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I hereby recommend that the thesis prepared under my supervision by Mack Tyner Jr.

entitled A Study of Polar Liquids

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

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A STUDY OF POLAR LIQUIDS

A dissertation submitted to the

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by

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CONTENTS

LIST OF SYMBOLS

$\vec{B}$ Magnetic induction

c the velocity of light

$\vec{D}$ Electric displacement

$\vec{E}$ Electric field intensity

$\vec{e}$ microscopic field intensity

$f = \frac{n^2+2}{3} \cdot \frac{2\varepsilon+1}{2\varepsilon+n^2}$

$\vec{G}$ Cavity electric field

$\vec{H}$ Magnetic field intensity

$\vec{h}$ Microscopic magnetic field intensity

$\vec{i}$ Current

k Boltzmann's constant

L Avogadro's number

$\vec{M}$ Magnetic moment per c.c.

$\vec{m}$ Magnetic moment per molecule

N Number of molecules per c.c.

n index of refraction

$\vec{P}$ Electric moment per c.c.

$\vec{p}$ Electric moment per molecule

$\vec{R}$ Reaction field

T Absolute temperature

V Molar volume

x Mol fraction

α A constant independent of density, $= \frac{3}{4\pi N} \frac{n^2-1}{n^2+2}$

$\beta = \frac{2\pi N}{9kT} \mu^2$

σ Conductivity of dielectric phase

$\delta = (n^2+2)^{-1}$

ε Dielectric constant

η Loss angle defined as $\eta = \frac{\pi}{2} - \theta$

θ Power factor angle

ρ Electric charge density

τ Relaxation time

μ Permanent moment of the molecule. Also in part II only, μ is magnetic permeability

χ Susceptibility

FOUN DATIONS OF CLASSICAL THEORY OF DIELECTRICS

The conventional Maxwell equations are called the "macroscopic field equations" because they do not aim to take direct cognizance of the molecular theory of matter. The Maxwell equations are: (vectors are designated by an arrow over the symbol)

$$\text{curl } \vec{E} = -\frac{1}{c}\,\partial E/\partial t \qquad \text{curl } \vec{H} = \frac{1}{c}\,(4\pi\vec{i} + \partial D/\partial t) \quad (1)$$

$$\text{div } \vec{D} = 4\pi\rho \qquad \text{div } \vec{B} = 0 \quad (2)$$

where $\vec{E}$ is the electric intensity defined by $\vec{F}/q$

(force / unit charge)

$\vec{D}$ is the electric displacement

ρ is the electric charge density per unit volume

$\vec{B}$ is the magnetic induction

$\vec{H}$ is the magnetic intensity (analogue of $\vec{D}$)

$\vec{i}$ is the current density

c is the velocity of light.

The magnetic equations are given to show how the two properties, magnetic and electric, parallel each other. As will be seen later this parallelism probably led to the first great step toward the explanation of the electric properties of polar substances from the accepted magnetic theory. In addition to the Maxwell equations, there exists the equations between the four field vectors which may be regarded as defining

the dielectric constant ε and the magnetic permeability μ.

$$\vec{D} = \varepsilon \vec{E} \qquad \vec{B} = \mu \vec{H} \qquad (3)$$

The ratios ε and μ are, except for ferromagnetic media, independent of the field strength for sufficiently small fields; and in general one must have such an independence, or a known dependence on the field strength before equations (1) and (2) become unambiguous enough to be useful. It is supposed that all media discussed here are isotropic, i.e. properties are not directional.

The ratios ε and μ depend on many factors, notably on the temperature, density, chemical constitution, and the frequency, as well as the field strength, if great. The theoretical description of their modes of dependence is accomplished by means of the molecular theory of matter, and especially by means of the dynamics governing the electrons within each atom or molecule. The twentieth century produced the electrical origin of matter, unknown to Clark Maxwell when he developed his macroscopic equations in 1861-73. The electrical origin of matter implied that by considering the subatomic distances it should be possible to formulate the equations of electrodynamics in terms of charges in vacuo, without the introduction of dielectric and magnetic media. Therefore, H.A.Lorentz proposed and studied what are called the "microscopic field equations",

$$\text{curl } \vec{e} = -\frac{1}{c}\,\partial\vec{h}/\partial t \qquad \text{curl } \vec{h} = \frac{1}{c}(4\pi\rho'\vec{v} + \partial\vec{e}/\partial t) \qquad (4)$$

$$\text{div } \vec{e} = 4\pi\rho' \qquad \text{div } \vec{h} = 0 \qquad (5)$$

which are similar in structure to the macroscopic equations in a vacuum, except that instead of the current density $\vec{i}$ Lorentz introduced the convection current density $\rho'\vec{v}$ due to motion of the charge with the velocity $\vec{v}$. The microscopic fields, $\vec{e}$, $\vec{h}$, and charge ρ' are not the same as the macroscopic fields or charge.

Equations (4) and (5) are more fundamental than equations (1), (2), and (3), as (4) and (5) are supposed to hold at every point either inside or outside the molecule; whereas equations (1), (2) and (3) are statistical in nature, and the expressions $\vec{E}$, $\vec{D}$, $\vec{H}$, $\vec{B}$, and which they involve must be correlated in some way with averages of microscopic fields and charges over a large number of molecules. It turns out that $\vec{E}$ and $\vec{B}$ are identical with the microscopic fields averaged over a "physically small" element of volume, so that

$$\vec{E} = \vec{e}_{average} \qquad \text{and} \qquad \vec{B} = \vec{h}_{average} \qquad (6)$$

In order to describe the statistical significance of $\vec{D}$ and $\vec{H}$, or of the constitutive relations in terms of the microscopic theory, it is necessary to write, as customary,

$$\vec{D} = \vec{E} + 4\pi\vec{P} \qquad \vec{B} = \vec{H} + 4\pi\vec{M} \qquad (7)$$

The expressions $\vec{P}$ and $\vec{M}$ so defined are called the electric and magnetic polarisations respectively, and the quotients

$$\vec{P}/\vec{E} = (\epsilon-1)/4\pi = \chi_e \qquad \vec{M}/\vec{H} = (\mu-1)/4\pi = \chi_m \quad (8)$$

are called the electric and magnetic susceptibilities. In order to get the electric charge per molecule, form the general expression

$$e_{mol} = \iiint_{1\,Molecule} \rho' \, dv, \text{ and} \quad (9)$$

$$\vec{p} = \iiint_{1\,Molecule} \rho' \vec{r} \, dv \qquad \vec{m} = 1/2c \iiint_{1M} \rho' (\vec{r} \times \vec{v}) dv \quad (10)$$

in which the integration is to include only the charge which belongs to a single molecule. In general molecules may overlap each other, but it is assumed that the charges of a given molecule can still be identified as such. The origin for the radius vector $\vec{r}$ is taken as the center of gravity of the molecule and its velocity is supposed negligible. If the molecule is electrically neutral, the integral in (9) vanishes and the origin for $\vec{r}$ is immaterial in the first integral of equation(10). The expressions for $\vec{p}$ and $\vec{m}$ defined by equation (10) are called the electric and magnetic moments of the molecule. In the conventional electron theory it is customary to suppose the dimensions of the electrons and nuclei are negligible, then the integrations may be replaced by summations over all the discrete charges making up the molecule, giving

$$e_{molecule} = \sum_i e_i \; ; \qquad \vec{p} = \sum_i e_i \vec{r_i} \; ; \; \vec{m} = 1/2c \sum_i e_i (\vec{r_i} \times \vec{v_i}) . \quad (11)$$

The contribution of a particle to the magnetic moment differs from its angular momentum $m_i(\vec{r}_i \times \vec{v}_i)$ only by a factor $\frac{e_i}{2m_ic}$.

The expressions $\vec{P}$ and $\vec{M}$, as defined in equation (7), are equal respectively to the average electric and magnetic moments $\vec{p}_{av.}$ and $\vec{m}_{av.}$ per molecule multiplied by the number of molecules per c.c., so that

$$\vec{P} = N\vec{p}_{average} \qquad \vec{M} = N\vec{m}_{average} \qquad (12)$$

Then the desired correlation equations for $\vec{D}$ and $\vec{H}$ are

$$\vec{D} = \vec{e}_{av.} + 4\pi N\vec{p}_{av.} \qquad \vec{H} = \vec{h}_{av.} - 4\pi N\vec{m}_{average} \qquad (13)$$

The term average moment per molecule means the molecular moment averaged over all the molecules in a "physically small" volume element. This is equivalent to the time average moment for an individual molecule if all the molecules are alike but for phase. The information conveyed by equation (13) must be regarded as a very important theorem on the physical or macroscopic significance of the mean molecular moments for it interprets the distinction between $\vec{D}$ and $\vec{E}$, or between $\vec{B}$ and $\vec{H}$, in terms of simple properties (equation 10) of the molecules. Equation (12) underlies all theories of dielectrics and magnetic media. This concept of the polarisation of the molecule as the cause of the departures of ε and μ from unity is not new and was intimated by Faraday in his

studies.

To complete the correlation of the macroscopic and the microscopic equations it must be stated how the currents and charges are connected. The convection current arises entirely from the migration of conduction electrons, rather than molecular ions, if the velocity of the center of gravity of a molecule is negligible, then the current and charge densities are given by

$$\vec{i} = -N_c e (\vec{v_c})_{average} \qquad \rho = N (e_{mol})_{average} - N_c e$$

where N_c is the number of conduction electrons per c.c., and $\vec{v_c}$ is their velocity. Similarly N denotes the number of molecules per c.c. and $(e_{mol})_{av}$ is the mean value of their net charges (equation 9).

It is desirable to know the effective average field to which a molecule is subjected when a macroscopic field $\vec{E}$ is applied. This effective field is not the same as the macroscopic field despite the fact that by equation (6) the the vector $\vec{E}$ is the space average of $\vec{e}$ over a "physically small" volume element. This effective field within a molecule may be resolved into two parts: (a) the internal field exerted by other charges within the same molecule, and (b) the remainder due not only to the applied electric field but also tot the attractions and repulsions by

other molecules, usually polarized under the influence of the external field. This second part is termed the local field and it is calculated differently depending upon the specific suppositions made.

The above is true for all dielectric and magnetic madia and it is now necessary to get toward the point of the discussion. For the study of dielectric phenomena, molecules are divided into two groups- polar and nonpolar. A molecule is polar if it has an electrical moment which is on the time average different from zero even in the absence of external electric fields. To find theppermanent moment one must retain out of the total moment $\sum_i e_i \vec{r}_i$ only the constant part which remains on averaging over the "internal" motions of the electrons relative to the nuclei. The mean square of the electric moment is not zero, for all atoms and molecules contain instantaneous moments which fluctuate with the positions of the electrons; but the square of the means may vanish, and if it does the molecule is nonpolar.

THE DEBYE-CLAUSIUS-MOSSOTTI EQUATION

Under certain simplifying assumptions the local field can be shown to be

$$\vec{e}_{local} = \vec{E} + 4\pi/3\ \vec{P} \qquad (14)$$

where $\vec{P}$ is the total electric moment per c.c., and

$\vec{E}$ is the electric intensity.

This expression is the Clausius-Mossotti formula for the local field and is the basis of the Debye theory of molecular dielectrics. The usual derivations of this expression for the local field assume that the molecule in question can be considered to be located at the center of a spherical cavity in the dielectric and that the diameter of the cavity is large compared to the size of a molecule. One must remember that the field within a cavity is a function of the shape of the cavity. It has the value (14) at the center of a spherical cavity, a value $\vec{E}$ within a needle-shaped cavity whose axis is parallel to $\vec{E}$, and a value $\vec{D} = \vec{E} + 4\pi\vec{P}$ within a slab-shaped cavity whose surfaces are perpendicular to $\vec{E}$. The term $4\pi/3\ \vec{P}$ in equation (14) is sometimes called the "inter-molecular field", and is a correction for the fact that the other molecules of the dielectric exert an average force on the given molecule (induced polarisation) when the dielectric

is subject to an electric field. The idea of induced polarization is an old one, as it was used in Mossotti's theory of susceptibility.(2)

At ordinary field strengths for nonpolar liquids the average electrical moment may be taken proportional to the local field, thus:

$$\vec{P}_{average} = \alpha \vec{e}_{local} \qquad (15)$$

where α is a constant independent of the density. By elimination of $\vec{p}$ and $\vec{P}$ by means of equations (8) and (12) one obtains a form of the Lorenz-Lorentz formula:

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

The number of molecules per c.c. is proportional to the density d, hence for nonpolar media, in general,

$$\frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{1}{d} = \frac{4\pi}{3} \frac{N}{d} \alpha \quad , \text{ a constant independent of density.} \qquad (16)$$

This is the well-known Lorenz-Lorentz formula as it was proposed by L. Lorenz and H.A. lorentz, both in 1880. Equation (16) is also known in the same form as above with ε replaced by n^2, the square of the index of refraction. This exchange is permissible provided that the magnetic permeability is unity, for the index of refraction is related with the dielectric constant and magnetic permeability according to this equation

$$n^2 = \varepsilon \mu$$

provided the term dielectric constant is used in a generalized sense to mean the ratio of $\vec{D}$ to $\vec{E}$ in periodic fields rather than in the restricted sense to denote this ratio in static phenomena.

If the dielectric constant can be considered independent of the field strength, P. Debye[3] showed that the electric susceptibility for polar media (gases only) is given by the expression

$$\chi_e = \frac{3}{4\pi}\frac{\varepsilon-1}{\varepsilon+2} = N\left(\alpha + \frac{\mu^2}{3kT}\right) \approx \frac{\varepsilon-1}{4\pi} \quad (\varepsilon \approx 1) \qquad (17)$$

which is called the Langevin-Debye formula. In this equation N is the number of molecules per c.c., T the absolute temperature, k is Boltzmann's constant, μ is now the magnitude of the permanent moment of the molecule not the magnetic permeability (as will be true throughout the remainder of the discussion), and is a constant given by equation (16). The existence of a susceptibility requires that the molecule have an average electrical moment in the direction of the applied field. The suggestion that part of the electric susceptibility might be due to alignment of the permanent moments, restricted by temperature agitation, did not appear until 1912, when Debye[3] used this idea in developing his theory of polar molecules. A magnetic susceptibility due entirely to orientation of permanent moments was suggested in 1905

by Langevin and the second term of equation (17) is thus an adaptation to the electric case of Langevin's magnetic formula. By equating equations (8) and (17) one obtains the customary Langevin-Debye-Clausius-Mossotti formula: $\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi N}{3}\left(\alpha + \frac{\mu^2}{3kT}\right)$

By a slight generalization of this equation, it was applied to dilute solutions of polar molecules in nonpolar solvents. If the molecules are supposed to have no effect on each other, then

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi}{3}\sum_i N_i\left(\alpha_i + \frac{\mu_i^2}{3kT}\right) \qquad (18)$$

where the subscript i denotes the ith species of molecule present in the solution.

The dielectric properties of gases can be satisfactorily accounted for in terms of molecular constants by means of the Debye-Clausius-Mossotti equation. Also it holds quite accurately for nonpolar liquids, and it gives values of permanent moments which are fairly consistent with those calculated from dielectric constants of polar gases when applied to dilute solutions of polar molecules in nonpolar solvents.[3] But in concentrated solutions and in pure polar liquids equation (18) becomes entirely inapplicable, as may be seen by close inspection of

the expression. Equation (18) predicts for polar liquids many properties which they do not possess,[4,5,6] e.g.it predicts a critical temperature analogous to a "Curie point", the theory predicts a stable state of permanent electric polarisation, all of which are not phenomena common to many polar liquids. The expression predicts points of great instability as to variations of electric susceptibility with pressure, temperature, volume, and field strength which are not experimentally observed.

The Debye-Clausius-Mossotti theory evidently contains several fundamental inaccuracies. Among these are: (1) the assumption of an unvarying moment for the molecule in solution, (2) the inclusion of the reaction field in the total orienting field acting on the molecule, and (3) the value of the internal field $\left(\frac{\epsilon+2}{3}\right)\vec{E}$ being inadequate. This value of the internal field has been derived rigorously only for cubic crystals and for very dilute gases.[1] The success that the equation has in explaining the properties of polar gases is no evidence for its general validity since the internal polarization of gases is negligible.

THE ONSAGER EQUATION

A number of empirical equations have been suggested to avoid the inadequaces of the Debye-Clausius-Mossotti theory and to account for the high electric susceptibilities of polar liquids. The most successful attempt to do this was the equation proposed by van Arkel and Snoek[7]

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi N}{3}\left(\alpha + \frac{\mu^2}{CN\mu^2 + 3kT}\right) \qquad (19)$$

This equation differs from equation (18) only in the term $CN\mu^2$, which was deliberately introduced to reduce the importance of the dipole orientation term $\frac{\mu^2}{3kT}$. With the exception of the hydrogen bonding liquids, the value of C does not vary greatly from one polar liquid to another and it is only slightly temperature dependent and for concentrated solutions of a given polar substance in nonpolar solvents it varies but little with the nature of the solvent. Müller[8] concludes that the term $CN\mu^2$ is three-halves of the energy of the dipole in its own reaction field, i.e.

$$CN\mu^2 = \tfrac{3}{2} R\mu \qquad (20)$$

whereas, Böttcher[9] found that the term is just equal to the energy μR, and that Onsager's theory predicts that value for upon substituting $CN\mu^2 = \mu\vec{R}$ into equation (19) and using Onsager's value of the reaction field $\vec{R}$, he obtained Onsager's equation for dielectricconstants.

In 1936 Lars Onsager[5] noting that the Clausius-Mossotti internal field was inadequate, derived an alternate expression for it. He represented 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 medium of dielectric constant ε; the radius $\underline{a}$ of the cavity is of the order of the radius of the molecule. For this model, it is found by classical electrostatics that the internal field acting on the dipole may be represented as the resultant of two fields $\vec{G}$ and $\vec{R}$; the reaction field $\vec{R}$ is caused by polarization of the surrounding medium by the field of the dipole (it acts parallel to the instantaneous dipole $\vec{p}$ and exists even in the absence of an applied field); the cavity field $\vec{G}$ is caused by, and acts parallel to, the applied field $\vec{E}$. These fields are found by calculation to have the following values

$$\vec{R} = \frac{2(\varepsilon-1)}{2\varepsilon+1}\,\frac{1}{a^3}\,\vec{p} \qquad \vec{G} = \frac{3\varepsilon}{2\varepsilon+1}\,\vec{E} \tag{21}$$

where $\vec{p}$ represents the instantaneous magnitude and direction of the dipole and $\underline{a}$ is the radius of the cavity. Onsager pointed out that the value of the reaction field obtained by his calculations is not strictly applicable to any liquid because of the simplified molecular model.

Under the influence of the fields $\vec{R}$ and $\vec{G}$, the molecule will be polarized so that its dipole moment will be, not the permanent moment μ, but

$$\vec{p} = \mu \vec{u} + \frac{3\epsilon}{2\epsilon+1} \alpha \vec{E} + \frac{2(\epsilon-1)\alpha}{(2\epsilon+1)a^3} \vec{p} \qquad (22)$$

where $\vec{u}$ is a unit vector in the direction of the permanent dipole μ. After this expression is solved for $\vec{p}$, it is easy to calculate the potential energy of the dipole as a function of its orientation in the applied field, and by the application of Boltzmann's statistics to evaluate $\vec{p}_{average}$, the average moment in the direction of the applied field. The substitution of this value of average $\vec{p}$ in equation (12) will give the Onsager equation.

It is convenient, so that the equation will reduce to the Debye equation for nonpolar liquids, to substitute

$$\frac{4\pi N}{3} a^3 = 1 \text{ cm}^3 \qquad (23)$$

and for the polarizability α, the index of refraction

$$\frac{n^2-1}{n^2+2} = \frac{4\pi N}{3} \alpha = \frac{d}{M} (P_{electronic} + P_{atomic}) \qquad (24)$$

where M/d is the molar volume of the substance.

Then Onsager's equation for the dielectric constant of polar liquids with the added supposition that terms involving powers of $\vec{E}$ higher than the first are negligible is

$$\frac{\epsilon - n^2}{\epsilon} \cdot \frac{2\epsilon + n^2}{(n^2+2)^2} = \frac{4\pi N}{3} \frac{\mu^2}{3kT} \qquad (25)$$

In the development of the theory no account was taken of the optical anisotropy of the polar molecule. 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. Onsager realized that this method can give only a rough approximation to the value of the reaction field for several reasons: (1) the treatment of the molecule as a sphere containing a point dipole, (2) the treatment of the environment as a homogeneous continuum, (3) neglect of dielectric saturation in considering the effect of strong fields in the vicinity of the dipole, (4) and the arbitrary choice of the value of a, the radius of the cavity.

Böttcher[10] found by use of equation (25) that permanent moments calculated by this formula are sufficiently independent of temperature and are in good agreement with values determined in gases and in dilute solutions except with associating liquids (water, alcohols, and organic acids) and in cases where the dipole moment is changed by mechanical interaction of the molecules (esters, etc.). He found that for liquids

possessing high dielectric constants the method was better than determining the permanent moment in dilute solutions.

Kirkwood[11] devised a very elegant theoretical treatment which takes into account the effect of association and placed the theory on a firmer foundation. For a liquid made up of molecules of permanent moment and polarizability zero (i.e., $n^2=1$), he derived an equation of the same form as Onsager's but with n^2 replaced by unity and μ^2 replaced by $\vec{\mu}\cdot\vec{\bar{\mu}}$. $\vec{\bar{\mu}}$ is the average resultant of the moments of all molecules included within a spherical volume, of radius large compared to molecular dimensions, circumscribed about a given dipole as a center. Then the value of $\vec{\mu}\cdot\vec{\bar{\mu}}$, calculated by statistical methods, formally accounts for dipole association in his theory. Association of polar liquids has not been studied further in this discussion.

George Jaffé[12] has applied two propositions in the calculus of probabilities to the analysis of the local field in polarized dielectrics. He found an implicit formula for the dielectric constant which represents the extension of Onsager's result to dielectrics of

variable densities down to the densities of gases. There is a formal similarity of Jaffé's results with those of Kirkwood's modification of Onsager's theory, but it is apparent that Kirkwood's treatment is superior to Jaffé's as regards the atomic and molecular picture. However, Jaffé established a more general connection between the actual permanent moment μ_o in vacuo and the μ in solution than did Onsager.

DISPERSION AND ABSORPTION

An anomalous dispersion for liquids for relatively long waves, i.e. a decrease of dielectric constant with increasing frequency, was first observed by P. Drude[13], who found that the effect existed only for a certain kind of molecule where special groups, -OH, $-NH_2$, existed. P. Debye[3] noted that the characteristic property of the liquids with anomalous dispersion is the polarity of their molecules, and that the effect represented the transition of the combined orientation and distortion polarization to a pure distortion polarization of the molecules. The dividing line between the two effects occurs at a frequency ω defined by $\omega\tau = 1$, where τ is the time of relazation of the liquid, or the time required for the moments of the molecules to revert to a random distribution after removal of the imposed field. In his analysis Debye found that for periodic fields the factor determining the orientation part of the dielectric constant should be multiplied by a complex factor $\frac{1}{1+i\omega\tau}$. The meaning of the complex factor is that there exists a phase difference between the moment and the internal force. This phase difference between field intensity and polarization is always accompanied by energy absorption. Therefore, as a result of the existence of

of a finite relaxation time one will not only encounter dispersion but also absorption intimately connected with it.

Debye[3] applied this idea to the Debye-Clausius-Mossotti equation for dielectrics and it is the object of this section of the discussion to apply the same idea to the Onsager equation and thereby obtain dispersion and absorption equations for polar liquids.

The Onsager equation is

$$(\varepsilon - n^2)\,\frac{2\varepsilon + n^2}{\varepsilon} = \frac{4\pi N}{3}(n^2+2)^2\,\frac{\mu^2}{3kT} \qquad (25)$$

In order to simplify the equation to one of the first degree in ε to facilitate its solution, it is supposed that ε is sufficiently large that

$$\frac{2\varepsilon + n^2}{\varepsilon} = 2 + \frac{n^2}{\varepsilon} \approx 2$$

Then multiplying the moment by the complex factor $\frac{1}{1+i\omega\tau}$ and substituting the complex dielectric constant, $\varepsilon = \varepsilon' - i\varepsilon''$, one obtains the following equation which contains both an absorption equation and a dispersion equation:

$$\varepsilon' - i\varepsilon'' - n^2 = \frac{\beta\delta}{1+i\omega\tau} \qquad (26)$$

where $\beta = \frac{2\pi N}{9kT}\mu^2$ and $\delta = (n^2+2)^2$. Now by equating the real terms and the imaginary terms of each side, these equations result:

for dispersion $$\varepsilon' = n^2 + \frac{\beta\delta}{1+\omega^2\tau^2} \qquad (27a)$$

for absorption $$\varepsilon'' = \frac{\omega\tau\beta\delta}{1+\omega^2\tau^2} \qquad (27b)$$

It can be seen by differentiation of the above equations that equation (27a) does not show a maximum value for

the dielectric constant but that equation (27b) does possess a maximum value, $\varepsilon''_{max.}$, at a value of $\omega\tau = 1$. There is no suitable experimental data available to enable one to discriminate between these equations and the Debye equations but in view of the success of the Onsager equation one will prefer these equations. Both these and the Debye equations give curves of the general form of the experimental data available on solids and highly associating liquids, both of which are excluded from the theory. If ε'_{max} is the value of the dielectric constant at the frequency where ε'' has the value $\varepsilon''_{max.}$, then

$$\varepsilon''_{max} = \frac{\beta\delta}{2} \qquad \text{and} \qquad \varepsilon'_{max} = n^2 + \frac{\beta\delta}{2} \qquad (28)$$

By applying the fundamental theorems of electricity and supposing that the direct current conductivity of the dielectric is negligible, one can show that if, as in polar liquids, the medium has a complex dielectric constant, $\varepsilon = \varepsilon' - i\varepsilon''$, then the liquid has a complex conductivity, $\gamma = \gamma' + i\gamma''$, where

$$\gamma' = \frac{\varepsilon''\omega}{4\pi} \qquad \text{and} \qquad \gamma'' = \frac{\varepsilon'\omega}{4\pi} \qquad (29)$$

Generally, the alternating current conductivity is not referred to but instead one uses the loss angle η defined as $\eta = \frac{\pi}{2} - \theta$ where θ is the phase angle between the instantaneous

current and voltage vectors. Then

$$\tan \eta = \frac{\varepsilon''}{\varepsilon'} = \frac{\gamma'}{\gamma''}$$

and the familiar power factor is given by

$$\cos \theta = \frac{\varepsilon''}{\sqrt{\varepsilon''^2 + \varepsilon'^2}} = \frac{\gamma'}{\sqrt{\gamma'^2 + \gamma''^2}}$$

The scalar product of the current and voltage vectors gives the instantaneous power consumed by the system and the mean power can be obtained by integration over a whole number of half periods giving:

mean power per second $= \gamma' \frac{E_o^2}{2}$ ergs/sec.

mean power per cycle $= \varepsilon'' \frac{E_o^2}{4}$ ergs/cycle

where E_o is the amplitude of the voltage vector. (E_o here is not to be confused with $\vec{E}$ the electric intensity).

It is easily seen that since the loss factor ε'' depends on the frequency, that by equation (29) the conductivity factor γ' will also depend on the frequency according to $\gamma' = \frac{\beta \delta}{4\pi} \cdot \frac{\omega^2 \tau}{1+\omega^2 \tau^2}$

A study of this equation shows that the conductivity of any dielectric to which the equation applies should always increase with the frequency, where it changes at all. The most interesting feature of this equation is that as the frequency increases indefinitely, γ' approaches a limiting value γ'_∞,

$$\gamma'_\infty = \frac{\beta \delta}{4\pi} \cdot \frac{1}{\tau} \qquad (30)$$

According to E. Murphy and S. Morgan[14], the leveling off of the conductivity curve at high frequencies is not observed in all materials. For many materials the

conductivity continues to increase as the frequency becomes higher, although the rate of increase is often not great. The equation was obtained by making the simplest assumptions which could be made regarding the structure of a dielectric and it is to be expected that many complex materials will not have a conductivity which obeys these equations.

The comparison of equation (30) with equation(28) brings out the contrast between the maximum dielectric loss per cycle ε''_{max} and the maximum dielectric loss per second δ'_∞. The maximum dielectric loss per cycle is completely determined by the difference between the static dielectric constant and the optical dielectric constant, n^2.

$$\varepsilon_s - n^2 = \beta\delta$$

On the other hand, the dielectric loss per second, ε'_∞, depends as well on τ. τ usually varies with temperature whereas $\beta\delta$ changes comparatively slowly with temperature. The temperature dependence of the maximum dielectric loss per cycle is related to the polarizability of the material; whereas, the temperature variation of the maximum dielectric loss per second is primarily a measure of the change of internal friction with temperature.

A METHOD FOR DETERMINING DIPOLE MOMENTS FROM SOLUTION DATA

The Onsager equation can be applied to solutions of any number of components of liquids both polar and nonpolar. The equation for solutions of polar liquids does not yield any interesting results because of the presence of the electric moments for all the polar molecules; however, in case one of the components has a nonpolar molecule, then the two component equation should yield a method of calculating the electric moment of the polar molecule.

The general Onsager equation for an n-component solution is

$$\frac{\epsilon-1}{4\pi}V = \frac{\vec{P}}{\vec{E}}V = \sum_i N_i\left(\frac{\mu_i\mu_i^*}{3kT} + \frac{\epsilon(n_i^2+2)}{2\epsilon+n_i^2}\alpha_i\right); \quad i = 1,2\cdots n, \tag{31}$$

where $\frac{\epsilon-1}{4\pi}V$ is the molal polarizability of the solution

α_i is the polarizability of ith molecule

$$\alpha_i = \frac{n_i^2-1}{n_i^2+2}a_i^3, \text{ and } a_i^3 = \frac{3}{4\pi}\frac{x_i V_i}{N_i}$$

V is the total volume of solution

ϵ is the dielectric constant of the solution

V_i is the molar volume of ith component, $V_i = \frac{M_i}{d_i}$

x_i is the mol fraction of ith component in solution, $x_i = \frac{N_i}{N_1+\cdots N_i}$

Then the equation for a two-component system made

up of a nonpolar solvent and a polar solute will be as follows:

$$\frac{\varepsilon-1}{4\pi}V = N_1\frac{\varepsilon(n_1^2+2)}{2\varepsilon+n_1^2}\alpha_1 + N_2\left(\frac{\mu_2\mu_2^*}{3kT} + \frac{\varepsilon(n_2^2+2)}{2\varepsilon+n_2^2}\alpha_2\right) \quad (32)$$

where $\alpha_1 = \frac{n_1^2-1}{n_1^2+2}\cdot\frac{3}{4\pi}\frac{x_1V_1}{N_1}$ and $\alpha_2 = \frac{3}{4\pi}\frac{n_2^2-1}{n_2^2+2}\cdot\frac{x_2V_2}{N_2}$

and the subscripts 1 and 2 refer to nonpolar and polar molecules respectively.

A new equation can be obtained by differentiating this equation with respect to the polar molecule concentration and by applying this differential equation in the limit as the polar molecule concentration approaches zero. Then for the pure nonpolar solvent $\varepsilon = n_1^2$. The simplified equation for a nonpolar component and a polar component is

$$\frac{\varepsilon-1}{4\pi}V = \frac{3\varepsilon}{4\pi}\left[\frac{N_1x_1V_1}{N_1}\cdot\frac{n_1^2+2}{2\varepsilon+n_1^2}\cdot\frac{n_1^2-1}{n_1^2+2} + \frac{N_2x_2V_2}{N_2}\cdot\frac{n_2^2+2}{n_2^2+2\varepsilon}\cdot\frac{n_2^2-1}{n_2^2+2}\right] + N_2\frac{\mu_2\mu_2^*}{3kT}$$

Remembering that $x_2 = \frac{N_2}{\sum_i N_i} = \frac{N_2}{L}$, or $N_2 = x_2L$, then

$$\frac{\varepsilon-1}{4\pi}V = \frac{x_2L}{3kT}\mu_2\mu_2^* + \frac{3\varepsilon}{4\pi}\left[x_1V_1\frac{n_1^2-1}{2\varepsilon+n_1^2} + x_2V_2\frac{n_2^2-1}{2\varepsilon+n_2^2}\right] \quad (33)$$

Differentiation of the right hand side of the above equation gives

$$\frac{d}{dx_2}\left(\frac{\varepsilon-1}{4\pi}V\right) = \frac{L\mu\mu^*}{3kT} + \frac{3}{4\pi}\left\{V_1(n_1^2-1)\left[x_1\frac{n_1^2}{(2\varepsilon+n_1^2)^2}\frac{d\varepsilon}{dx_2} + \frac{\varepsilon}{2\varepsilon+n_1^2}\frac{dx_1}{dx_2}\right]\right.$$
$$\left. + V_2(n_2^2-1)\left[x_2\frac{n_2^2}{(2\varepsilon+n_2^2)^2}\frac{d\varepsilon}{dx_2} + \frac{\varepsilon}{2\varepsilon+n_2^2}\right]\right\} \quad (34)$$

Since $x_1+x_2 = 1$, then $\frac{dx_1}{dx_2} = -1$. In the right hand

side of the above equation let x_2 approach zero, then $x_1 \rightarrow 1$ and also $\epsilon = n_1^2$ (nonpolar) which gives

$$\frac{d}{dx_2}\left(\frac{\epsilon-1}{4\pi}V\right) = \frac{L}{3kT}\mu_2\mu^* + \frac{3}{4\pi}\left\{V_1(n_1^2-1)\left[\frac{1}{9\epsilon}\frac{d\epsilon}{dx_2} - \frac{1}{3}\right] + V_2(n_2^2-1)\left[\frac{\epsilon}{2\epsilon+n_2^2}\right]\right\} \quad (35)$$

Now differentiate the left hand side of equation (34) to obtain

$$\frac{d}{dx_2}\left(\frac{\epsilon-1}{4\pi}V\right) = \frac{1}{4\pi}\left[(\epsilon-1)\frac{dV}{dx_2} + V\frac{d\epsilon}{dx_2}\right]$$

and assume that $V = (1-x_2)\frac{M_1}{d_1} + x_2\frac{M_2}{d_2}$,

whence $$\frac{dV}{dx_2} = \frac{M_2}{d_2} - \frac{M_1}{d_1} = V_2 - V_1$$

so that one obtains

$$\frac{d}{dx_2}\left(\frac{\epsilon-1}{4\pi}V\right) = \frac{1}{4\pi}\left[V\frac{d\epsilon}{dx_2} + (\epsilon-1)(V_2-V_1)\right] \quad (36)$$

Then the final equation becomes

$$\left(V\frac{d\epsilon}{dx_2} + (\epsilon-1)(V_2-V_1)\right) = \frac{4\pi L}{3kT}\mu_2\mu_2^* + \left\{V_1(n_1^2-1)\left[\frac{1}{3\epsilon}\frac{d\epsilon}{dx_2} - 1\right] + 3V_2(n_2^2-1)\frac{\epsilon}{2\epsilon+n_2^2}\right\}$$

or

$$\frac{2\epsilon V_1 + V_1}{3\epsilon}\cdot\left.\frac{d\epsilon}{dx_2}\right|_{x_2\rightarrow 0} + \frac{(2\epsilon+1)(\epsilon-n_2^2)}{2\epsilon+n_2^2}V_2 = \frac{4\pi L}{3kT}\mu_2\mu_2^* \quad (37)$$

This is the equation which may be used to calculate electric moments from experimental data on solutions of polar molecules in nonpolar solvents.

To get values of electric moments in solution, one must note that Onsager gives for μ_s in solution

$$\mu_s = \sqrt{\frac{2\epsilon+1}{3\epsilon}}\mu_2\mu_2^*, \text{ and } \mu_s = \frac{n^2+2}{3}\cdot\frac{2\epsilon+1}{2\epsilon+n^2}\mu_0 \quad (38)$$

where μ_s is the electric moment in an environment of dielectric constant ϵ. Then the final equation is

$$V_1\left.\frac{d\epsilon}{dx_2}\right|_{x_2\rightarrow 0} + \frac{3\epsilon(\epsilon-n_2^2)}{2\epsilon+n_2^2}V_2 = \frac{4\pi L}{3kT}\left(\frac{3\epsilon}{2\epsilon+1}\right)^2\mu_2^2 \quad (39)$$

It appears that this equation will give very

accurate values of permament electric moments provided accurate data are available from dielectric constant measurements of dilute solutions of polar molecules in a series of nonpolar solvents. One of the chief difficulties in applying this equation is the evaluation of $\frac{d\varepsilon}{dx_2}$ as $x_2 \to 0$. This can be overcome somewhat by evaluating $\frac{d}{dx_2}\left(\frac{\varepsilon-1}{4\pi}V\right)\Big|_{x_2 \to 0}$ since $\frac{\varepsilon-1}{4\pi}V$ at low polar molecule concentrations is approximately a linear function of the concentration for many polar molecules.

F. Muller[15] and others[16,17] have shown that the value of the permanent 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 permanet moment of a free polar molecule from studies on its dilute solutions it is necessary to make measurements using a variety of solvents and to extrapolate to dielectric constant of unity. S. Sugden[17] has suggested a convenient method for performing this extrapolation. Onsager gives the effect of surrounding matter of dielectric constant ε and refractive index n upon the electric moment μ_o, in free space, as

$$\mu_{solution} = \frac{n^2+2}{3} \cdot \frac{2\varepsilon+1}{2\varepsilon+n^2} \cdot \mu_o = f \cdot \mu_o \qquad (40)$$

In this equation f is always greater than unity and it indicates that the most satisfactory solvent to use for electric moment determinations would be one of low refractive index as well as low dielectric constant. This equation was derived for liquids. If the density of the solution differs greatly from a normal density of liquids, the results of G. Jaffé's[18] theoretical treatment of the local field in polarized dielectrics may be used. Jaffé obtained, as a general connection between the actual electric moment μ at variable densities and the moment μ_0 in free space, the equation

$$\varphi(z_1, q) = \mu/\mu_0 = 1 + q\, e^{z_1 - q} \int_{z_1 - q}^{\infty} \frac{e^{-t}}{t}\, dt \qquad (41)$$

where $z_1 = \frac{4\pi N}{3} s_1^3$

s_1 is the nearest distance of approach for two molecules,

q is $\frac{2(\epsilon - 1)}{2\epsilon + 1} \cdot \frac{4\pi N}{3} \alpha$

α is the polarizability of the molecule,

t is a parameter,

$\int_{z_1 - q}^{\infty} \frac{e^{-t}}{t} dt$ is the logarithmic integral $-Ei(z_1 + q)$ which may be evaluated from mathematical tables.

For liquids z_1 is usually put equal to unity, then the general equation (41) becomes

$$\varphi(1, q) = \mu/\mu_0 = 1 + q\, e^{1 - q} \int_{1 - q}^{\infty} \frac{e^{-t}}{t}\, dt \quad . \qquad (42)$$

If in case Jaffé's implicit formula for the dielectric constant is to be the same as Onsager's equation, then Jaffé's function must be the same as Onsager's relation between μ and μ_o or

$$\varphi(z_1, g) = \mu / \mu_o = \frac{n^2+2}{3} \cdot \frac{2\varepsilon+1}{2\varepsilon+n^2} \qquad (43)$$

Throughout this paper Onsager's μ_o and Jaffé's μ_o mean the permanent moments in free space. Equation (39) is used to calculate the permanent moment value in solution, then equation (40) is used to find Onsager's μ_o in free space and equation (42) is used to find Jaffé's μ_o in free space. Onsager's μ_o and Jaffé's μ_o are the result of application of two different theories of solvent effect to permanent moment values in solution calculated by equation (39).

CALCULATIONS

The equation for calculating permanent moments from dielectric constant measurements is

$$V_1 \left.\frac{d\epsilon}{dx_2}\right|_{x_2 \to 0} + \frac{3\epsilon(\epsilon - n_2^2)}{2\epsilon + n_2^2} V_2 = \frac{4\pi L}{3kT} \left(\frac{3\epsilon}{2\epsilon + 1}\right)^2 \mu^2$$

Take as an example for calculation the recent data on benzene-morpholine system measured by Smyth and Lewis who obtained a permanent moment value of $\mu = 1.58$. (J. Am. Chem. Soc. 61, 3067 (1939)). Partington and Coomber (Nature, 141, 918 (1938)) obtained a value of $\mu = 1.48$ in benzene . Graphically, from a plot of ϵ vs. x_2, the value of $\left.\frac{d\epsilon}{dx_2}\right|_{x_2 \to 0}$ was calculated as 3.50. Other properties of benzene and morpholine as given by Smyth and Lewis are:

benzene	morpholine
$V_1 = 89.4$ cm^3	$V_2 = 87.4$ cm^3
$\epsilon = 2.276$ at 25.°c	$n_2^2 = 2.11$

Then $89.4(3.50) + \frac{6.84}{6.67}(0.17)\,87.4 = 6.22 \times 10^{37} \left(\frac{6.84}{\sqrt{5.54}}\right)^2 \mu^2$

or $\mu = 1.86 \times 10^{-18} = 1.86$ D

By the Onsager theory: $\mu_o = \frac{1.86}{1.16} = 1.60$ D

By the Jaffé equation: $\mu_o = \frac{1.86}{1.09} = 1.71$ D

Onsager's μ_o and Jaffé's μ_o are the direct results of this thesis and they are to be compared to the accepted permanent moment values.

Here are some additional calculations made from data obtained from the recent literature.

This data on ethyl bromide in carbontetrachloride solution is from Goss (J.Chem.Soc. 752 (1940)). The temperature was 20°C. and the slope $d\varepsilon/dx_2$ was obtained by numerical interpolation. He obtained a value of $\mu = 1.98$ and the accepted value is about $\mu = 2.00$.

$CCl_4 \begin{cases} V_1 = 96.5 \\ \varepsilon = 2.24 \end{cases}$; Ethyl bromide $\begin{cases} V_2 = 74.4 \\ n_2^2 = 2.03 \end{cases}$; $\frac{d\varepsilon}{dx_2} = 4.65$

$$96.5(4.65) + \frac{6.72}{6.57}(0.21)94.4 = 6.33 \times 10^{37}(1.45)\mu^2$$

$\mu = 2.24$ D and (Onsager) $\mu_0 = 1.95$ D ; (Jaffé) $\mu_0 = 2.07$ D.

This data on chloroform in carbontetrachloride solution was measured at 20°C. by Goss. He obtained a value of $\mu = 1.05$.

$CCl_4 \begin{cases} V_1 = 96.5 \\ \varepsilon = 2.24 \end{cases}$; $CHCl_3 \begin{cases} V_2 = 80.3 \\ n_2^2 = 2.09 \end{cases}$; $\frac{d\varepsilon}{dx_2} = 1.59$

$$96.5(1.59) + \frac{6.72}{6.57}(0.15)80.3 = 6.33 \times 10^{37}(1.50)\mu^2$$

$\mu = 1.32$ D ; Onsager's $\mu_0 = 1.15$; Jaffé's $\mu_0 = 1.22$

For a comparison of measurements made in two solvents, take Goss's measurements made on ethanol in both carbontetrachloride and benzene. In benzene at 20°C, he obtained

benzene $\begin{cases} V_1 = 89.4 \\ \varepsilon = 2.28 \end{cases}$; ethanol $\begin{cases} V_2 = 58.4 \\ n_2^2 = 1.85 \end{cases}$; $\frac{d\varepsilon}{dx_2} = 3.88$

$$89.4(3.88) + \frac{6.84}{6.41}(0.43)58.4 = 6.33 \times 10^{37}(1.51)\mu^2$$

$\mu = 1.98$ D and Onsager's $\mu_0 = 1.91$ D ; Jaffé's $\mu_0 = 1.81$ D

In carbontetrachloride at 20°C, he obtained

$CCl_4 \begin{cases} V_1 = 96.5 \\ \varepsilon = 2.24 \end{cases}$ - ethanol $\begin{cases} V_2 = 58.4 \\ n_2^2 = 1.85 \end{cases}$; $\frac{d\varepsilon}{dx_2} = 2.95$

$$96.5(2.95) + \frac{6.72}{6.33}(0.39)58.4 = 6.33 \times 10^{37}(1.45)\mu^2$$

$\mu = 1.85$ D and Onsager's $\mu_0 = 1.61$ D ; Jaffé's $\mu_0 = 1.71$ D.

Data on tetranitromethane in carbontetrachloride solution by Smyth and Lewis (J. Am. Chem. Soc. 61, 3067 (1939)) at 25°C. gives

$V_1 = 97.4$; $V_2 = 121.0$, $\left.\frac{d\epsilon}{dx_2}\right|_{x_2 \to 0} \approx 0.31$

$\epsilon = 2.24$; $n_2^2 = 2.06$

$$97.4(0.31) + \frac{6.72}{6.54}(0.18)\,121.0 = 6.22 \times 10^{37}(1.70)\,\mu^2_{soln}$$ and

$\mu_{soln.} = 0.75\,D$. Onsager's $\mu_o = 0.65$ and Jaffé's $\mu_o = 0.69$

Smyth and Lewis found $\mu = 0.71$ and added that the permanent moment might be attributed to the unaccounting for atomic polarization in their equations. Coop and Sutton (J.Chem.Soc. 1269 (1938)) found $\mu = 0.39$ in the gas and Williams (Physik.Z. 29, 27 (1928)) found $\mu = 0.20$ in benzene. It appears that this method gives as good values as does the present Debye dilute solution equation. Neither the Debye equation nor the Onsager equation take formal account of atomic polarization in complex molecules. Therefore this dipole moment value does not definitely catalogue tetranitromethane as a polar compound. It is included not to settle a controversy but to illustrate the results of this new method as compared to the present method for calculating polar moments.

Data on nitrobenzene in benzene solution by Williams (Landolt-Bornstein Tables, Vol. 2, pt. 2, p.1002) at 25°C. gives $V_1 = 88.5$; $V_2 = 102.5$; $\left.\frac{d\epsilon}{dx_2}\right|_{x_2 \to 0} \approx 22.4$

$\epsilon = 2.28$; $n_2^2 = 2.33$

so that $88.5(22.4) + \frac{6.84}{6.89}(-0.05)102.5 = 6.22 \times 10^{37}\ \mu^2_{soln.}\ (1.51)$

and $\mu_{soln.} = 4.60$. Onsager's $\mu_0 = 3.97$ and Jaffé's $\mu_0 = 4.21$ D. Goss found $\mu = 4.38$ and the accepted value in the gas is $\mu = 4.23$.

Data on hydrogen persulfide in benzene solution at 25°C. measured by Smyth, Lewis, Grossman and Jennings (J.Am.Chem.Soc. 62, 1219 1940) gives

$$v_1 = 88.5 \quad \epsilon = 2.28 \quad ; \quad v_2 = 49.6 \quad n_2^2 = 2.64 \quad ; \quad \left.\frac{d\epsilon}{dx_2}\right|_{x_2 \to 0} \approx 2.10$$

$$88.5(2.10) + \frac{6.84}{7.20}(-0.36)49.6 = 6.22 \times 10^{37}(1.51)\ \mu^2_{soln}$$

$\mu_{soln.} = 1.34$ D. Onsager's $\mu_0 = 1.16$ and Jaffé's $\mu_0 = 1.23$ D. They obtained a permanent moment value of 1.17.

Data on n-propyl borate measured at 25°C. in benzene solution by Smyth and Lewis (J.Am.Chem.Soc. 62, 1529 (1939)) gives

$$v_1 = 89.5 \quad \epsilon = 2.28 \quad v_2 = 220. \quad n_2^2 = 1.94 \quad \left.\frac{d\epsilon}{dx_2}\right|_{x_2 \to 0} \approx -0.05$$

$$89.5(-0.05) + \frac{6.84}{6.50}(0.34)220 = 6.2 \times 10^{37}(1.51)\ \mu^2_{soln.}$$

$\mu_{soln.} = 0.89$. Onsager's $\mu_0 = 0.77$, Jaffé's $\mu_0 = 0.82$ Their calculations from the benzene solution data gave a permanent moment value of 0.77.

Data on i-butyl borate measured in benzene solution at 25°C. by Smyth and Lewis (J.Am.Chem.Soc. 62, 1529 1939)

gives

$V_1 = 89.5$ $\quad V_2 = 274.0$ $\quad \left.\frac{d\epsilon}{dx_2}\right|_{x_2 \to 0} \approx -0.03$

$\epsilon = 2.28$ $\quad n_2^2 = 1.968$

$$89.5\,(-0.03) + \frac{6.8\alpha}{6.53}(0.31)\,274.0 = 6.2 \times 10^{37}\,(1.51)\,\mu^2_{soln.}$$

$\mu_{soln.} = 0.97$ $\quad$ Onsager's $\mu_0 = \frac{0.97}{1.16} = 0.84$ $\quad$ Jaffé's $\mu_0 = \frac{0.97}{1.089} = 0.89$

They calculated $\mu = 0.85$ in benzene solution.

Data on acetonitrile measured at 25°C. in benzene solution by Smyth and Lewis (J.Chem.Phys. 7, 1085 1939) gives

$V_1 = 89.5$ $\quad V_2 = 52.8$ $\quad \left.\frac{d\epsilon}{dx_2}\right|_{x_2 \to 0} \approx 15.8$

$\epsilon = 2.28$ $\quad n_2^2 = 1.805$

$$89.5(15.8) + \frac{6.8\alpha}{6.37}(0.47)\,52.8 = 6.2 \times 10^{37}\,(1.51)\,\mu^2_{soln.}$$

$\mu_{soln.} = 3.91$ D. $\quad \mu_0$ (Onsager) $= 3.37$. $\quad$ Jaffé's $\mu_0 = 3.60$

They calculated $\mu = 3.51$ in benzene and $\mu = 3.45$ in hexane.

Data on n-butanol measured at 20°C. in carbontetrachloride solution by Rodebush, Eddy and Eubank (J.Chem. Phys. 8, 890 (1940)) gives

$V_1 = 96.5$ $\quad V_2 = 91.5$ $\quad \left.\frac{d\epsilon}{dx_2}\right|_{x_2 \to 0} \approx 3.35$

$\epsilon = 2.24$ $\quad n_2^2 = 1.96$

$$96.5\,(3.35) + \frac{6.72}{6.44}(0.28)\,91.5 = 6.33 \times 10^{37}\,(1.45)\,\mu^2_{soln.}$$

$\mu_{soln} = 1.95$. $\quad$ Onsager's $\mu_0 = \frac{1.95}{1.14} = 1.69$ $\quad$ Jaffé's $\mu_0 = \frac{1.95}{1.08} = 1.80$

Goss gives a value of the moment of 1.68 corrected for the solvent influence by his method and the accepted value of the moment in gas is 1.66.

The following table gives a summary of the calculations made from recent data in the literature. The first column contains the accepted values of dipole moments in the gaseous phase. Column two contains the values of permanent moments as corrected by Goss. Columns three and four give the permanent moments as calculated in this thesis by applying the Onsager solvent effect correction (in column three) and the Jaffe solvent effect correction (in column four).

	μ_{Gas}	μ_{Goss}	$\mu_{Onsager}$	$\mu_{Jaffé}$
Acetonitrile		3.51*	3.37	3.60
n-Butanol	1.66	1.68	1.69	1.80
i-Butyl borate		0.85*	0.84	0.89
Ethanol	1.68	1.68	1.61	1.71
Chloroform	1.02	1.05	1.15	1.22
Ethyl bromide	2.01	1.94	1.95	2.07
Hydrogen persulfide			1.16	1.23
Morpholine		1.58*	1.60	1.71
Nitrobenzene	4.23	4.38	3.97	4.21
n-Propyl borate		0.77*	0.77	0.82
Tetranitromethane	0.39	0.71*	0.66	0.69

* From calculations made by Smyth and others.

The results seem to agree very well with the accepted permanent moment values.

Values of the Solvent Effect Factor

Both the Onsager and the Jaffé solvent effect factors were calculated for several common nonpolar solvents. Properties of these solvents were obtained from Müller's data (Physik. Z. 38,286 (1937). The values were measured at 20°C. and the index of refraction is for the Na-D line. Jaffé's solvent effect function is always smaller than Onsager's function and both are always greater than unity. This indicates that the influence of the solvent is always to increase the permanent moment of the polar molecule in solution.

Here are the values for Jaffé's $\varphi(1,q)$ and Onsager's f.

$$\varphi(1,q) = 1 + q e^{1-q} \int_{1-q}^{\infty} \frac{e^{-t}}{t}\, dt \qquad \text{where } q = \frac{2(\varepsilon-1)}{2\varepsilon+1} \cdot \frac{n^2-1}{n^2+2}$$

$$f = \frac{n^2+2}{3} \cdot \frac{2\varepsilon+1}{2\varepsilon+n^2}.$$

For pentane:	$\varepsilon = 1.835$	and	$\varphi = 1.050$
	$n^2 = 1.839$		$f = 1.082$
For hexane:	$\varepsilon = 1.908$	and	$\varphi = 1.056$
	$n^2 = 1.910$		$f = 1.096$
For benzene:	$\varepsilon = 2.284$	and	$\varphi = 1.089$
	$n^2 = 2.253$		$f = 1.160$
For CCl_4:	$\varepsilon = 2.236$	and	$\varphi = 1.080$
	$n^2 = 2.132$		$f = 1.140$

CONCLUSIONS

This thesis contains the general theory of dielectric and magnetic media up to the pointwhere specific suppositions must be made. Then the study was limited to dielectric phenomena. Next, specific assumptions were made and the Debye-Clausius-Mossotti and Onsager equations were discussed and criticised to some extent.

Using the Onsager equation as the best approximation to actual conditions yet proposed, an absorption and a dispersion equation was discussed and related to the alternating current conductivity of the medium.

In the last section an equation for calculating permanent moments from dilute solution measurements was derived and tested. The use of this formula together with a suitable accounting for the solvent effect offers to give the most accurate permanent moment values available at this time.

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