ELECTRIC POLARIZATION OF ONSAGER FLUIDS. I. DIPOLE POLARIZATION. 1. ELECTRIC MOMENTS OF FREE MOLECULES

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An attempt was made to modify the model Onsager theory. A polarizable molecular dipole enclosed in a spherical cavity is substituted for a rigid one submerged in the polarizable medium which fills the cavity. The local dielectric permittivity of the Heaviside type is replaced for the oscillating, rapidly damping function of the Fresnel integral. The analytical expressions deduced allow to estimate dipoles of free molecules, starting from the results of dielectrometry of polar fluids. The obtained values are as close as possible to the experimental data on a great variety of pure organic liquids. PACS numbers: 35.20.My, 31.70.Dk

1. Introduction

The problem of correct determination of electric and optical characteristics of molecules of dielectric fluids can actually be brought to the problem of description of the effective internal field which consists of the field induced by external sources and of the cumulative electric field of molecules of the medium including intermolecular interactions. Numerous attempts employing quantum-chemical and molecular-statistical approaches to solve the problem lead to general judgments and cannot give a systematic analysis of entire variety of the experimental data. Furthermore, in final step which is comparison with experiments, any theory, no matter how fundamental its basic principles are, has to use simple models. That is why theories based on macroscopic thermodynamics in the approximation of self-consistent field (SCF) are applicable.

The rational choice of the internal field model which would reflect the main features of electric polarization of fluids is the subject of greatest importance in the molecular physics of liquids. The Onsager model is a good example of a successful and purposeful search, though it is not free from serious drawbacks. Validity of the Onsager approach to the experimental data on dielectrometry of polar liquids has been demonstrated in several papers. It seems also obvious that the theory requires further development.

2. Model description of the internal field and orientational polarization

Let us modify the Onsager model [1] of a polar molecule in a dielectric fluid. The rigid, free-orienting dipole μ_0 is centrosymmetrically submerged in a polarizable matrix with polarizability α equal to the dynamic polarizability of the molecule. The Onsager cavity with the radius *a* is repleted with the matrix and is enclosed in a dielectric continuum. An obvious consequence of such transformation is a modification of the Onsager fields (cavity field G = gE, reactive field R = tm, and internal field E = G + R) and the effective molecular moment $(m = \mu_0 + \alpha E_e)$ which leads to the expressions

$$E_{\rm e} = G^* + R^*, \qquad G^* = gE^*, \qquad R = tm^*, \qquad G^* - G = l(\alpha G^*),$$

$$R^* - R = t(\alpha R^*), \qquad m = \mu_0^* + \alpha G^*, \qquad \mu_0^* - \mu_0 = \alpha(t\mu_0^*), \tag{1}$$

where the factors g and f are defined in [1]. Therefore, if E = 0, $\mu_0 \neq 0$, then $E_e = G^*$, $m^* = \alpha G^*$; if $E \neq 0$, $\mu_0 = 0$, then $E_e = R^*$, $m^* = \mu_0^*$, and if E, $\mu_0 \neq 0$, then

$$E_{e}^{2} = (G^{*})^{2} + (R^{*})^{2} + 2G^{*}R^{*}\cos\vartheta,$$

$$|G^{*}| = G^{*} + R^{*}\cos\vartheta, \qquad |R^{*}| = R^{*} + G^{*}\cos\vartheta,$$

$$m^{2} = m_{E}^{2} + m_{\mu}^{2} + 2m_{E}m_{\mu}\cos\vartheta.$$
(2)

The vectors m_E and m_{μ} are defined as follows:

 $|m_E| = \alpha(G^* + R^* \cos \vartheta) = \alpha |G^*|,$

$$|m_{\mu}| = \mu_0^* + \alpha (R^* + G^* \cos \vartheta) = \mu_0^* + \alpha |R^*|.$$

 ϑ denotes an instantaneous angle between the vectors E and μ_0 .

These expressions enable us to write down the integrally averaged (over all equally probable values of the angle ϑ from the interval $[0...\pi]$) quantity of the orientational energy of the effective moment m_{μ} in the field G^* :

$$U = -m_{\mu}G^* \cos \vartheta = -\mu_0^* G^* (1 + 1.5\alpha l) \cos \vartheta.$$
(3)

Therefore, the statistically averaged (Boltzmann) value $\langle \cos \vartheta \rangle$ determined with the help of the Langevin function L(x), x = U/kT when $U \ll kT$ (which is always true in the dielectrometry of liquids), is

$$\langle \cos \vartheta \rangle = \mu_0^* G^* (1 + 1.5\alpha t) (3kT)^{-1}$$

According to (2) the averaged (over ϑ) magnitude of the dipole moment m_{μ} projection on the direction of the field G^* and the corresponding orientational polarization of the fluid of identical polar molecules are as follows:

$$\langle m_{\mu} \rangle = m_{\mu} \langle \cos \vartheta \rangle = \alpha G^* + \mu_0^* G^* (1 + 1.5\alpha t) (3kT)^{-1},$$

$$P = N_i \langle m_\mu \rangle_E = \frac{\varepsilon - 1}{4\pi} E. \tag{4}$$

And finally, the relationship between the free-molecule dipole and the macroscopic characteristics of the dielectric fluid is established by the following equation:

$$\mu_0^2 = \frac{3kT}{4\pi N} \frac{(1-\alpha t)^2}{(1+1.5\alpha t)} \left[\frac{(\varepsilon-1)(1-\alpha t)}{g} + 3\frac{\varepsilon_{\infty} - 1}{\varepsilon_{\infty} + 2} \right].$$
 (5)

N is the number of molecules in the unit volume of a fluid, ε_{∞} , ε are high- and low-frequency dielectric permittivities of a medium at the absolute temperature T; k is the Boltzmann constant.

Studying dipole polarization of dielectric fluid within the framework of the Onsager model, Levin [2] introduced into consideration the limited body surrounding the Onsager cavity. The induction of the body in an external electric field is determined by the effective local dielectric permittivity $\varepsilon_1(r) \neq \varepsilon$, ε_{∞} individual for each fluid, which allows, if properly chosen, to calculate the magnitude μ_0 equal to the gaseous phase molecular dipole μ_g . Developing this idea, we introduce spherically (related to the fixed molecule) isotropic distribution of non-interacting molecules of the molecular fluid in the layer consisting of several coordinative spheres, in the form of the structural quasi-periodic arrangement of densely packed $(4\pi Na^3 = 3)$ Onsager bodies. The local, radially symmetrical dielectric permittivity function $\varepsilon_1(r)$ of such arrangement is assigned empirically and takes the form of the rapidly damping (at long distances from the center of the body) oscillating function [3]:

$$\varepsilon_1(r) = A(\varepsilon, \varepsilon_\infty) S_1(\pi r^2/2) + B(\varepsilon, \varepsilon_\infty) S_2(\pi r^2), \tag{6}$$

 $\lim \varepsilon_1(r) = \varepsilon$ when $r \gg a$ and $\varepsilon_1(r) = \varepsilon_\infty$ when $r \leq r_0$, $S(\pi r^2) = \varepsilon_\infty/2\varepsilon$, where $S_i(\pi r^2)$ are the Fresnel integrals. Then the electric induction of the inner Onsager body and its nearest surroundings is represented by the smooth function of r:

 $\operatorname{div} D(r) = \operatorname{div} [\varepsilon_1(r)E] = 0.$

To calculate the field factors g and t, we are to solve this equation. Expressing the radial component of the potential $\zeta(r)$ of the field E as $\zeta(r) = \text{const} \cdot F(r) \cos \vartheta$, in the polar coordinates, we can rewrite it in the following way:

$$\frac{\mathrm{d}^2 F(r)}{\mathrm{d}r^2} + \left[\frac{2}{r} + \frac{\mathrm{d}}{\mathrm{d}r}\ln\varepsilon_1(r)\right]\frac{\mathrm{d}F(r)}{\mathrm{d}r} - \frac{2}{r^2}F(r) = 0.$$

As this equation contains the logarithm derivative, it is impossible to achieve the general solution in the explicit form. Therefore, we look for the solution only in the region where r satisfies the condition

$$\lim_{\Delta r \to 0} \left[\sum_{j} (-1)^{j} \ln \varepsilon_{1j} (r+j\Delta r) \right] = 0.$$

Now the problem is reduced to the trivial search of the special solutions

$$\zeta_1(r) = \sum_l C_l r^l P_l(\cos \vartheta) \quad \text{and} \quad \zeta_2(r) = \sum_l T_l r^{-(l+1)} P_l(\cos \vartheta),$$

where $P_l(\cos \vartheta)$ are the Legendre polynomials. The coefficients C_l and T_l determine the quantities g and t [3].

3. Dipole moments of free molecules of pure organic liquid dielectrics

Assessment of reliability of free molecule dipole moments calculated on the basis of Eq. (5) with the local dielectric permittivity function (6), starting from the data on dielectrometry of about fifty pure organic compounds with general formulas $C_i H_j O_k X_l$ and $C_i H_j O_k N_m$ (X — halogen, i = 1...57, j = 1...110, k = 0...9, l = 0...16, m = 1...6), was made by comparison with the corresponding gaseous phase values μ_g .

All the measurements were performed at the temperature $T = 298 \pm 0.05$ K. Dielectric constant ε and density ρ of the liquids were found with the aid of the standard dielectrometer "Dipole", and refraction index n with the help of the refractometer IRF-23. High-frequency permittivity ε_{∞} was taken equal to $(1.05...11)n^2$.

Figure 1 presents correlations of the calculated dipole moments μ_0 with the experimental gaseous phase moments μ_g in the coordinates: $\Delta \mu = |\mu_0 - \mu_g|\mu_g^{-1}$ vs. $\varepsilon/\varepsilon_{\infty}$. The latter value is the dielectric constant of the fluid, normalized by the high-frequency permittivity. In the same figure we display the data of the analogous calculations according to Onsager and according to [4] with $\varepsilon_1(r)$ being inversely proportional to the exponent of r.

We also compare the outcomes of our approach and of the exact molecularstatistic theory of polarizable liquid dielectrics, viz. the hard-spheres model by



Fig. 1. Relationship between the values of dipole moments of free molecules calculated according to Onsager (i = 3), according to [4] (i = 2) and to Eq. (5) with $\epsilon(r)$ given by (6) (i = 1), and corresponding gaseous phase values for organic compounds of the types $C_iH_jO_k$ and $C_iH_jN_m$.



Fig. 2. Relationship between the values of Δy_i , calculated according to Onsager (i = 3), according to the model [4] (i = 2) and to Eq. (5) with $\epsilon(r)$ given by (6) (i = 1) (the data on y obtained by Onsager and Wertheim are presented in the insertion), and the corresponding results after [5]. Here $y = 4\pi N \mu_0^2 (9kT)^{-1}$.

Wertheim. Direct testing of the theory [5] by experiment is impossible. That is why we conducted calculations on the assumption that both the dipole μ_0 and the medium filling the Onsager cavity are non-polarizable. Besides, we equalize the radii of the Onsager cavity and that of the Wertheim hard molecular spheres. The results of the comparison are shown in Fig. 2, where y denotes $4\pi N\mu_0^2(9kT)^{-1}$.

4. Discussion

It may be seen from Fig. 1 that the smallest differences in the calculated dipole moments μ_0 in relation to the gascous phase ones μ_g are achieved within the limits of the modification of the Onsager theory which was presented here. The features of our approach are as follows:

First, the components of the internal field defined in the paper: the cavity field G^* directed along the external field E and the reactive field R^* oriented parallel to the molecular dipole μ_0 , differ from those in the Onsager theory by additional terms. These terms give more precise description of the reactive fields of the induced dipole moments (1).

Second, the orientational energy (3) varies from that used by Onsager by the factor $(1+1.5\alpha t)(1-\alpha t)^{-1}$. The factor accounts for the fact that polarization is a three-dimensional, spherical phenomenon. Consequently, the magnitudes and projections of the effective moment m_{μ} and field $E_{\rm e}$ on the directions of μ_0^* and E are closer to the actual values.

Third, when calculating the total orientational polarization (4) of a substance, we take account of the fact that the orienting effect of the field G^* is acting not on the dipole μ_0 of the isolated molecule but to the effective one m_{μ} which results from μ_0^* under influence of the reactive G^* and cavity R^* fields. All of the reasons mentioned above lead to the final conclusion (5) related to the known result of Onsager (μ_{Ons}) in the following way:

$$\mu_0^2 = (1 - \alpha t)(1 + 1.5\alpha t)\mu_{\text{Ons}}^2.$$

The bulk dielectric constant ε is used in the Onsager theory to characterize the permittivity of the cavity. It is assumed that it is constant right to the border of the cavity

$$\varepsilon_1(r) = \varepsilon \vartheta(x) + \vartheta(y), \qquad x = r - a, \qquad y = a - r,$$

where $\vartheta(\zeta)$ is the Heaviside function, r is the distance from the center of the cavity. Being one of the essential imperfections of the theory, it leads to noticeable errors in the dipoles of the slightly ($\varepsilon/\varepsilon_{\infty} < 5$) and strongly ($\varepsilon/\varepsilon_{\infty} > 15$) polar substances. But in the model with $\varepsilon_1(r)$ given by (6) the errors are considerably smaller. This fact agrees with the calculations of the field factors g and t in [3].

The validity of our approach has found another confirmation. Analytical differentiation of the non-linear equations g, l, $\mu_0 = f(\varepsilon, \varepsilon_{\infty})$ displays the bend points with the abscissae $\varepsilon/\varepsilon_{\infty} \equiv \varepsilon^*$. The magnitudes of ε^* are individual for each approach:

the Onsager theory	$\varepsilon^* pprox 2.6,$
the model [4]	$\varepsilon^* pprox 3.6$,
our approach	$\epsilon^* \approx 4.2.$

Our modification of the Onsager theory gives the bend points with the abscissae very close to that on the curve $\mu_g(\varepsilon, \varepsilon_{\infty})$, which was built upon the established values of the gaseous phase dipoles of the compounds studied. Minor inaccuracies in the dipoles calculated within the limits of our model for the substances with $\varepsilon/\varepsilon_{\infty} < 5$ and $\varepsilon/\varepsilon_{\infty} > 15$ are probably bound with the prevailing contributions of dispersive and strong dipole-dipole interactions to the energy of inductive polarization. Thus, when we assume that both the dipole μ_0 and the medium which occupies the Onsager cavity cannot be polarized and these contributions are negligibly small, our values of y are in fine accordance with the results of the exact Wertheim theory (Fig. 2).

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