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Dielectric Properties of Low-Polarity Substances and Their Description Taking into Account Intermolecular Interactions

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Abstract—Optical and dielectric properties of low-polarity liquids (benzene, xylene, toluene, carbon tetrachloride, carbon disulfide) are considered. A generalized equation of dielectric polarization is suggested to describe these properties; its specific feature is the correction for the kind and intensity of intermolecular interaction. This correction is determined on the basis of the model of the molecular electronic shell expanding owing to cross self-polarization of molecules. A material equation improving the agreement of the calculated quantities with the experiment is obtained.

Low-polarity liquids, strictly speaking, can be classed neither with polar nor with nonpolar substances. They have certain characteristic features such as the so-called solvent effect, frequency variance of the dielectric permittivity, and increased (compared to nonpolar liquids) dielectric permittivity. These compounds are characterized by the occurrence of additional atomic polarization along with the main electronic polarization. Typical representatives of low-polarity liquids are benzene, dioxane, and carbon tetrachloride. The Maxwell equation $\varepsilon = n^2$ does not hold for these compounds, and the Clausius–Mossotti equation is not always valid.

One of the possible causes of deviations from the Maxwell equation, observed with low-polarity liquids, may be their finite dipole moment giving rise to the orientation polarizability and to the corresponding contribution to the dielectric permittivity. The orientation contribution to the dielectric permittivity of liquids can also originate from dipole associates formed in a liquid. Substances that exhibit orientation polarization along with deformation polarization are usually described by a Clausius–Mossotti–Debye type equation [1–3]

$$\frac{\varepsilon - 1}{\varepsilon + 2\rho}\frac{\mu}{\rho} = \frac{4}{3}\pi N_A(\alpha_e + \alpha_a + \alpha_{or}), \qquad (1)$$

where μ is the relative molecular weight; ρ, density; α_e, α_a, and α_{or}, electronic, atomic, and orientation polarizabilities, respectively; and N_A, Avogadro number.

The sum $\alpha_e + \alpha_a$ is the deformation polarizability δ_d, and in analysis of experimental data it is usually considered as an entity. The orientation polarization is by definition equal to $p^2/3kT$, where p is the dipole moment of a molecule; k, Boltzmann constant; and T, temperature. At relatively large dipole moments, the deformation and orientation contributions can be separated experimentally [3]. As the dipole moment decreases (in going to low-polarity liquids), the error of its determination rapidly grows. At $\alpha_{or} \to 0$, Eq. (1) transforms into the Clausius–Mossotti equation:

$$\frac{\varepsilon - 1}{\varepsilon + 2\rho}\frac{\mu}{\rho} = \frac{4}{3}\pi N_A\alpha_d. \qquad (2a)$$

The Clausius–Mossotti equation is also applicable to describing purely electronic polarization, which is frequency-independent up to frequencies of the optical range. In this case, the measured quantity is the refractive index n:

$$\frac{n^2 - 1}{n^2 + 2}\frac{\mu}{\rho} = \frac{4}{3}\pi N_A\alpha_e. \qquad (2b)$$

Preliminary analysis of the applicability of Eqs. (1) and (2) to certain typical low-polarity substances shows that the error in calculation by these equations is in most cases large (several percents). On the other hand, the error of the Clausius–Mossotti equation applied to nondipolar substances is estimated at 0.2–0.5%. Apparently, to reach this level of accuracy, it is necessary to improve the accuracy of determining the dipole contribution to the dielectric permittivity.

In this connection, let us consider an alternative description of the dielectric polarization [4] based on introducing a correction for intermolecular interac-

Experimental and calculated dielectric constants of low-polarity substances

Substance	μ, g mol^{-1}	ρ, g cm^{-3} (20°C)	ε [6, 7] (20°C)	n^2 [6, 8] (20°C)	$\varepsilon_g - 1$[a] (20°C)	$n^2 - 1$[b] (20°C)	$(\alpha_e + \alpha_a) \times 10^{24}$, $\alpha_e \times 10^{24}$, cm^3	*p*, D
Benzene	78.0	0.8792	2.284	2.239	0.937	2.320	11.0, 10.4	0
p-Xylene	106.2	0.861	2.264	2.224	0.919	2.159	15.1, 14.3	0
m-Xylene	106.2	0.8642	2.367	2.228		2.228		0.3–0.4
o-Xylene	106.2	0.8802	2.594	2.253	0.919	2.350	15.1, 14.2	0.62
Toluene	92.1	0.867	2.392	2.226	0.883	2.302	12.7, 11.2	0.36
CCl_4	153.8	1.595	2.2363	2.124	0.8758	2.2366 2.104	11.16, 10.24	0
Dioxane	88.1	1.033	2.218	2.017	0.862	2.0176	8.56	0.4
CS_2	76.1	1.263	2.642	2.618	1.113	2.562	8.866, 8.08	0

[a] Calculated by Eq. (3). [b] Calculated by the Clausius–Mossotti equation.

tions into a material equation for an ideal substance. We will start our consideration from the gas equation of dielectric polarization, valid for the ideal state of a substance (when intermolecular interactions can be neglected) [5]:

$$\varepsilon_g - 1 = 4\pi N\alpha. \tag{3}$$

where ε_g is the dielectric permittivity of a hypothetical substance corresponding to the ideal state; N is the molecular density (number of molecules in unit volume).

This equation has the same sense as the equation of the ideal state of a gas in thermodynamics. It is assumed that the molecules preserve their individual electronic structure and, correspondingly, their polarizability. The values of $\varepsilon_g - 1$, calculated by Eq. (1) from the "gas" polarizabilities α and the densities ρ corresponding to those of the real substance, are listed in the table. All these values are systematically underestimated as compared to the experimental values of $\varepsilon - 1$. Equation (1) should be modified by introducing a certain correction associated in some way or other with molecular interaction forces. Indeed, condensation of a substance results in shortening of intermolecular distances and in the corresponding growth of the intermolecular interaction forces; this fact forms the basis for the concept of the condensed state of a substance. It is also the basis of the comprehensively approbated thermodynamic method for studying intermolecular interactions, the method of virial expansion of the compressibility coefficient in a power series in density [9]. If we accept this obvious principle, it will become necessary to reject the postulate that the molecular polarizability is constant. It should be noted that in Eq. (3) the dielectric properties of a substance (and, correspondingly, the dielectric permittivity) at a given composition are determined exclusively by the polarizability. Therefore, it would be quite logical to ascribe the experimentally observed difference between ε and ε_g to variation of the molecular polarizability proper in the course of condensation, i.e., if applied to condensed media, Eq. (3) should be supplemented by the correction $\Delta\alpha/\alpha$ characterizing the intermolecular interactions:

$$\varepsilon - 1 = 4\pi N\alpha(1 + \Delta\alpha/\alpha). \tag{4}$$

Here the quantity $Z_\varepsilon = 1 + \Delta\alpha/\alpha$ is the so-called dielectric coefficient of compressibility, directly following from comparison of Eqs. (3) and (4). Like the thermodynamic compressibility coefficient Z_p, Z_ε is the measure of intermolecular interactions. Deviations of Z_ε from unity may be indicative of perturbation of molecular electronic shells and hence of changes in the molecular polarizability.

The correlation between the polarizability and size of the electronic shell is the simplest in atomic systems. The atomic polarizabilities are usually calculated within the framework of Bohr or Thomson's model [10, 11] (both models lead to the same result). This is usually done by constructing the balance equation for forces acting on electric charges of the atom. On the one hand, an external field E perturbs the electronic shell of an atom with the force $F_e = qE$. On the other hand, the counteracting Coulomb attraction forces give rise to the Hookean force F_C. The origin of this force is associated with redistribution of the intraatomic fields due to perturbation of the electronic shell of an atom; the criterion of this redistribution is the change in the atomic radius a by Δa. This force can be found as the difference between the forces acting in the atom before and after perturbation:

$$F_C = q_eE_{a0} - q_eE_{aE} = \frac{q_eq_n}{a^2} - \frac{q_eq_n}{(a+\Delta a)^2} = \frac{2q_eq_n\Delta a}{a^3},$$

where q_e and q_n are the effective charges of electrons and nucleus; E_{a0} and E_{aE} are the intensities of the electric field generated by the nucleus before and after perturbation.

Let us take into account the determining equation for the induced electric moment p_i, $p_i = \alpha_eE$, where E is the intensity of the external electric field, equal in this case to the intensity of the effective field E_a acting on a given molecule and generated by its nearest atomic surrounding. Let us also assume $q_e = q_n = q$ and $p_i = 2q\Delta$a, where the coefficient 2 reflects the action on the atomic charges q_e and q_a of the force couple $F_C = \pm qE_a$. By solving the force balance equation $F_e = F_C$, we obtain the known relationship [8, 10]

$$\alpha_e = a_e^3. \tag{5}$$

Here the subscript e at the atomic radius a_e denotes the polarization radius. It should be noted that Eq. (5) is valid for hydrogen-like atoms only [10]. However, in going to molecular systems, the atomic extension effect is preserved. This means that each molecule, generating an electric field, exerts a polarizing effect on its nearest atomic surrounding. This effect is due to dispersion interaction forces resulting in that all atoms in each molecule, being affected by the surrounding atoms, are subject to all-round extension; as a result, the size of each molecule increases by a certain effective quantity Δa. In the process, the molecular fields E_a make the polarization work, which is equal to $u_m = p_iE_a$. This work is spent for deformation (Δa) of the electronic shell with the effective charge q_e. As a result, an induced dipole moment $p_i = q_e\Delta a$ arises in the direction perpendicular to the molecular surface. A similar hypothesis of an increase in the electronic shell volume was put forward by Litinskii [12] who considered the universal model of intermolecular interactions.

On the other hand, the stability of atoms in a molecule is provided by the Coulomb attraction forces; their energy is $u_C = –q_nq_e/a$, where q_b is the effective radius of the nucleus of an atom in the molecule. The relative perturbation of the electronic shell is determined by the ratio of u_C and u_m:

$$u_m/u_C = p_iE_aa/q_nq_e = (\Delta a/a)^2. \tag{6}$$

When deriving this equation, we used the known relationships $p_i = \alpha E_a$ and $\alpha = a^3$ [Eq. (5)].

According to Eq. (6), condensation of a medium results in an increase in the molecular size, implying the corresponding increase in the molecular polarizability. A peculiar self-polarization of molecules caused by mutual effects of their electric fields is observed. The relationship between the relative changes in α and a can be obtained by differentiation of the relationship $\alpha = a^3$:

$$\Delta\alpha/\alpha = 3(\Delta a/a). \tag{7}$$

By substituting $\Delta\alpha/\alpha$ in Eq. (4), taking into account relationships (6) and (7), we obtain the virial expression for dielectric polarization:

$$\varepsilon - 1 = 4\pi N\alpha_e[1 + 3(u_m/u_C)^{1/2}]. \tag{8}$$

The intermolecular interactions are cooperative, i.e., all the surrounding molecules participate in extension of the electronic shell; for molecular systems in the condensed state, the coordination number η is ~11–12. The effective polarization energy is constituted by the energies of pair interactions u_d between the central (selected) molecule and molecules of its nearest surrounding. The pair interaction forces are always directed normally to the surface of the selected molecule. The resultant force acting on the surface of the selected molecule in any point is equal to the sum of projections of the pair interaction forces on the direction normal to the molecular surface. To determine the effective polarization energy, it is necessary to know the effective number of pair interactions taking part in deformation of the electronic shell in any point. For this purpose, we take into account the fact that the polarization energy is equal to 1/4 of the total energy of ηu_d, because of the uniform distribution of this energy in space in mutually perpendicular planes corresponding to the directions up–down (relative to the selected molecule) and left–right (for molecules lying in the same plane with the selected molecule). Hence, the effective polarization energy can be found as $u_m = \eta u_d/4$. In molecular systems, the intermolecular interaction energy, to a first approximation, is determined by the dispersion energy [13, 14]:

$$u_m = \frac{\eta}{4}u_d = -\frac{3\alpha^2I\eta}{16r^6}, \tag{9}$$

where I is the ionization potential and r is the distance between the centers of the interacting molecules.

Let us then take into account the fact that the binding energy of valence electrons in molecules is equal to the ionization potential, $u_C = I$ [15], and substitute u_m and u_C in Eq. (8), considering that the molecular volume V_m (equal to $1/N$), i.e., the volume per molecule, is equal to the elementary volume r^3. Also, for definiteness sake, let us assume the coordination number $\eta = 12$, which is maximum possible for molecular systems. As a result, we obtain the “virial” (i.e., based on the concept of force interactions) equation of the dielectric polarization:

$$\varepsilon - 1 = 4\pi N\alpha_e\left(1 + \frac{9\alpha_e N}{2}\right) = 4\pi N\alpha_e\left[1 + \frac{9(\varepsilon - 1)}{8\pi}\right]. \tag{10a}$$

Here, for definiteness sake, we put the subscript denoting the electronic polarization at the polarizability α_e. This equation becomes more compact when written using dielectric susceptibility χ:

$$\frac{2\chi}{9\chi + 2} = \alpha_e N, \tag{10b}$$

where $\varepsilon - 1 = 4\pi\chi$.

This equation is valid for nonpolar substances; it was approbated with noble gases as examples.

Equation (10) resembles in its structure the Clausius–Mossotti equation presented in the following form:

$$\varepsilon - 1 = 4\pi N\alpha\left[1 + \frac{\varepsilon - 1}{3}\right]. \tag{10c}$$

Equations (10a) and (10c) differ only in the factors at $\varepsilon - 1$: 0.358 in (10a) and 0.333 in (10c). Comparison of Eqs. (10c) and (10a) with (4) leads to a conclusion that the expressions in brackets are corrections that are essentially corrections for intermolecular interactions in both cases. It can be shown that the difference between these expression originates from the difference between the assumed coordination numbers. Indeed, by taking in Eq. (8) the coordination number given by the relationship $\eta^{1/2} = 16\pi/(9 \times 3^{1/2})$ (i.e., $\eta \sim 11$), we obtain in the brackets the expression equal to the Lorentzian correction $(\varepsilon + 2)/3$ entering into the Clausius–Mossotti equation, whereas Eq. (10a) was obtained in the approximation $\eta = 12$.

Equations (10) describe electronic polarization and do not take into account atomic polarization. To take into account the contribution of atomic polarization to the resultant dielectric permittivity or refractive index, it is necessary to refine the above-accepted molecular model in which the interatomic bonds were assumed to be absolutely rigid. However, in real molecules the covalent bond energy is finite. Furthermore, it is always lower than the ionization potential of the constituent atoms. Therefore, the elasticity of a chemical bond is also finite, giving rise to an additional polarization mechanism, atomic polarization.

The difference between the mechanisms of the atomic and electronic polarization should be manifested in the frequency variance of the dielectric permittivity. The electronic (faster) polarization is manifested at high frequencies also, whereas the atomic (slower) polarization is manifested only at low frequencies. This means that, at optical frequencies, only the electronic polarization contributes to the dielectric permittivity. This contribution is usually expressed via the refractive index; according to Eq. (10), we obtain for this case expression (11), with the coordination number η assumed to be 12:

$$n^2 - 1 = 4\pi N\alpha_e\left[1 + \frac{9(n^2 - 1)}{8\pi}\right]. \tag{11}$$

In the general case, we obtain Eq. (12):

$$n^2 - 1 = 4\pi N\alpha_e\left[1 + 3\sqrt{3\eta}\,\frac{(n^2 - 1)}{16\pi}\right]. \tag{12}$$

In this equation, we took into account the dependence of the correction for intermolecular interactions on the structural factor η.

In many cases, molecules in liquids are associated and form a fairly ordered supramolecular structure. For example, the benzene molecules are arranged in mutually perpendicular planes, and the structure resembles that of the solid benzene lattice. In this case, the expression for the intermolecular interaction energy is as follows:

$$u_m = -\frac{3\alpha_\perp\alpha_\parallel\nu u_C}{4r^6}. \tag{13}$$

where $\alpha_\parallel$ and $\alpha_\perp$ are the longitudinal and transverse polarizabilities, respectively; η, coordination number; and r, mean intermolecular distance. In view of (13), Eq. (11) can be transformed to the following form:

$$n^2 - 1 = 4\pi N\alpha_e\left[1 + \frac{3N}{2}\sqrt{3\alpha_\parallel\alpha_\perp\eta}\right]. \tag{14}$$

The dielectric permittivity and refractive index of low-polarity substances can be measured with a high accuracy, which opens the principal possibility of determining low and very low dipole moments. If it is possible to separate the orientation and atomic contributions, then the effective dipole moments can be calculated with Eq. (15):

$$\varepsilon - n^2 = 4\pi N\alpha_{\mathrm{or}} = \frac{4\pi\rho N_{\mathrm{A}} p_{\mathrm{eff}}^2}{3kT\mu}, \qquad (15)$$

where $\alpha_{\mathrm{or}} = p_{\mathrm{eff}}^2/3kT$ is the orientation polarizability; p_{eff}, effective dipole moment; μ, relative molecular weight; ρ, density; k, Boltzmann constant; and T, temperature.

Let us consider the applicability of these equations to low-polarity substances.

Dioxane. Dioxane is the only “nonpolar” solvent infinitely miscible with water. This allows smooth variation of the dielectric properties of a solution in a wide range of dielectric permittivities. The water–dioxane system shows abnormal trends in variation of dielectric properties [16]. Another characteristic feature of dioxane is the so-called “dioxane” effect [17]. The unusual properties of dioxane are due to its characteristic structure. Dioxane has two conformations: *boat* and *chair*. Relatively large charges on the surface of the oxygen atoms provide fairly strong interaction of dioxane with solute molecules and hence good solvency of dioxane. This is also favored by certain small dipole moments of molecules in the *boat* conformation. The prevailing nondipolar *chair* conformation determines the “nonpolar” properties of dioxane. This is confirmed by the fact that the refractive index calculated by the Clausius–Mossotti equation is in good agreement with the experiment (see table). In calculations, we took reference data on the polarizability of dioxane molecules in the gas phase [17] and the refractive index extrapolated to infinite wavelength according to [8]. The same value was taken for comparison with the calculation results, as specifically corresponding to the electronic polarization. ‘The difference $\varepsilon - n^2 = 0.2$ between the measured static dielectric permittivity (ε) and refractive index squared (n^2) is the frequency variance, which is due to the total contribution from dipolar molecules and atomic polarization of all the molecules. The solvent polarity is determined by the effective dipole moment p_{eff}, equal to 0.4 D according to published data [18]. The corresponding contribution to the dielectric permittivity according to Eq. (15) is $\Delta\varepsilon$ 0.12. The remaining fraction of the frequency variance, 0.08, should be apparently ascribed to variance of the dielectric permittivity due to atomic polarization. If all these corrections are taken into account, the Clausius–Mossotti equation becomes applicable to dioxane; this became possible after separation of particular contributions to the polarization. The applicability of the Clausius–Mossotti equation to dioxane suggests that the molecules in the liquid are weakly structured, and their coordination number is $\eta \approx 11$.

Benzene. According to available data on polarization $\prod$ and refraction R in the gas phase (see table) [19], benzene shows the frequency variance of the dielectric permittivity. In the liquid phase, this is confirmed by fairly strong IR absorption [20]. From data on $\prod$ and R, we determined the deformation polarizabilities of the benzene molecules and then the quantities ε and n^2 according to Eqs. (1) and (2). Both quantities appeared to be overestimated, with the values of $\varepsilon - 1$ and $n^2 - 1$ differing from the experimental values by ~5%. This error is very large for the Clausius–Mossotti equation, and it can be explained by taking into account the above-mentioned nature of the Lorentzian correction for intermolecular interactions according to Eq. (10). The disagreement with the experiment is due to specific features of the electronic structure of benzene molecules, determining the specific features of intermolecular interactions in benzene. It is known that liquid benzene shows features of a quasicrystalline structure [21], which is due to significant polarizability anisotropy. This should cause the coordination number to decrease. Taking the coordination number η 8 and using Eq. (12) (with the reference value of polarization $\prod$), we obtain ε 2.288. This result much better agrees with experiment (the error is ~0.5%). The expected orientation contribution originating, according to the hypothesis put forward in [22], from formation of weak dipole associates in liquid benzene is absent. The same conclusion follows from the effective dipole moment of liquid benzene, p_{eff} ~0.1 D, estimated by Eq. (15); its contribution to the dielectric permittivity according to Eq. (12) is of the order of calculation error. A small difference between the calculated [by Eq. (12), using the reference value of refraction R] and experimental optical quantities n^2 (2.210 and 2.239) is apparently due to the error in extrapolation of the refractive index to infinite wavelength corresponding to purely electronic polarization according to Eq. (12). A qualitatively similar result is obtained using Eq. (14) with substitution of the known values, $\alpha_{\parallel}$ 6.4, $\alpha_{\perp}$ 12.4 Å^3, and η 8.

It is interesting to consider how variation of the structure (relative to that of benzene molecule) affects the dielectric properties and, correspondingly, polarity of a substance. For this purpose, we chose the benzene derivatives, **xylene** and **toluene**. For toluene and three isomers of xylene, we calculated the frequency variance of the dielectric permittivity and the dipole moment; also we assessed the applicability of the Clausius–Mossotti equation and Eq. (10a) to their dielectric properties.

Let us first discuss *p*-xylene. Its axial symmetry suggests the absence of the dipole moment. Nevertheless, the variance $\varepsilon - n^2 = 0.04$ of *p*-xylene is significant and equal to that of benzene. This fact suggests that the supramolecular structure of *p*-xylene is similar to that of benzene. The relatively high stability of both structures is attributable to the increased energy of the dispersion interaction of molecules, which is, in turn, due to fairly high transverse polarizability of benzene as a result of delocalization of electrons on its π bonds. The effective dipole moment of liquid *p*-xylene, like that of benzene, is close to zero. The variances for *o*- and *m*-xylene are appreciably higher than those for benzene and *p*-xylene, which is due to the axial asymmetry of *o*- and *m*-xylene molecules and appearance of permanent dipole moments. The dipole moment suggests the orientation contribution to the dielectric permittivity. The p_{eff} of *m*-xylene is 0.35 D [18], which corresponds to the orientation contribution $\Delta\varepsilon$ 0.049. With this contribution taken into account, the static and optical dielectric permittivities become appreciably closer. A similar result is obtained with *o*-xylene whose dipole moment is still higher: p_{eff} 0.62 D [18]. After correcting for the orientation contribution to the dielectric permittivity, the quantity $n^2 - 1$ calculated by Eq. (12) appears to be very close to the experimental value (see table).

Toluene, in which the molecular symmetry is distorted by the methyl substituent, is also structurally similar to benzene. The axial asymmetry of the toluene molecule leads to the dipole moment p_{eff} 0.36 D [18]. The frequency variance is also fairly high ($\varepsilon - n^2 = 0.166$) and is primarily due to the intrinsic dipole moment of toluene molecules. The orientation polarizability calculated from the dipole moment allows the dielectric permittivity to be corrected for the orientation contribution, to determine the theoretical dielectric permittivity. Calculation by the Clausius–Mossotti equation gives $n^2 - 1 = 1.236$, which is fairly well consistent (with ~1% error) with the experimental value, $n^2 - 1 = 1.226$. This means that the coordination number of toluene is close to 11. This fact suggests that deviations from the symmetry of molecule enhance their coordination power.

Carbon disulfide. The dielectric permittivity of carbon disulfide, ε 2.642, is exceedingly high for nondipolar molecular systems. This is due to the relatively high polarizability at relatively low molecular weight. The variance of the dielectric permittivity of CS_2 in the gas phase ($\prod$ 22.36, R 20.17 cm^3 [19]) suggests the presence of vibrational degrees of freedom in the IR range. This fact is confirmed by the relatively strong IR absorption of liquid CS_2 [20]. The values of ε and n^2 calculated from $\prod$ and R [by Eqs. (1) and (2), respectively] significantly differ from the experimental values (relative error ~5%). Such a difference can be explained by improper choice of the correction for intermolecular interactions in Eqs. (1) and (2), corresponding to η ~11. The high coordination numbers are typical for spherical molecules rather than for linear molecules like CS_2. The linear structure of CS_2 molecules with the pronounced anisotropy should result in structuring of the liquid. Assuming the coordination number η 8, typical for such molecules, and turning back to Eq. (12), we obtain the calculated value ε 2.647. A small deviation from the experimental value ($\Delta\varepsilon$ 0.005) may be due to formation in the liquid of weak associates with the effective dipole moment p_{eff} ~0.1 D.

Carbon tetrachloride. Carbon tetrachloride, like benzene, shows both electronic and atomic polarization. The atomic contribution can be determined from the polarization $\prod$ and refraction R of CCl_4 in the gas phase [19]. It can be calculated with Eq. (2) by substituting the corresponding values of $\prod$ and R. It appears to be significant, $\Delta\varepsilon$ 0.133, and virtually coinciding with the experimental variance $\varepsilon - n^2 = 0.112$. Hence, the orientation contribution to the resultant polarization of CCl_4 is insignificant. This suggests that CCl_4 molecules have no dipole moment. This result cast doubts on the hypothesis that liquid CCl_4 contains dipole associates supposedly formed owing to strong interaction between chlorine atoms [22]. Calculation of the dielectric permittivity of CCl_4 by Eq. (2) gives n^2 2.2366, which only slightly exceeds the experimental value of ε, 2.2363. The applicability of the Clausius–Mossotti equation (η ~11) to the dielectric permittivity of CCl_4 is consistent with the fact that its globular molecules provide high coordination.

Analysis of the dielectric properties of low-polarity liquids confirms the previous conclusion that correct description of the dielectric properties of substances requires an equation reflecting the dependence of the dielectric permittivity on the nature and intensity of intermolecular interactions. In the case of low-polarity substances, the dependence of the dielectric permittivity on intermolecular interactions is associated with the increase in polarizability due to cross self-polarization of molecules. In turn, the self-polarization efficiency depends to similar extent on the polarizability of a molecule and number of molecules in its nearest surrounding (i.e., coordination number). The polarizability can be measured with a fairly high accuracy [3, 4]. Therefore, it appears possible to determine fairly accurately the coordination number using virial equation (12). On the other hand, if the coordination number is known, the energy of intermolecular interaction can be determined directly with this equation.

Published data show that the dielectric properties of low-polarity substances depend on the ratio of the polarizability components and on the extent of sphericity of their molecules. The following classes of substances can be distinguished with respect to polarity:

(1) Nondipolar ("nonpolar") substances for which the orientation polarizability is small compared to the deformation polarizability, i.e., $\alpha_d >> \alpha_{or}$. This class includes substances with the effective dipole moment $p_{eff} \leq 0.1$ D.

(2) Low-polarity liquids for which the deformation and orientation polarizabilities may be comparable, so that $\alpha_d \geq \alpha_{or}$.

(3) Polar liquids for which the orientation contribution becomes prevalent, i.e., $\alpha_{or} \geq \alpha_d$.

The dipole moment p_{eff} ~1 D can be taken as the borderline between low-polarity (p_{eff} < 1 D) and polar (p_{eff} > 1 D) substances.

The specific feature of "low-polarity liquids" is the necessity of taking into account all kinds of polarization (electronic, atomic, orientation) to attain the high accuracy of the description. The applicability of the Clausius–Mossotti equation to low-polarity liquids appears to be limited, and it seems better to use the equation of dielectric polarization derived in this work, in which the energy of intermolecular interactions and the structural factor are introduced as parameters of the theory along with the polarizability.

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