 + \vartheta_s \frac{(n_m{}^2 + 2)}{(n_s{}^2 + 2)} (n_s{}^2 - n_m{}^2) \qquad (47)$$

These formulas are seen to agree with Eqs. 42–44 in two cases: when $n_m = 1$ and when $n_m = n_s$. For values of n_m between these limits, Eqs. 42–44 predict larger increments of the "refractive index" and of the dielectric constant than does the classical theory. On the other hand, for $n_m > n_s$, the new formulas predict a *smaller decrement* of the refractive index, n, and a *smaller increment* of $\epsilon - n^2$, the susceptibility due to orientation. The quantitative relations between the two theories can be summarized as follows

$$(n^2 - n_m{}^2)_{\text{new}}/(n^2 - n_m{}^2)_{\text{old}} = f$$
$$(\epsilon - n^2)_{\text{new}}/(\epsilon - n^2)_{\text{old}} = f^2 = (\mu_{\text{app}}/\mu_0)^2 \qquad (48)$$
$$f = f(\epsilon_m, n_s{}^2) = 3\epsilon_m(n_s{}^2 + 2)/(2\epsilon_m + n_s{}^2)(\epsilon_m + 2)$$

Here, μ_{app} denotes the "electric moment" computed by means of the classical formula, Eq. 1, from the dielectric constant of a solution which conforms to the present theory. The function $f(\epsilon, n^2)$ is represented in Fig. 1. Some of its important properties are

$$f(\epsilon, n^2) - 1 = 2(\epsilon - n^2)(\epsilon - 1)/(2\epsilon + n^2)(\epsilon + 2)$$
$$f(1, n^2) = f(n^2, n^2) = 1 \qquad (49)$$
$$f(\epsilon, n^2) \lessgtr f(n, n^2) = 1 + 2((n - 1)/(n + 2))^2$$
$$f(\epsilon, n^2) = f((n^2/\epsilon), n^2)$$

Discussion

The present development of the theory is by no means complete. One open question is the proper choice of the molecular "radius" a. The assumption that the molecules fill the whole volume of the liquid (Eqs. 23, 37), is a makeshift; and its application to the extreme case of a gas would be quite absurd. Assuming that our molecular model is adequate, it would appear better to find a suitable basis for the determination of constant "a." Then in order to allow for changes of volume due to thermal expansion or other causes it would only be necessary to consider the "void" as a constituent of a mixture. This point of view is in perfect accord with our Eq. 36, where the "void," of dielectric constant unity, enters quite symmetrically with the other constituents. Nevertheless, it appears that the development of the theory along these lines will involve careful consideration of molecular arrangements, and probably some arbitrary exercise of judgment.

Similar questions would arise in a generalization of the present theory to molecules of shapes other than spherical, in which case the ratios μ/μ_0, μ^*/μ_0 and μ^*/μ will be greater the shorter the dipole axis compared to other dimensions of the molecule. As far as dilute solutions in non-polar solvents are concerned, it is only necessary to compute the ratio μ^*/μ_0 as a function of ϵ_m; then μ^* determines the increment of the dielectric constant according to Eq. 38. On the other hand, for an imaginary polar liquid of refractive index unity the electric susceptibility must be proportional to the product $\mu\mu^*$, rather than to $(\mu^*)^2$. Fortunately, the difference between the two results is not in general very large. The paradox which it represents is capable of solution, but only by taking into account the reciprocity of neighborhood relations between non-spherical molecules!

The computation of the molecular radius (a) from the total volume of the liquid should lead to an underestimate of the dielectric constant for the given molecular model. The error ought not to be very large, except when a liquid is considered close to its critical point. The assumption of spherical molecules can cause positive or negative errors, perhaps about equally often. With this in mind we should inquire whether the present theory can

furnish a reasonably good description for the *average* dielectric behavior of polar liquids and their solutions.

As regards the former, we have available Wyman's analysis[3] of an extensive material which he has compiled without apparent prejudice and without any knowledge of the theory to be tested. Wyman has summarized his conclusions in the formula

$$p = (\epsilon + 1)/A$$

where p measures the total "polarization" per unit volume, in our notation

$$p = \frac{4\pi}{3} \sum N \left(\alpha + \frac{\mu_0^2}{3kT} \right)$$

The value of the factor A is derived from measurements of ϵ together with measurements of μ_0 in the vapor in non-polar solvents. For a great number of liquids Wyman finds $A \sim 8.5$, with a certain spread given by the limits $A = 6.2$ and 11.

Wyman's formula is practically the same as our Eq. 29

$$\epsilon/A = 2\epsilon/(n^2 + 2)^2 \sim 4\pi N \mu_0^2/9kT \qquad (29)$$

We obtain $A = (n^2 + 2)^2/2$, and Wyman's typical value $A = 8.5$ corresponds to a refractive index

$$n = 1.46$$

which is very reasonable indeed. The range

$$6.2 < A < 11$$

corresponds to

$$1.275 < n < 1.64$$

A comparison with individual refractive indices has not been attempted; it would hardly be significant without allowance for molecular shape. Incidentally, our "refractive index" should include the "atomic polarization" due to elastic displacement of the atomic nuclei by the electric field.

According to Wyman's analysis, one group of liquid dielectrics deviates very markedly from the rest, in that they exhibit much larger dielectric constants than they ought to have. This group includes water, alcohols and ammonia; on the whole, it coincides with the liquids which on the basis of unusual thermodynamic behavior have long been considered as "associated."

There is good cause for the view that we are dealing here with a type of molecular interaction which does not admit of adequate description in terms of permanent and induced dipoles. A promising scheme for coördination of the phenom-

ena is the "proton bond" theory,[6] which has recently been given considerable attention by Hildebrand[7] and by Pauling.[8]

If the dielectric behavior of the substances in question is to be explained along these lines, then an important part of the present theory may still be applicable. As a starting point, Eq. 26 can hardly be far from the truth; its derivation is almost phenomenological. Moreover, it is not likely that in a liquid like water, the ratio μ^*/μ will differ much from its normal value of 3/2; in order to account for the large anomalies in question, it would have to equal 3. Thus we are led to abandon Eq. 19, and that involves only a quite reasonable addition to the basic hypothesis of the proton bond theory: *The formation of a "hydrogen bond" increases the electric moment of the group which carries the hydrogen.*

On the basis of this general picture, we can estimate that a water molecule in the liquid has a dipole moment of the order $\mu \sim 3 \times 10^{-18}$ e. s. u., with $\mu^*/\mu \sim 3/2$. The increment from $\mu_0 = 1.8 \times 10^{-18}$ in the vapor could hardly be accounted for by ordinary homogeneous induction. The properties of water as a solvent for electrolytes appear to harmonize well with our assumption of a large electric moment.

This explanation for the anomaly of "proton bond" liquids differs from the "association theory" in the assumption of a large ratio μ/μ_0, while the "association theory" would call for an anomalous ratio μ^*/μ.

For dilute solutions of polar substances in non-polar solvents, the present theory expects in accordance with experience that the "apparent" dipole moments computed on the basis of the Clausius–Mosotti equation should not in general differ much from those found in vapors of the same substances.

An important theoretical advance is the reconciliation of this empirical rule with the expectation of increased dipole moments in solutions; in our picture $\mu_{app.}$ is only a fictitious quantity with a complicated meaning.

According to Eq. 18, the apparent electric moments of a given molecule should be somewhat dependent on the solvent, so as to decrease with increasing dielectric constant of the environment. The researches of H. Mueller[2,9] have shown that

(6) Latimer and Rodebush, THIS JOURNAL, **42**, 1419 (1920).

(7) Hildebrand, *Science*, **83**, 21 (1936).

(8) Pauling, THIS JOURNAL, **57**, 2680 (1935); *ibid.*, **58**, 94 (1936).

(9) H. Mueller, *Physik. Z.*, **35**, 346 (1934).

in spite of occasional irregularities, a general effect of this type exists. The effect is of the expected order of magnitude. Mueller's results[9] for the temperature dependence of μ_{app} in solutions support the view that the "radius" a should be treated as a molecular constant. It is worth pointing out that the present theory gives a precise interpretation for the dielectric constants of dilute solutions: except for the susceptibility due to elastic polarization (refractive index), the increment of the dielectric constant is a measure for $(\mu^*)^2$, as given by our Eq. 42. We should also mention that the recent calculations by R. M. Fuoss[10] of the dielectric properties and of molecular interaction of salt molecules in non-polar solvents are in accord with the present theory, if only his electric moments, which he denotes by μ, are identified with our "external" electric moments μ^*.

As regards the electrostatic interaction of polar molecules in dilute solutions, Fuoss' computations are carried to a higher degree of approximation. A comparison with his results shows that in cases of extremely strong molecular interaction, the predictions of the present, simpler theory are subject to considerable modification. This disagreement should be taken as a warning against uncritical application of the present theory, which purports to be no more than a first approach to the complete description of dielectrics.

In our computations, the neighborhood of a molecule is considered as a continuum, thus neglecting its actual discrete structure. Moreover, the polarization of the neighboring liquid by a given molecule was considered as proportional to the field, while actually this relation might be modified by compression and by some sort of dielectric saturation. In spite of these shortcomings, the theory apparently accounts for a considerable field of experience, and there is some indication that an outstanding class of discrepancies are due to the physical assumptions involved in the conventional molecular model, and not to the mathematical approximations.

Summary

1. The dipole theory of dielectrics, as originally developed with the aid of Mosotti's formula

(10) R. M. Fuoss, THIS JOURNAL, **56**, 1027, 1031 (1934).

for the "internal field," leads to the expectation of electrical Curie points, with attendant instability for liquids of high dielectric constants. This prediction is not verified by experience.

2. The field which acts upon a molecule in a polarized dielectric may be decomposed into a *cavity field* G, given by the shape of the molecule and proportional to the external field intensity, and a *reaction field* R, which is proportional to the total electric moment, and depends on the instantaneous orientation of the molecule.

3. The mean orientation of a molecule is determined by the orienting force-couple exerted by the cavity field G upon the electric moment of the molecule. The earlier naïve application of the Mosotti formula is equivalent to the assumption that the effective orienting field equals the average of (G + R), and incorrect because R never exerts a torque upon the molecule.

4. Since all real molecules are electrically deformable, the reaction field R will cause an enhancement of the electric moment of any molecule immersed in a dielectric. The induced moment due to the cavity field G will be similarly enhanced by the corresponding component of R.

5. The electric moment μ of a spherical molecule is computed as a function of the dielectric constant ϵ of the environment. In addition, it is convenient to consider an "external" electric moment μ^*, which determines the interaction of the molecule with all distant charges and long range fields in the dielectric. For spherical molecules, the ratio μ^*/μ increases from unity to 3/2 as the dielectric constant of the environment increases from 1 to ∞. Both μ and μ^* approach limits, which depend on the deformability of the molecule, for $\epsilon \longrightarrow \infty$. Accordingly, no Curie point is expected.

6. For simplicity, the computations are restricted to spherical molecules. The resulting formulas for the dielectric constants of pure polar liquids are similar to those proposed on empirical grounds by Wyman. For solutions of polar molecules in non-polar liquids the predictions of the earlier theory are largely upheld, but with certain minor modifications which are in qualitative agreement with the experiments of Horst Mueller.

NEW HAVEN, CONN.   RECEIVED JUNE 1, 1936