Temperature Dependence of Dielectric Constants and Dipole Moments in Polar Liquids

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It is pointed out that, for a number of polar liquids, the relation of the static dielectric constant ε to the temperature T is expressed generally by an empirical formula $\varepsilon = a + b/T$.

Attempts are made to relate the coefficient b to the entropy change due to the dipole orientation. The following expression is derived;

$$\frac{\partial \varepsilon}{\partial(1/T)} = \left[\frac{\varepsilon(n^2+2)}{2\varepsilon + n^2} \right]^2 \frac{4\pi N}{3k} \mu^2,$$

Where μ, n and N are the dipole moment, the refractive index and the number of molecules per cc., respectively.

The dipole moments calculated from this equation are in good agreement with those obtained from gas or solution methods. In the case of associated liquids, the calculated dipole moments show too large values. This fact may be attributed to the entropy change due to molecular association.

INTRODUCTION

It has already been known that the static dielectric constants for most of polar liquids decrease with increasing temperature except a few cases such as acetic and butyric acids[1][2]. Several investigators[3~6] proposed an empirical formula to express this temperature dependence of the dielectric constant for a few kinds of polar liquid as follows:

$$\varepsilon = a + b\frac{1}{T}, \tag{1}$$

where ε denotes the dielectric constant, T the absolute temperature, and a and b are the empirical constants characteristic of each liquid.

A closer examination of the experimental data on the temperature dependence of dielectric constants discloses that this empirical formula holds not only for a number of non-associated polar liquids but also for the strongly associated liquids such as water and alcohols.

Typical examples of such a linear relation of ε to $1/T$ are shown in Fig. 1. The values of the intercept a at $1/T = 0$ and the slope b in Eq.(1) for a number of organic liquids, are listed in Table 1.

According to Debye's[7] theory the relation between the dielectric constant ε of gas and the temperature T is expressed as follows,

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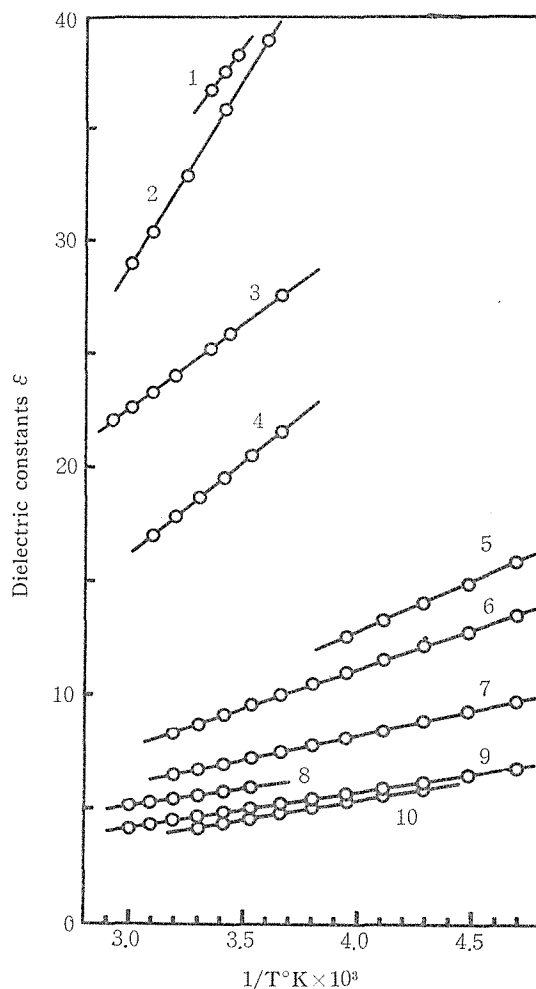
Fig. 1. Temperature dependence of the dielectric constant for some polar liquids.
1. CH_3CN ; 2. $C_6H_5NO_2$; 3. C_6H_5CN ; 4. $(CH_3)_2CO$; 5. CH_3Cl ;
6. CH_2Cl_2 ; 7. CH_3I ; 8. C_6H_5Cl ; 9. $CHCl_3$; 10. $(C_2H_5)_2O$.

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

where N is the number of dipole in a unit volume, k Boltzmann's constant, μ the dipole moment and α the polarizability of molecule.

Since it was found that this Debye equation does not hold quantitatively for pure polar liquids, alternative theories were proposed by several investigators. Debye[8] modified his original equation on the basis of the restriction of molecular rotation. Onsager[9] computed electrostatically the internal field, and obtained the following expression:

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

where n denotes the optical refractive index. Wilson[10] modified Onsager's theory by taking into account the optical anisotropy of molecule.   Kirkwood[11] developed

statistically a dielectric theory of polar liquids. Further, Fröhlich[12] developed a general theory applicable to any dielectric subsatnce.

However, there are few appropriate interpretations for the temperature dependence of the dielectric constant of polar liquid as given in Eq.(1). Yasumi and Komooka[13] proposed a theory concerning the linear relation of ε to $1/T$ by using their expression for the internal field. In all theories mentioned above, the expressions concerning the dielectric constant were derived through the calculation of the average value of electric moment of molecule.

In the present study, attempts are made to discuss the temperature dependence of dielectric constants in terms of the entropy change due to the dipole orientation.

THEORY

A. Thermodynamic Representation of Dielectric Phenomena[14]

According to the thermodynamics and the electrostatics, the electric polarization P is related to the thermodynamic quantities per unit volume of a dielectric material by the equation

$$P = \frac{\varepsilon - 1}{4\pi} E = \left(\frac{\partial A}{\partial E} \right)_T = \left(\frac{\partial U}{\partial E} \right)_T - T \left(\frac{\partial S}{\partial E} \right)_T, \qquad (4)$$

where E is the electric field strength, A the Helmholtz free energy, U the internal energy and S the entropy. Then we have

$$\varepsilon = \left[\frac{4\pi}{E} \left(\frac{\partial U}{\partial E} \right)_T + 1 \right] - \frac{4\pi T}{E} \left(\frac{\partial S}{\partial E} \right)_T. \qquad (5)$$

This equation means that the dielectric constant consists of two terms, i. e. the first term due ro a change in internal energy and the second due to the entropy change.

From the thermodynamic relation, we obtain

$$\left(\frac{\partial S}{\partial E} \right)_T = \frac{E}{4\pi} \left(\frac{\partial \varepsilon}{\partial T} \right)_E = -\frac{E}{4\pi T^2} \left(\frac{\partial \varepsilon}{\partial(1/T)} \right)_E. \qquad (6)$$

Hence Eq.(5) becomes

$$\varepsilon = \left[\frac{4\pi}{E} \left(\frac{\partial U}{\partial E} \right)_T + 1 \right] + \frac{1}{T} \left(\frac{\partial \varepsilon}{\partial(1/T)} \right)_E. \qquad (7)$$

It is seen from Eq.(7) that if the plot of ε against $1/T$ is a straight line, the intercept at $1/T = 0$ and the slope correspond to the first and the second term of Eqs.(5) and (7) respectively. Thus, the empirical constants a and b in Eq.(1) are related to the thermodynamic quantities by

$$a = \frac{4\pi}{E} \left(\frac{\partial U}{\partial E} \right)_T + 1 \qquad (8)$$

$$b = \left(\frac{\partial \varepsilon}{\partial(1/T)} \right)_E = -\frac{4\pi T^2}{E} \left(\frac{\partial S}{\partial E} \right)_T. \qquad (9)$$

B. Statistical Treatment of the Dipole Assembly

Eq.(6) shows that if $\partial \varepsilon/\partial T$ is negative, the entropy is decreased by the field. In such a case it may be considered that the external field orientates the dipoles,

creating order in polar liquids and thus leading to the decrease in the entropy of the state.

We shall consider an assembly of N independent non-localized dipoles, each of which carries an electric dipole of strength μ. The potential energy of the dipole in the internal field F is

$$U_j = -\mu F \cos \theta_j, \tag{10}$$

where θ_j denotes the inclination of the dipole to the direction of the field and the subscript j refers to the dipole of the j th kind. If we assume that n_j is the number of dipoles whose directions fall within the infinitesimal solid angle $\Delta\omega_j$, the total number Ω of different states of the assembly and the corresponding entropy S are given by

$$\Omega = \frac{1}{\prod_j n_j!} \prod_j (\Delta\omega_j)^{n_j} \tag{11}$$

$$S = k \ln \Omega, \tag{12}$$

where k is Boltzmann's constant.

According to Boltzmann's distribution law the relation between n_j and $\Delta\omega_j$ is given by

$$n_j = CN \exp\left(-\frac{U_j}{kT}\right) \cdot \Delta\omega_j, \tag{13}$$

where C is the normalization factor to be determined by the condition

$$N = \sum_j n_j. \tag{14}$$

Calculation leads to

$$C = \frac{1}{4\pi} \frac{x}{\sinh x}, \quad x = \frac{\mu F}{kT}. \tag{15}$$

Substituting Eqs.(11) and (13) into Eq.(12), we obtain

$$S = -kNx\left(\coth x - \frac{1}{x}\right) + kN \ln\left(\frac{\sinh x}{x}\right) + kN(1 + \ln 4\pi - \ln N). \tag{16}$$

Therefore we have

$$\left(\frac{\partial S}{\partial E}\right)_T = \frac{\mu N}{T}\left(x \operatorname{cosech}^2 x - \frac{1}{x}\right)\frac{\partial F}{\partial E}. \tag{17}$$

From Eqs.(17) and (6), the following expression is obtained concerning the slope of ε versus $1/T$ under the approximation $x \ll 1$,

$$\frac{\partial \varepsilon}{\partial(1/T)} = -\frac{4\pi N \mu^2}{3k}\frac{F}{E}\left(\frac{\partial F}{\partial E}\right) = -\frac{4\pi N_A \rho \mu^2}{3kM}\frac{F}{E}\left(\frac{\partial F}{\partial E}\right). \tag{18}$$

where N_A is Avogadro's number, ρ the density and M the molecular weight.

For the field F we assume the internal field given by Onsager and take up only the component parallel to the external field E. Then we obtain

$$F = \frac{\varepsilon(n^2 + 2)}{2\varepsilon + n^2} E, \tag{19}$$

where n is the refractive index.

Substituting Eq.(19) into Eq.(18), we have

$$\frac{\partial \varepsilon}{\partial (1/T)} = \left[\frac{\varepsilon(n^2+2)}{2\varepsilon+n^2} \right]^2 \frac{4\pi N_A \rho}{3kM} \mu^2. \tag{20}$$

In the case of gas, $\varepsilon \simeq 1$ and $n^2 \simeq 1$. Thus Eq.(20) becomes a simple expression as follows:

$$\frac{\partial \varepsilon}{\partial (1/T)} = \frac{4\pi N_A \rho}{3kM} \mu^2. \tag{21}$$

DISCUSSION

The values of dipole moment μ_{cal} calculated from b at $20°$ by using Eq.(20), are shown in Table 1 together with μ_{Ons}, the values calculated from Onsager's Eq.(3), μ_{gas} and μ_{sol}, those obtained from the gas and the solution method. As seen in Table 1, the agreement between μ_{cal} and μ_{gas} or μ_{sol} is fairly good, being better for smaller values of the dipole moment. If the more appropriate estimate is given for the internal field, still better agreements would be obtained.

It should be remarked that Eq.(20) gives a relation of the dipole moment to the temperature coefficient of the dielectric constant, whereas Onsager's Eq.(3) gives a relation of the dipole moment to the dielectric constant at a fixed temperature.

We shall consider the mutual relation between the expressions of Debye, Onsager and the present authors concerning the slope of dielectric constant against $1/T$.

Differentiating both sides of Eq.(2) with respect to $1/T$, we have

$$\frac{\partial \varepsilon}{\partial (1/T)} = \left(\frac{\varepsilon+2}{3} \right)^2 \frac{4\pi N}{3k} \mu^2. \tag{22}$$

Strictly speaking, Debye's theory is valid for polar gas, where the dielectric constant is so close to unity that Eq.(22) is identical with Eq.(21). Therefore, Eq.(21) may be applicable to the evaluation of dipole moment from the gas measurement.

It is noteworthy that Eq.(20) is useful for the determination of dipole moments from the temperature dependence of the dielectric constant in the liquid state, while Eq.(22) is applicable to the temperature method in the gaseous state.

The differentiation of both sides of Eq.(3) with respect to $1/T$ leads to the following:

$$\frac{\partial \varepsilon}{\partial (1/T)} = \frac{\varepsilon^2(n^2+2)^2}{3(2\varepsilon^2+n^4)} \frac{4\pi N}{3k} \mu^2. \tag{23}$$

Eq.(20) differs from Eq.(23) only in a factor $3(2\varepsilon^2+n^4)/(2\varepsilon+n^2)^2$. Since this factor has values between 1 and 1.5, the values of dipole moment calculated from Eq.(23) are always larger than μ_{cal} obtained from Eq.(20), provided that the same experimental value of b is adopted. Therefore it is noticed from Table 1 that Eq.(20) gives a value of the dipole moment nearer to μ_{gas} than does Onsager's Eq.(23).

For associated liquids such as alcohol, glycerol, glycol and water, μ_{cal} shows a considerable deviation from μ_{gas} and μ_{sol}. Such a tendency of μ_{cal} is similar to that of μ_{Ons}. In the present theory, the entropy is derived from Eqs.(11) and (12) on

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Table 1. Values of constants a and b in Eq.(1) and comparison of μ_{cal} calculated from Eq.(20) at 20°, μ_{Ons} calculated from Eq.(3), μ_{gas} and μ_{sol} obtained from gas and solution measurements respectively, in D. U.

	Intercept a	Slope b	μ_{cal}	μ_{Ons}	μ_{gas}	μ_{sol}	Lit.[a]
n-$C_{16}H_{33}Br$	1.33	700.0	1.98	1.80[b]	——	——	b
n-$C_{14}H_{29}Br$	1.43	716.7	1.92	1.78[b]	——	——	b
n-$C_{12}H_{25}Br$	1.16	866.6	2.01	1.79[b]	——	——	b
$CHBr_3$	1.08	940.0	1.21	1.0[c]	——	1.0[c]	c
$CH_3OC_6H_5$	0.97	1010.4	1·49	1.5[c]	1.2[c]	1.2–1.3[c]	c
n-$C_9H_{19}Br$	1.26	1033.3	1.95	1.81[b]	——	1.89[b]	b
n-$C_{10}H_{21}Br$	0.92	1050.0	2.08	1.79[b]	——	1.90[b]	b
n-$C_8H_{17}Br$	0.90	1216.6	1.99	1.81[b]	——	1.96[b]	b
m-$C_6H_4Cl_2$	0.88	1235.7	1.59	1.4[c]	1.6[h]	1.4–1.5[c]	c
C_6H_5Br	1.20	1258.5	1.50	1.4[c]	1.5–1.7[c]	1.4–1.5[c]	c
n-$C_7H_{15}Br$	0.69	1383.3	2.02	1.81[b]	2.15[b] ^{l}	——	b
$CHCl_3$	-0.37	1518	1.55	1.2–1.3[c]	1.1[h]	1.1–1.3[c]	c
C_6H_5Cl	0.58	1522	1.64	1.5–1.6[c]	1.6–1.7[c]	1.5–1.6[c]	c
n-$C_6H_{13}Br$	0.28	1650	2.06	1.83[b]	—	1.97[b]	b
$(C_2H_5)_2O$	-1.60	1748	2.00	1.4–1.5[c]	1.1–1.2[c]	1.1–1.2[c]	c
n-$C_5H_{11}Br$	-0.29	1967	2.09	1.82[b]	——	1.95[b]	b
CH_3I	-0.33	2147	1.48	1.3[c]	1.3–1.6[c]	1.4[c]	c
$C_6H_5NH_2$	-0.37	2158	1.74	1.5[c]	1.5[c]	1.5–1.6[c]	c
C_2H_5I	0.31	2199	1.69	1.5–1.7[c]	1.6–2.0[c]	1.7–1.8[c]	c
$CH_3CO_2 \cdot C_2H_5$	-0.99	2203	2.05	1.8[c]	1.8[c]	1.8–1.9[h]	c
n-C_4H_9Br	-0.56	2233	2.04	1.80[b]	2.15[b]	2.0[h]	b
Quinoline	-0.48	2826	2.16	2.1[c]	—	2.1–2.2[c]	c
n-C_3H_7Br	-2.12	3033	2.16	1.83[b]	2.15[b]	2.0[h]	b
CH_2Br_2	-3.60	3220	1.85	1.4[c]	1.9–2.3[h]	1.4[c]	c
CH_3Br	-2.08	3291	1.61	1.6[c]	1.8[c]	1.5[c]	c
C_2H_5Br	-1.88	3308	2.04	1.8–1.9[c]	1.8–2.1[c]	1.8–1.9[c]	c
CH_2Cl_2	-2.13	3320	1.90	1.7[c]	1.6[h]	1.5–1.8[c]	c
o-$C_6H_4Cl_2$	-3.28	3936	2.56	2.2[c]	2.2–2.5[h]	2.2–2.3[c]	c
CH_3Cl	-4.94	4425	1.86	1.8[c]	1.7–1.8[c]	1.6–1.8[c]	c
Pyridine	-3.53	5019	2.43	2.3[c]	—	2.1–2.2[c]	c
$C_6H_5COCH_3$	-6.57	7227	3.40	3.2[c]	3.0[h]	2.9–3.0[c]	c
C_6H_5CN	0.52	7377	3.16	3.6–3.7[c]	4.4[c]	3.9[c]	c
$(CH_3)_2CO$	-7.81	8022	3.11	3.0–3.1[c]	3.0[c]	2.7–2.8[c]	c
$CH_3COC_2H_5$	-8.57	8043	3.41	3.2[c]	—	2.7–2.8[c]	c
o-$CH_3C_6H_4NO_2$	-10.83	11220	4.12	3.9[c]	3.6[c]	3.7[c]	c
CH_3CN	-9.40	13745	3.39	3.6[c]	3.9[c]	3.1–3.5[c]	c
$C_6H_5NO_2$	-22.66	17138	4.69	4.2[c]	4.2[c]	3.9–4.0[c]	c
CH_3NO_2	-40.76	23500	4.39	3.7[c]	3.4–3.8[c]	3.0–3.1[c]	c
C_2H_5OH	-18.66	12447	3.43	2.8–3.1[c]	1.7[c]	1.7[c]	c
$CHOH (CH_2OH)_2$	-21.23	18330	4.21	4.00	—	2.7[h]	d
CH_2OHCH_2OH	-28.75	20700	4.02	3.64	2.3[h]	2.3[h]	e
H_2NNH_2	-20.65	21570	3.00	3.01	—	1.8[h]	f
H_2O	-35.03	33830	3.12	3.0–3.1[c]	1.8–1.9[c]	1.7–2.0[c]	g

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the assumption of independent non-localized dipoles. Hence, in the case of associated liquids, the entropy term due to the association mechanism must be taken into account in Eq.(16).

The dielectric properties of a few liquids such as acetic and butyric acids whose dielectric constants increase with increasing temperature may be attributed to the formation of a ring dimer and its self-ionization[15].

The negative value of a as shown in Table 1 may be ascribed to the physical sturcture inherent in the condensed state, though Cole et al.[5] suggested that the negative value of a have no physical meaning. The internal energy U used in Eq. (7) may not be the sum of the interaction energy between the dipole and the external field as given in Eq.(10), but be the sum of the mutual potential energy between dipoles.

Although Fowler and Guggenheim[16] derived Debye's formula for gases by using the partition function corresponding to the dipole orientation, their method is unable to explain the negative value of a when applied to the liquid state.

CONCLUSION

It is concluded that the temperature coefficient of the dielectric constant of polar liquids can be elucidated in terms of the entropy change due to the dipole orientation.

ACKNOWLEDGMENT

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