On the Dielectric Constant of Polar Liquid

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(Received November 15, 1955)

Introduction

The Debye's theory for the dielectric constant of polar fluids seems to be inadequate to explain quantitatively most of the experimental results for the polar liquids.

The origin of the failure of the theory has been discussed by many authors⁽¹⁾. It is concluded that the inadequacy of the assumption concerning the local field adopted by Debye⁽²⁾ plays the most important role.

Assuming an simplified model for the polar liquid, Onsager has obtained a quite different expreession for the local field and succeeded in deriving a formula for the dielectric constant of polar liquid⁽¹⁾. In spite of the rather over-simplified model, the Onsager's formula seemed to be able to eliminate the difficulties appearing in Debye's theory⁽¹⁾. Although the Onsager's theory succeeded in explaining the experimental results (at least semiquantitatively), the problem of the local field in polar liquid seems not to have been solved completely.

In the present work, we have obtained an expreession for the local field, from the point of view of the classical electrodynamics in the continuous medium. Using this expersion for the local field we have obtained also an expression for the dielectric constant. [section 2–A]

The result is as follows: a Wyman type relation between dielectric constant ε and absolute temperature T exists, i.e. $\varepsilon \sim 1/T$.

If we take into account the fluctuation of the internal field, a slightly different expression is obtained. [section 2–B]

The Internal Field and the Dielectric Constant

We assume that polar fluid is continuous and that its dipolar density $\vec{p}$ is expressed as follows:

$$\vec{p} = \vec{\mu}/v \tag{1}$$

where v is the volume element in the polar liquid and $\vec{\mu}$ is the dipole moment of this volume element. If we assume that the shape of the molecule of which the dipolar substance consists is the sphere of the radius a, we may choose $\frac{4}{3}\pi a^3$ as volume element v, and μ may be considered as the dipole mo-

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1) L. Onsager, *J. Am. Chem. Soc.*, 58, 1486 (1936). J.H. Van Vleck, *Ann. N.Y. Acad. Sci.*, 40, 289 (1940). S. Oka, "Theory of Dielectrics", Iwanami-shoten, (in Japanese) (1954).

2) The local field adopted by Debye is sometimes called Lorentz field. However, Lorentz applied this field only to the case of induced polarization. As shown below, the Lorentz field is correct when applied within this limitation.

ment of the molecule i. e.

$$v=\frac{4}{3}\pi a^3 \ . \tag{2}$$

[A] The case when we do not take into account the fluctuation of the internal field.

The electric field, the external field, the internal field and the self-field of the volume element v are denoted by $\vec{E}$, $\vec{E_0}$, $\vec{F}$, $\vec{E_S}$, respectively. The expression of the $\vec{E_S}$ is determined when we know the type of the self-field (i. e. dipolar, quadrupolar, etc.).

On the other hand the expression of the internal field, which is the vector sum of the external force and the forces of all other volume elements in the dielectric medium, may have a complicated form.

However, in the continuous medium, the expression of the internal field may be obtained as follows.

In the continuous medium the electric field $\vec{E}$ is resolved into the internal field and the self-field, i. e.[3,4]

$$\vec{E}=\vec{F}+\vec{E_S} \ . \tag{3}$$

If the self-field $\vec{E_S}$ is assumed to be dipolar and if the Eq. (2) is valid, $\vec{E_S}$ is represented as[4]:

$$\vec{E_S}=-\frac{4\pi}{3}\vec{p}=-\frac{\vec{\mu}}{a^3} \ . \tag{4}$$

The dipole moment of a molecule consists of two parts i. e. the permanent dipole moment $\vec{\mu_0}$ and the induced dipole moment $\alpha\vec{F}$,

$$\vec{\mu}=\vec{\mu_0}+\alpha\vec{F} \tag{5}$$

where α is the polarizability of the molecule.

The case when the molecule has not a permanent moment (non-polar molecule), the following equation holds

$$(n^2-1)\vec{E}=4\pi\vec{p} \tag{6}$$

where n is the refractive index.

In this case

$$\vec{E_S}=-\frac{(n^2-1)}{3}\vec{E} \ . \tag{7}$$

From the Eqs. (3), (4) (6) and (7) $\vec{F}$ is represented as:

$$\vec{F}=\vec{E}+\frac{n^2-1}{3}\vec{E}=\frac{n^2+2}{3}\vec{E} \ . \tag{8}$$

This is the Lorentz-Lorenz internal field.

On the other hand from the Eqs. (7), (1) and (2) (taking $\mu_0=0$)

$$\vec{p}=\frac{\alpha\vec{F}}{(4/3)\pi a^3} \ . \tag{9}$$

From the Eqs. (5) and (9)

$$\frac{\alpha}{a^3}=\frac{n^2-1}{n^2+2} \ . \tag{10}$$

Eq. (10) is the well-known Lorentz-Lorenz formula.

For the case of the polar liquid, the internal field $\vec{F}$ is expressed as: (Eqs. (3), (4) and (5) being used)

$$\vec{F}=\frac{1}{(1-\alpha/a^3)}\left[\frac{\vec{\mu_0}}{a^3}+\vec{E}\right]. \tag{11}$$

Putting (10) into (11), we obtain.

$$\vec{F}=\frac{n^2+2}{3}\left[\frac{\vec{\mu_0}}{a^3}+\vec{E}\right]. \tag{12}$$

Using this equation and the Eq. (5) we have,

$$\vec{\mu}=\frac{n^2+2}{3}(\vec{\mu_0}+\alpha\vec{E}) \ . \tag{13}$$

The component of $\vec{\mu}$ along the direction of $\vec{E}$ is denoted by μ_E, and the mean value of μ_E is denoted by $<\mu_E>$.

Assuming Boltzman statistics, we have the following equation,

$$<\mu_E>=\int\mu_E\cdot e^{-\frac{U}{kT}}d\Omega\Big/\int e^{-\frac{U}{kT}}d\Omega \tag{14}$$

where U is the potential energy of the dipole $\vec{\mu}$ in the electric field and $d\Omega$ is an elementary solid angle. U has the following expression.

$$U=-\left\{\frac{1}{2}\alpha F^2+(\vec{\mu_0}\cdot\vec{F})\right\} \ . \tag{15}$$

Let the angle between $\vec{E}$ and $\vec{\mu_0}$ be θ,

$$\mu_E=\frac{n^2+2}{3}(\mu_0\cos\theta+\alpha E) \ . \tag{16}$$

Inserting (15) and (16) in (14) and making a simple calculation we have the following expression for $<\mu_E>$,

$$<\mu_E>=\frac{n^2+2}{3}\alpha E+\left(\frac{n^2+2}{3}\right)^3\frac{\mu_0^2}{3kT} \ . \tag{17}$$

In this calculation $e^{-\frac{U}{kT}}$ is expanded in the power series of E, and only the terms proportional to E are retained.

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

$$(\varepsilon-1)E=\frac{4\pi N}{V}<\mu_E> \ , \tag{18}$$

where N is Avogadro's number and V is

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[3] J. H. Van. Vleck, "Theory of Electric and Magnetic Susceptibilities".

[4] H. Fröhlich, "Theory of Dielectrics". Oxford (1949).

molecular volume. In our model of the dipolar molecule,

$$\frac{N}{V}=\frac{1}{(4\pi/3)a^3}\ . \tag{19}$$

Using the Eqs. (18), (17), (19) and (10), we have

$$\varepsilon-n^2=\frac{4\pi N}{V}\left(\frac{n^2+2}{3}\right)^3\frac{\mu_0{}^2}{3kT}\ . \tag{20}$$

J. Wyman proposed the following simple experimental formula for the dielectric constant of polar liquids[5],

$$\varepsilon+1=K_{\rm w}\bar{p}\ , \tag{21}$$

where

$$\bar{p}=\frac{4\pi}{3}\cdot\frac{N}{V}\cdot\frac{\mu_0{}^2}{3kT}\ . \tag{22}$$

$K_{\rm w}$ represents a constant and amounts to about 8.5 for most of normal polar liquids.

In the case when ε is much greater than n^2, the form of the Eq. (20) is similar to that of the Eq. (21), i. e.

$$\varepsilon\simeq3\left(\frac{n^2+2}{3}\right)^3\bar{p}\ . \tag{23}$$

Moreover if $n=1.5$ the factor of $\bar{p}$ $\left(\text{i. e } 3\left(\frac{n^2+2}{3}\right)^3\right)$ amounts to about 8.5. Since the refractive index of most of the liquid is about 1.5 the validity of the Wyman's relation is explained by our theory.

[B] The case when the fluctuation is taken into account.

In the above-mentioned treatment, we have assumed that the local field is expressed by means of the self-field and the electric field. However, actually the form of the local field may be very complicated, since it is the sum of the external field and the fields of all other molecules. It is beyond our ability to treat this problem rigorously.

We attempt to solve this problem making an assumption for the form of the fluctuating local field $\vec{F_{\rm f}}$, when it is slightly different from its mean value $\vec{F_{\rm m}}$.

Consider at first the static equilibrium. In this case, $\vec{F_{\rm m}}=\vec{F}$. Next we imagine that the molecule considered changes its orientation by some action. In this case we assume that the arrangement of the sorrounding molecules does not change. That is to say, the magnitude of $F_{\rm f}$ is equal to that of $F_{\rm m}$, but its orientation is not the same as in the static equilibrium.

In other words, the direction of $\vec{F_{\rm f}}$ can take any direction independent of the direction of $\vec{\mu_0}$. Moreover we assume that the probability of orientation is regulated by Boltzmann's factor.

The expression for $\vec{F_{\rm f}}$ and $\vec{\mu}$ may have the following forms:

$$\vec{F_{\rm f}}=\left(\frac{n^2+2}{3}\right)\left(\vec{E}+\frac{\mu_0}{a^3}\vec{u_1}\right) \tag{24}$$

$$\vec{\mu}=\alpha\vec{F_{\rm f}}+\mu_0\vec{u_2}\ , \tag{25}$$

where $\vec{u_2}$ is the unit vector along the direction of $\vec{\mu_0}$, and $\vec{u_1}$ represents the unit vector along the direction of the fluctuating local field. In this case, the electric field (denoted by $\vec{E_{\rm f}}$) also fluctuates about the direction of $\vec{E}$.

$$\vec{E^{\rm f}}=\vec{F_{\rm f}}+\vec{E_{\rm S}}=\vec{E}+\frac{\mu_0}{a^3}(\vec{u_1}-\vec{u_2})\ . \tag{26}$$

In the case of absence of the fluctuation $u_1=u_2$, then $\vec{E_{\rm f}}$ coincides with $\vec{E}$.

The potential energy of a molecule assumes the following form:

$$U=-\left\{\frac{1}{2}\alpha F_{\rm f}{}^2+\mu_0(\vec{u_2},\ \vec{F_{\rm f}})\right\}\ . \tag{27}$$

In this case $<\mu_{\rm E}>$ is expresses as:

$$<\mu_{\rm E}>=\iint(\vec{\mu},\ \vec{\mu_0})e^{-\frac{U}{kT}}d\Omega_1 d\Omega_2\Big\backslash\iint e^{-\frac{U}{kT}}d\Omega_1 d\Omega_2 \tag{28}$$

where $\vec{u_0}$ denotes the unit vector along $\vec{E}$. $d\Omega_1$ and $d\Omega_2$ represent the elementary solid angles the around directions of $\vec{u_1}$ and $\vec{u_2}$ respectively.

A calculation transforms the Eq. (28) to the following expression:

$$<\mu_{\rm E}>=E\left[\frac{n^2+2}{3}\alpha+\frac{\mu_0{}^2}{3kT}\left(\frac{n^2+2}{3}\right)\right.$$
$$\left.\times\left\{1+\left(\frac{n^2-1}{3}\right)^2\right\}+\frac{2\mu_0{}^2}{3kT}\left(\frac{n^2-1}{3}\right)\left(\frac{n^2+2}{3}\right){\rm L}(y)\right] \tag{29}$$

$$y=\frac{n^2+2}{3}\ \frac{\mu_0{}^2}{a^3kT}\ , \tag{30}$$

where ${\rm L}(y)$ denotes Langevin function. As in the previous case, $e^{-\frac{U}{kT}}$ is expanded in the power series of E and only the terms proportional to E are retained.

Inserting this expression for $<\mu_{\rm E}>$ to the Eq. (18) we have this expression for ε,

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[5] J. Wyman, *J. Am. Chem. Soc.*, 58, 1482 (1936).

$$\varepsilon-n^2=\frac{4\pi N}{V}\frac{\mu_0^2}{3kT}\left(\frac{n^2+2}{3}\right)\left\{1+\left(\frac{n^2-1}{3}\right)^2\right\}$$
$$+\frac{4\pi N}{V}\frac{2\mu_0^2}{3kT}\left(\frac{n^2+2}{3}\right)\left(\frac{n^2-1}{3}\right)\mathrm{L}(y). \quad (31)$$

For the large value of y, $\mathrm{L}(y)$ is approximately equal to 1. Then the Eq. (31) coincides with the Eq. (20).

For the value of y greater than 3, $\mathrm{L}(y)\fallingdotseq 1-1/y$. In this case the Eq. (31) is approximated as follows:

$$\varepsilon-\frac{n^2+2}{3}=\frac{4\pi N}{V}\frac{\mu_0^2}{3kT}\left(\frac{n^2+2}{3}\right)^3. \quad (32)$$

For most of polar liquids, the approximate Eq. (32) is sufficient, because the values of y are greater than 3 for them.

TABLE I

THE DIELECTRIC CONSTANTS OF ESTERS, CHLORIDES AND NITROCOMPOUNDS

Name	n	$3\left(\frac{n^2+2}{3}\right)^3$	$\bar{p}$	$\varepsilon(Y-K)$	$\varepsilon(W)$	ε(obs.)*
Ethyl formate	1.358	6.35	1.21	9.2	9.3	8.6
Isobutyl formate	1.386	6.67	0.93	7.5	6.9	8.0
Methyl acetate	1.359	6.35	1.03	7.8	7.8	7.3
Isobutyl acetate	1.391	6.76	0.81	6.7	5.8	5.6
Ethyl salysilate	1.525	8.85	1.55	15.2	12.2	8.6
Ethyl cinnamate	1.544	9.20	0.95	10.2	7.1	6.6
Methyl benzoate	1.518	8.73	0.87	9.0	6.7	6.9
Ethyl nitrate	1.385	6.68	2.4	17.3	19.4	19.7
Acethyl chloride	1.390	6.75	2.38	17.5	19.2	15.9
Ethylidene chloride	1.417	7.15	1.15	9.5	8.8	10.9
Allyl chloride	1.415	7.10	1.27	10.3	9.8	8.2
p-Chlorotoluene	1.519	8.75	0.89	9.2	6.6	6.2
tert-Amyl chloride	1.408	6.98	1.04	8.5	7.9	9.5
Nitromethane	1.381	6.60	3.82 5.81	26.5 39.7	31.5 43.4	39.4
Nitroethane	1.390	6.75	3.26 4.76	23.3 33.3	26.7 39.5	30.0?
Nitrobenzene	1.553	9.40	3.05 3.74	30.1 36.6	24.9 30.8	36.1
o-Nitrotoluene	1.547	9.32	2.78	27.4	22.6	27.4

* $\varepsilon(Y-K)$ is the value calculated with our formula.
$\varepsilon(W)$ is the value calculated with the formula of Wyman.
ε(obs.) is the observed value.

Comparison of Our Formula with Experiments

The coefficient K_w in the Wyman's formula, takes the value 8.5 for most of the normal polar liquids but fluctuates from 6.2 to 11. K_w corresponds to $3\left(\frac{n^2+2}{3}\right)^3$ in our formula (32). $3\left(\frac{n^2+2}{3}\right)^3$ takes the value 6.2 when $n=1.34$, and 11 when $n=1.62$.

For example, we calculate the dielectric constant of some of the polar liquids referred to in Wyman's paper[5], by means of our formula (32).

In Table I, the dielectric constants of esters, chlorides and nitro-compounds calculated with the Eq. (32) are given, and compared with those calculated with the Wyman's formula (21). The observed values are also given. The values of $\bar{p}$ are taken from the Wyman's paper[5].

The values of refractive indices for sodium D line n are taken from "International Critical Tables" and are also given in Table I.

As Wyman has stated[5], the values of $\bar{p}$ are not satisfactorily reliable. Accordingly, we cannot bring up detailed discussion with the above-described comparison. We can only say that from the experimental point ot view, our formula (32) has applicability comparable to that of Wyman.

Next we calculate the dielectric constants of benzonitrile, nitrobenzene, ethyl bromide, ethyl iodide and chlorobenzene.

For these substances the dielectric constants in the liquid state have been measured over a considerably wide range of temperature[6]. The values are given in Table II. The densities are calculated with the equa-

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[6] R. J. W. Le Fevre, *Trans. Faraday Soc.*, **34**, 1127 (1938).

tion referred to in "International Critical Tables".

The refractive indices are calculated from the value of molecular refraction7) according to the Lorentz-Lorenz formula.

a) **Benzonitrile.**—The values of ε are calculated with the Eq. (32).

TABLE II-1

THE DIELECTRIC CONSTANTS OF BENSONITRILE

$\mu_0=4.39$ D8)

t(°C)	d	n	$3\left(\frac{n^2+2}{3}\right)^3$	$\bar{p}$	ε(calcd.)	ε(obs.)
0	1.0228	1.539	9.26	4.23	40.7	27.6
18	1.0070	1.529	9.07	3.94	37.3	25.85
25	1.0018	1.526	9.02	3.83	36.0	25.2
40	0.9874	1.517	8.85	3.60	33.2	24.0
50.3	0.9782	1.511	8.74	3.45	31.5	23.28
60	0.9697	1.506	8.64	3.32	30.2	22.7
70	0.9607	1.501	8.55	3.19	28.7	22.1

b) **Nitrobenzene.**—The values of ε are calulated with the Eq. (32).

TABLE II-2 9)

THE DIELECTRIC CONSTANTS OF NITROBENZENE

$\mu_0=4.19$ D10)

t	d	n	$3\left(\frac{n^2+2}{3}\right)^3$	$\bar{p}$	ε(calcd.)	ε(obs.)
10	1.222	1.563	9.75	3.98	40.3	37.9
25	1.168	1.550	9.48	3.76	37.1	34.9
30	1.193	1.547	6.42	3.68	36.2	34.0
40	1.183	1.542	9.32	3.53	34.3	32.3
60	1.163	1.531	9.12	3.26	31.2	29.1

c) **Ethyl Bromide.**—The values of ε are calculated with the Eq. (32).

TABLE II-3

Ethyl bromide

$\mu_0=2.01$ D11)

t	d	n	$3\left(\frac{n^2+2}{3}\right)^3$	$\bar{p}$	ε(calcd.)	ε(obs.)
−30	1.564	1.461	5.70	1.463	9.57	11.69
−20	1.543	1.454	5.64	1.359	8.97	11.20
−10	1.5215	1.446	5.58	1.290	8.56	10.68
0	1.5014	1.439	5.52	1.226	8.09	10.19
10	1.4813	1.433	5.47	1.166	7.73	9.71
25	1.4500	1.422	5.40	1.087	7.21	9.01

d) **Ethyl Iodide.**—The values of ε are calculated with the Eq. (32).

TABLE II-4

Ethyl iodide

$\mu_0=1.87$ D31)

t	d	n	$3\left(\frac{n^2+2}{3}\right)^3$	$\bar{p}$	ε(calcd.)	ε(obs.)
0	1.980	1.528	9.03	0.995	10.42	8.33
10	1.958	1.521	8.88	0.950	9.86	8.00
25	1.924	1.510	8.70	0.887	9.15	7.64
35	1.902	1.503	8.55	0.848	8.68	7.37
45	1.880	1.496	8.44	0.812	8.29	7.11
55	1.859	1.490	8.32	0.779	7.88	6.90
65	1.839	1.483	8.23	0.746	7.54	6.66

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7) "International Critical Tables", Vol. VII, p. 32.

8) L.G. Groves and S. Sugden, *J. Chem. Soc.*, **1934**, 1094.

9) The values of n and d are calculated as in the previous cases.

10) K.B. McAlpine and C.P. Smyth, *J. Chem. Phys.*, **3**, 55 (1934).

11) L.G. Groves and S. Sugden, *J. Chem. Soc.*, 158 (1937).

e) Chlorobenzene.—The values of ε are calculated with the Eq. (29).

TABLE II-5

Chlorobenzene

$\mu_0=1.70$ D[10]

t	d	n	ε(calcd.)	ε(obs.)
21	1.1053	1.524	6.05	5.67
25	1.1014	1.522	5.98	5.61
40	1.0847	1.512	5.69	5.37
48	1.0761	1.508	5.46	5.23
70	1.0520	1.495	5.10	4.89

Conclusions and Remarks

It is suprising that our theory can fairly explain the experimental data. For our theory is based upon the above-described over-simplified assumption.

As in the case of the Wyman's equation, our theory cannot be applied to the so-called abnormal liquids.

It seems that our Eqs. (31) and (32) become in better agreement with the experimental data near the boiling point than near the melting point.

The degree of coincidence of our theory with the experimental data seems to depend on the chemical structure of the molecule forming the liquid considered.

As stated by Wyman[5], if a linear relation between ε and $\bar{p}$ exists, the critical frequency ν_c will be represented as

$$2\pi\nu_c\tau=1\,, \tag{33}$$

where τ denotes the relaxation time, because the value of $\langle\mu_E\rangle$ in the case of an alternating field may be represented as:

$$\langle\mu_E\rangle=\left\{\frac{1}{1+i\omega\tau}\frac{\mu_0^2}{3kT}\left(\frac{n^2+2}{3}\right)+\left(\frac{n^2+2}{3}\right)\alpha\right\}E, \tag{34}$$

where ω denotes the angular frequency.

Inserting Eq. (34) into Eq. (18), ε (complex quantity) is obtained, and Eq. (33) is readily obtained.

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

Summary

An equation for the dielectric constant of polar fluids is obtained from the point of view of the classical theory of electricity in the continuous medium.

The obtained equation has a close relationship to the empirical equation of Wyman.

The comparison with the experimental data are represented.

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