Dielectric Constant of Liquid Consisting of Anisotropic Molecules

By Masasi YASUMI, Hideo OKABAYASHI and Hitoshi KOMOOKA

(Received November 11, 1957)

Recently we have derived a formula for the internal field of polar liquid consisting of isotropic spherical molecules[1].

Our idea is based upon the classical electrostatics of continuous medium. Accordingly, the internal field is expressed as follows:

$$\vec{F}=\vec{E}-\vec{E}_s \tag{1}$$

where $\vec{F}$ is the internal field, $\vec{E}$ the electric field and $\vec{E}_s$ the self-field of a molecule. If the self-field is assumed to be dipolar,

$$\vec{E}_s=-\frac{4\pi}{3}\vec{p} \tag{2}$$

where $\vec{p}$ is the dipolar density.

We have assumed that p is the momentary dipolar density, i. e.;

$$\vec{p}=\frac{\vec{\mu}}{v} \tag{3}$$

where $\vec{\mu}$ is the momentary electric moment of the molecule, and v is the volume of the molecule.

1) M. Yasumi and H. Komooka, This Bulletin, **29**, 407 (1956).

$$\vec{\mu}=\vec{\mu}_0+\alpha\vec{F} \tag{4}$$

$\vec{\mu}_0$ is the permanent moment and α is the polarizability of the molecule.

For the liquid consisting of isotropic spherical molecules, the final expression for the internal field is as follows:

$$\vec{F}=\frac{n^2+2}{3}\left(\frac{\vec{\mu}_0}{a^3}+\vec{E}\right) \tag{5}$$

n denotes the (isotropic) refractive index and a is the radius of the spherical molecule.

On the other hand, Debye's internal field is readily obtained from Eqs. 1 and 2, if we assume that the dipolar density is the macroscopic one; i.e.,

$$\vec{p}=\frac{\varepsilon-1}{4\pi}\vec{E} \tag{6}$$

Using (6) and (2), Debye's internal field has the following expression.

$$\vec{F}=\frac{\varepsilon+2}{3}\vec{E} \tag{7}$$

It is our opinion that in calculating the internal field the dipolar density must be taken as the momentary one and not to be taken as the statistical one, because according to the definition the concept of the internal

field is referred to the molecule in the momentary state and is not referred to the molecule in the statistical state.

Assuming our expression for the internal field, the formula for the dielectric constant of polar liquid is readily derived and has the following expression:

$$\varepsilon - n^2 = \frac{4\pi}{V}\left(\frac{n^2+2}{3}\right)^3 \frac{\mu_0^2}{3kT} \tag{8}$$

This relation is closely related to the empirical relation of Wyman[2].

In spite of the simplified assumption, our equation 8 can fairly explain the experimental facts.

However, if we compare the experimental data with our equation 8 in detail, we can see that the degree of coincidence seems to depend on the chemical structure of the molecule forming a liquid.

On the other hand, most of the real molecules, especially polar molecules are not to be assumed to have spherical shapes and isotropic polarizabilities in general.

In this paper, we extend our previous theory to the case when a molecule has the shape of an ellipsoid and an anisotropic polarizability.

Formula for the Internal Field and the Dielectric Constant

We assume that the molecule forming a liquid has an anisotropic polarizability and a shape of ellipsoid.

We assume that the directions of the three principal axes of the ellipsoid are coincident with the directions of the coordinate axes (x_1, x_2, x_3).

The directions of the principal axes of the polarizability ellipsoid are not the same as those of the ellipsoid determining the molecular shape in general. However, we assume that these two sets of directions are coincident.

Let the lengths of the principal axes of the ellipsoid be $2a_1$, $2a_2$ and $2a_3$ respectively.

The dipolar density $\vec{p}$ of the liquid is represented as follows:

$$\vec{p} = \frac{\vec{\mu}}{v} = \frac{\vec{\mu}}{\frac{4\pi}{3} a_1 a_2 a_3} \tag{9}$$

The electride field $\vec{E}$ at a point of the liquid is resolved into two parts, i. e. the internal field $\vec{F}$ and the self-field $\vec{E}_s$.

2) J. Wyman, *J. Am. Chem. Soc.*, **58**, 1482 (1936).

$$\vec{E} = \vec{F} + \vec{E}_s \tag{10}$$

The component of the self-field of the ellipsoid along the direction of a principal axis x_i is expressed as[3];

$$E_{si} = -\varphi_i p_i \tag{11}$$

where

$$\varphi_i = 2\pi a_1 a_2 a_3 \int_0^\infty \frac{du}{(a_i^2+u)\sqrt{(a_1^2+u)(a_2^2+u)(a_3^2+u)}} \tag{12}$$

Accordingly, the component of the internal field $\vec{F}$ is represented as:

$$F_i = E_i + \varphi_i p_i \tag{13}$$

On the other hand, the total dipole moment of the molecule consists of the permanent dipole moment and the induced dipole moment.

$$\mu_i = \mu_{0i} + \alpha_i F_i \tag{14}$$

where α_i stands for the component of the polarizability tensor along the direction of the principal axis x_i[4].

From the Eqs. 9, 13 and 14,

$$F_i = \left(1 - \frac{\varphi_i \alpha_i}{v}\right)^{-1}\left(E_i + \frac{\varphi_i \mu_{0i}}{v}\right) \tag{15}$$

If the number of the molecules in 1cc. of the liquid is denoted by N_c, then

$$1 = N_c v \tag{16}$$

and

$$\begin{aligned} F_i &= (1 - N_c \varphi_i \alpha_i)^{-1}(E_i + N_c \varphi_i \mu_{0i}) \\ &= \gamma_i (E_i + N_c \varphi_i \mu_{0i}) \end{aligned} \tag{17}$$

The component of the total dipole moment of the molecule is expressed as:

$$\mu_i = \gamma_i(\alpha_i E_i + \mu_{0i}) \tag{18}$$

The component of $\vec{\mu}$ along the direcion of $\vec{E}$ is denoted by μ_E, and the statistical mean value of μ_E is denoted by $\langle \mu_E \rangle$. Assuming Boltzmann statistics, we have

$$\langle \mu_E \rangle = \int \mu_E \cdot e^{-U/kT} d\Omega \Big/ \int e^{-U/kT} d\Omega \tag{19}$$

where U is the potential energy of the dipole under the influence of the electric field and $d\Omega$ is an elementary solid angle.

U has the following expression;

$$U = -\left\{\frac{1}{2}\sum \alpha_i F_i^2 + \sum \mu_{0i} F_i\right\} \tag{20}$$

3) e. g. Stratton, "Electromagnetic Theory", McGraw-Hill Book Company, Inc., 1st Ed. (1941), pp. 207-213, 257.

4) φ and α are tensor quantities. However, in our case when they are diagonalized, only diagonal elements (φ_1, φ_2, φ_3) (α_1, α_2, α_3) are necessary.

and

$$\mu_E=\sum\mu_i\frac{E_i}{E}=\sum\gamma_i(\alpha_iE_i+\mu_{0i})\frac{E_i}{E} \quad (21)$$

Inserting 20 and 21 in 19 and making a simple calculation, we have;

$$<\mu_E>=\left\{\frac{\sum\alpha_i\gamma_i}{3}+\frac{\sum\mu_{0i}^2\gamma_i^3}{3kT}\right\}E \quad (22)$$

In this calculation $e^{-U_i/kT}$ is expanded in the power series of E_i, and only the terms proportional to E_i are retained.

The dielectric constant ε is related to $<\mu_E>$ by the following equation:

$$(\varepsilon-1)E=4\pi N_c<\mu_E> \quad (23)$$

Accordingly, we have

$$\varepsilon-1=4\pi N_c\left\{\frac{\sum\alpha_i\gamma_i}{3}+\frac{\sum\mu_{0i}^2\gamma_i^3}{3kT}\right\} \quad (24)$$

Consider, for a while, a non-polar liquid.

The refractive index of the liquid may be denoted by n. Then

$$n^2-1=4\pi N_c\frac{\sum\alpha_i\gamma_i}{3} \quad (25)$$

We define the quantity n_i by the following equation;

$$n_i^2-1=4\pi N_c\alpha_i\gamma_i \quad (26)$$

n_i may represent the refractive index of the molecule along the direction of the principal axis x_i.

From the Eqs. 25 and 26, we obtain

$$n^2=\frac{1}{3}\sum n_i^2 \quad (27)$$

It must be noticed that according to Lorentz-Lorenz field,

$$\frac{n^2-1}{n^2+2}=\frac{1}{3}\sum\frac{n_i^2-1}{n_i^2+2} \quad (28)$$

in contrast to our equation (27).

The equation 24 is transformed to the following form;

$$\varepsilon=\frac{\sum n_i^2}{3}+4\pi N_c\frac{\sum\mu_{0i}^2\gamma_i^3}{3kT} \quad (29)$$

In the cases of simple molecules, it may be assumed that the direction of the dipole moment coincides with one of the directions of the principal axes of the molecular ellipsoid. We choose the direction of the axis a_1, as the direction of the dipole moment.

In this case, the equation 29 reduces to

$$\varepsilon=\frac{\sum n_i^2}{3}+4\pi N_c\frac{\gamma_1^3\mu_0^2}{3kT} \quad (30)$$

According to J. Wyman[2] we define the quantity $\bar{p}$ by the following equation[5]:

$$\bar{p}=\frac{4\pi}{3}N_c\left\{\frac{\sum\alpha_i}{3}+\frac{\mu_0^2}{3kT}\right\} \quad (31)$$

then

$$\varepsilon+\frac{4\pi N_c}{3}\left\{\sum\alpha_i(\gamma_i^3-\gamma_i)\right\}-1=3\gamma_1^3\bar{p} \quad (32)$$

The equation 32 corresponds to Wyman's empirical relation[2]

$$\varepsilon+1=K_w\bar{p} \quad (33)$$

K_w represents a constant, amounting to 8.5 for most of normal liquids.

The quantity $3\gamma_1^3$ in our equation 32 which corresponds to K_w is slightly dependent on temperature, but practically is constant in the limited range of temperature[1].

Our present theory can treat the gaseous state if we take v appearing in the equation 9 as the volume portioned to one molecule. The form of the space occupied by this volume is assumed to be an ellipsoid confocal to the molecular ellipsoid.

In the gaseous state $N_c\alpha_i$ is much less than unity so the value of γ_i approaches to 1.

The equation (32) reduces to

$$\varepsilon-1=4\pi N_c\left\{\frac{\sum\alpha_i}{3}+\frac{\mu_0^2}{3kT}\right\} \quad (34)$$

The equation 34 coincides with the Debye's equation in the limiting case of $\varepsilon-1\ll1$.

Comparison of Our Formula with Experiments

In order to compare the value calculated with our theoretical formula the Eq. 29 or the Eq. 30 with the experimental value, we must know the value of permanent dipole moment, that of the component of polarizability and that of the molecular dimension.

a) The value of the permanent dipole moment. We take as the value of the permanent dipole moment, the value determined by the experiment of Stark effect in micro-wave spectroscopy.

However, in the case when this value is not available, the value determined by the measurement of the dielectric constant in the gaseous state is used.

b) The value of the component of polarizability. Two factors contribute to

5) In our previous paper[1], we define

$$\bar{p}=\frac{4\pi}{3}N_c\frac{\mu_0^2}{3kT}$$

However in the Wyman's original paper[3], $\bar{p}$ is defined as in this paper.

the polarizability of a molecule, i. e., the electronic polarization and the atomic polarization.

To determine the value of the component of polarizability, the experimental result of refraction, that of depolarization of polarized light, and that of Kerr effect, should be known.

The latter phenomenon concerns both the electronic polarization and the atomic polarization. On the other hand, the two other phenomena concern only the electronic polarization.

We use as the value of component of polarizability the value referred to in the literature of Stuart for the gaseous state[6] and that of Le Fèvre for the solution[7], when the datum for the gaseous state is not available.

This value does not include the contribution from the atomic polarization.

c) Moreover, we need the value of the molecular dimension. We use as the values of the interatomic distances and the values of valence bond angles the values determined by the experiments of electron diffraction or of micro-wave spectroscopy.

As the dimension of atomic size we use the usual van der Waals' radii[8].

From these values we construct a molecular model. Then we approximate a molecule as an ellipsoid, and determine the lengths of the principal axes. They are denoted by $2a_1$, $2a_2$ and $2a_3$, respectively. The direction of axis a_1 is assumed to be the same as that of the dipole moment.

A symmetrical top molecule can be approximated as a spheroid. In this case the parameter which determines the shape of the spheroid is only one. (i. e., the ratio of axes $a_2/a_1=a_3/a_1$).

We choose the value of the parameter in order to fit the experimental values of dielectric constant, and compare this value with the obtained from the geometrical configuration.

In some cases, we also calculate the value of dielectric constant with our formula taking as the value of axial ratio the value determined with the molecular model.

In the case of a general ellipsoid two parameters (i. e. a_2/a_1 and a_3/a_1) are necessary. In this case we use the values of the parameters determined from the geometrical configuration. We calculate the value of dielectric constant with our equation using these values and compare them with the experimental one.

Our assumption that a molecule may be approximated as an ellipsoid may not hold strictly.

In our calculation, we assume that the ratio of the lengths of the axes of the ellipsoid is independent of the temperature. Strictly saying, this assumption is not correct.

However, in the limited range of temperature, at which the liquid state exists, this assumption may be used without serious error.

For about thirty substances, the value of dielectric constant calculated with our formula is compared with the experimental one. As shown in the following tables the coincidence is strikingly excellent.

For most of the symmetrical top molecules the error is within a small percentage and for most of the asymmetrical top molecules the error is within 10 per cent.

The exceptions are revealed in the cases of methyl fluoride, nitromethane, nitrobenzene and diethyl ether.

In the following, some remarks are made on the individual cases.

1) Non-polar Liquid

For the non-polar liquid, our formula becomes coincident with Lorentz-Lorenz formula, provided that the molecule has a spherical shape and an isotropic polarizability[1]. However, if the molecule forming a liquid has an ellipsoidal shape and an anisotropic polarizability, our equation 25 does not coincide with that of Lorentz and Lorenz.

For benzene and carbon dioxide, we can not determine whether the Lorentz-Lorenz formula or our formula fit the experimental results.

For carbon disulfide it is recognized that the better agreement between the experimental value and the theoretical value is achieved if we calculate with our formula instead of the Lorentz-Lorenz formula.

Moreover the value of the ratio of the axes ($a_2/a_1=a_3/a_1$) obtained with our formla using the experimental results, is 0.5 which is in agreement with the geometrical value 0.54.

The considerable discrepancy between the experimental value and the theoretical

6) H. A. Stuart, Landolt-Börnstein Tabellen, I. Band (1951) 510, 512.

7) C. G. Le Fèvre and R. J. W. Le Fèvre, *Reviews of Pure and Applied Chemistry*, 5, 261-318 (1955).

8) L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press 1st. ed. (1939).

value calculated with Lorentz-Lorenz formula exists for the liquid state under high pressure. Moreover, the discrepancy is systematic (i.e., the higher the pressure, the greater the discrepancy).

It is striking that in this case the value calculated with our formula is in excellent agreement with the experimental one.

2) Symmetrical Top Molecule

a) Derivatives of methane

For methyl chloride and methyl bromide the theoretical value is fairly in agreement with the experimental one. The assumed ratio of the axes for methyl chloride is 0.75 (if the Stuart's data for Kerr effect are used) or 0.85 (if the Le Fèvre's data are used). The geometrical value is 0.71.

For methyl bromide the same order of agreement is recognized.

For methyl iodide a somewhat smaller value for the ratio of axes (0.45) is assumed in order to fit the experimental result. The value of the ratio of the axes obtained with the molecular model is 0.64.

For methyl fluoride the value of dielectric constant in the liquid state under high pressure is compared with the value calculated with our formula. If we assume 1.7 as the value of the ratio of the axes which corresponds to an oblate spheroid, the calculated value is in excellent agreement with the experimental one over the wide range of temperature. On the other hand, methyl fluoride has a shape of a prolate spheroid whose axial ratio is 0.85.

The reason why the value of the axial ratio calculated from the value of dielectric constant is inconsistent with the value calculated with the molecualr model is as yet obscure.

b) Other symmetrical top molecules

In the case of acetonitrile, *tert*-butyl chloride and chloroform our theory may be regarded as satisfactory.

3) Asymmetrical Top Molecule

As stated above, as the value of the axial ratio the value determined with the molecular model is used.

a) Nitromethane

The calculated value of dielectric constant is considerably smaller than the experimental one.

b) Methylene chloride.

The agreement is satisfactory.

c) Diethyl ether

The molecular shape of diethyl ether is as yet not determined completely. In table 16 the values of dielectric constant calculated with our formula using various values of axial ratio are shown, and compared with the experimental value.

The planar zig-zag form does not fit. The oblate spheroid whose axial ratio is 0.5 fit to the experimental results very well[9].

d) Other ethers

For dimethyl ether our theory can explain the experimental results quite satisfactorily if we use as the values of axial ratios the values determined with the molecular model.

For *n*-propyl ether, it seems that the zig-zag model is suitable. However, the lack of complete data prevents us from furfher discussion.

e) Paraldehyde

The molecular model is assumed to be the chair-form. This substance has the great atomic polarization. Accordingly we have taken into account the atomic polarization[10].

f) Acetone

The agreement of theoretical value with the experimental one is fairly satisfactory if we use as the value of the axial ratio the ratio determined with the molecular model.

g) Other ketones

In these cases, the value of dipole moment is assumed to be the same as that of acetone. The molecular forms are assumed to be planar zig-zag forms. If other suitable molecular models are assumed, better agreements would be obtained.

h) Derivatives of benzene, pyridine and quinoline

Except nitrobenzene, the calculated value of the dielectric constant is considerably in agreement with the experimental one, if we use as the values of the axial ratios the values determined with the molecular model. Nitrobenzene is assumed to have a coplanar molecular shape.

For nitrobenzene, the calculated value is considerably smaller than the experimental one, as in the case of nitromethane.

Appendix

Evaluation of φ_i. Let the lengths of three

9) On the other hand, the zig-zag model fits the experimental result of the Kerr effect when our internal field is used. Detailed discussion will appear in the following paper.

10) We define the quantity f as follows;

$$\frac{P_E+P_A}{P_E}=\frac{45.2}{33.1}=f$$

where P_E and P_A stand for the electronic and the atomic polarization respectively. In the calculation of the dielectric constant, $f\alpha_i$ is used instead of α_i.

principal axes of an ellipsoid be 2a, 2b and 2c respectively, and $a \geqq b \geqq c$.

φ_i's are represented as follows:[11]

$$\varphi_a = \frac{4\pi \frac{b}{a}\frac{c}{a}}{\left\{1-\left(\frac{c}{a}\right)^2\right\}^{3/2}} \frac{F(k,\rho)-E(k,\rho)}{k^2}$$

$$\varphi_b = \frac{4\pi \frac{b}{a}\frac{c}{a}}{\left\{1-\left(\frac{c}{a}\right)^2\right\}^{3/2}} \frac{1}{k'^2}\left\{\frac{E(k,\rho)-k'^2F(k,\rho)}{k^2} - \frac{\frac{c}{a}\sqrt{1-\left(\frac{c}{a}\right)^2}}{\frac{b}{a}}\right\}$$

$$\varphi_c = \frac{4\pi \frac{b}{a}\frac{c}{a}}{\left\{1-\left(\frac{c}{a}\right)^2\right\}^{3/2}} \frac{1}{k'^2}\left\{\frac{b}{a}\tan\rho - E(k,\rho)\right\}$$

where

$$k^2 = \frac{1-\left(\frac{b}{a}\right)^2}{1-\left(\frac{c}{a}\right)^2}$$

$$k'^2 = 1-k^2$$

$$\sin^2\rho = 1-\left(\frac{c}{a}\right)^2$$

$$F(k,\rho) = \int_0^\rho \frac{d\theta}{\sqrt{1-k^2\sin^2\theta}}$$

$$E(k,\rho) = \int_0^\rho \sqrt{1-k^2\sin^2\theta}\, d\theta$$

i. e., $F(k,\rho)$ and $E(k,\rho)$ represent the elliptic integral of first kind and that of second kind respectively. The numerical values of each are shown in the numerical tables[12].

In the case of sphere,

$$\varphi_a = \varphi_b = \varphi_c = \frac{4\pi}{3}$$

In the case of spheroid:

i) $a=b>c$

if we define as:

$$e^2 = 1-\left(\frac{c}{a}\right)^2$$

then

$$\frac{\varphi_c}{4\pi} = \frac{1}{e^2} - \frac{(1-e^2)^{1/2}\sin^{-1}e}{e^3}$$

and

$$\varphi_a = \varphi_b = 2\pi(1-\varphi_c)$$

ii) $a>b=c$

if we define as:

$$e^2 = 1-\left(\frac{b}{a}\right)^2$$

then

$$\varphi_a = 4\pi\left(\frac{1}{e^2}-1\right)\left(\frac{1}{2e}\ln\frac{1+e}{1-e}-1\right)$$

and

$$\varphi_b = \varphi_c = 2\pi(1-\varphi_a)$$

11) W. Magnus and F. Oberbethinger, "Formel und Sätze für die Speziellen Funktionen der Mathematischen Physik", (1948) Springer-Verlag. p. 136.

12) Marcell Boll, "Tables Numeriques Universelles", 1947.

Summary

Our previous theory of dielectric constant of liquid consisting of spherical molecules having an isotropic polarizability is extended to the case when the molecule has an ellipsoidal shape and an anisotropic polarizability.

The theory is compared with experimental results for about thirty substances. The coincidence is quite satisfactory with few exceptions. For non-polar substance, better agreement between the experimental value and the theoretical value is achieved if we use our formula instead of the Lorentz-Lorenz formula.

We are grateful to Professor San-ichiro Mizushima for his kind encouragement throughout this work and to Professor Akira Kotera for his kind advice. Our thanks are also due to the Ministry of Education for a grant in aid of this research.

Institute of Science and Technology
University of Tokyo
Meguro-ku, Tokyo