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THEORY OF DIELECTRIC POLARIZATION OF A SUBSTANCE. CALCULATION OF DIELECTRIC PERMITTIVITY OF WATER, AMMONIA, AND CHLORINE

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A theory of dielectric polarization of a substance is developed. The theory is verified by experiment and by phenomenological relations that follow from the determination of polarization, molar polarization, and dielectric permittivity.

Neither the classical [1-4] nor the modern [5-13] theories of dielectric polarization of a substance are directly linked with the interaction energy or the electrical characteristics of molecules in dense media and therefore are practically unsuitable for concrete calculations.

In the present work, the problem of polarization is solved in energy terms, since polarization of dielectric molecules occurs in the intrinsic electric field simultaneously with the formation of an associated system (of a real gas, a liquid, a solid). An electric dipole is taken as a model of a molecule. If the molecule has a constant dipole p^0, the dipole moment of the molecule in the associated state is the vector sum of the constant and additional dipoles. With no constant dipole in the molecule, the dipole moment of the molecule is the additional dipole moment p_{add}. When associated molecular systems form, an internal electric field $\overline{F}$ is produced that alters the properties of single molecules. Under the action of this field, the system becomes self-polarized. With respect to polarizable molecules the field F acts as an external one, and therefore in what follows we will use relations obtained by phenomenological theory for the process of polarization of monomer molecules by an external electric field.

The process of self-polarization of a substance implies that the field F orients in space the dipole p, which changes in magnitude owing to deformation (the induction dipole) and correlation of the general motion (the dispersion dipole) of the electron density. Thus, three components of the intermolecular interaction (the orientation component, the induction component, and the dispersion component) correspond to the three contributions to the dipole moment of the molecule. The additional dipole is often called the polarization dipole, since the dispersion dipole is considered as the average induction dipole due to the fluctuating nonuniform electric field produced by each molecule at the location of another molecule. A characteristic of the dipole moment is electron polarizability. Since it is the total dipole p that is oriented in the field F, this polarization is purely dipole.

According to [14, 15], the internal electric field in condensed phases of water is about 10^{10} V·m^{-1} ($\approx 10^6$ cgs units), i.e., extremely strong. In strong electric fields, the dipole moment is written as

$$p = p^0 + \left[\alpha F + \frac{1}{2}\beta_1 F^2 + \frac{1}{6}\beta_2 F^3 + \frac{1}{24}\beta_3 F^4 + \ldots\right]\langle\cos\theta\rangle, \tag{1}$$

where $<\cos\theta>$ is the average value of the angle θ.

The change in energy for the system of molecules due to orientation in space, molecular deformation, and correlation of mutual motion of the electron density is equal to

$$dW = -\overline{P}\,d\overline{F} = -\chi\overline{F}\,d\overline{F}\,.$$

Since in the "ideal" gas–associated state transition the field strength and the polarization change from zero to F and P the change in energy in polarization in the intrinsic field is equal to

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$$W = -\int_0^F \overline{P}\,d\overline{F} = -\frac{\overline{P}\,\overline{F}}{2}. \tag{2}$$

The energy W changes in the process of initiation of interaction; therefore, at constant temperature and volume, W is equal to the density of the internal interaction energy. Allowing for this fact, for one molecule-dipole we write expression (2) as

$$pF\langle \cos\theta \rangle = 2\hat{u}. \tag{3}$$

We divide the process of self-polarization into two:

1) the dependence of the polarization $\overline{P}$ on $<\cos\theta>$ at constant p and F;

2) the dependence of $\overline{P}$ on the parameter x at a constant value of $<\cos\theta>$ where $x = pF/(kT)$ changes from zero to x.

The problem of finding $<\cos\theta>$ for the case of $p = \text{const}$ and $F = \text{const}$ was solved by Langevin. According to Langevin

$$\langle \cos\theta \rangle = l(x) = \frac{e^x + e^{-x}}{e^x - e^{-x}} - \frac{1}{x} = \operatorname{cth} x - \frac{1}{x},$$

where $l(x)$ changes from zero to 1. It is easily seen that in strong fields ($pF >> kT$) the function $l(x)$, to a high degree of accuracy, is equal to

$$l(x) \simeq 1 - \frac{1}{x} = 1 - \frac{kT}{pF}, \tag{4}$$

while for weak fields

$$l(x) \simeq \frac{x}{3} = \frac{pF}{3kT}. \tag{5}$$

The polarization of the substance in the case of the Langevin problem is equal to $P = npl(x)$; in an electric field F it is proportional to the factor x and is equal to

$$P = npxl(x). \tag{6}$$

From the widely known phenomenological relation

$$P = \frac{(\varepsilon_s - 1)F}{4\pi} \tag{7}$$

and expression (6) we obtain

$$\varepsilon_s = 1 + \frac{4\pi np^2 l(x)}{kT}. \tag{8}$$

Simultaneous solution of the phenomenological relations

$$P_{\mathrm{m}} = \frac{4\pi N_0}{3} a_{\mathrm{t}}, \tag{9}$$

$$P = na_{\mathrm{t}} F, \tag{10}$$

$$P_{\mathrm{m}} = \frac{(\varepsilon_s - 1) V_0}{3} \tag{11}$$

and expressions (3), (4), (6), and (8) enables us to obtain a series of equations useful for the polarization theory:

$$pFl(x) = 2\hat{u}\,, \tag{12}$$

$$P = \frac{2np\hat{u}}{kT}\,, \tag{13}$$

$$a_t = \frac{p^2 l(x)}{kT}\,, \tag{14}$$

$$P_m = \frac{4\pi N_0}{3} a_t = \frac{4\pi N_0}{3}\left[\frac{p^2 l(x)}{kT}\right], \tag{15}$$

$$F = \frac{8\pi np\hat{u}}{(\varepsilon_s - 1)\,kT}\,, \tag{16}$$

$$l(x) = \frac{2\hat{u}}{2\hat{u} + kT}\,, \tag{17}$$

$$F \simeq \left[\frac{6kT\hat{u}}{p^2}\right]^{1/2}. \tag{18}$$

Formula (18) is obtained from Eq. (3) with the proviso that $l(x) \approx x/3$ and therefore holds only for weak fields. Equation (17) is valid only for strong fields, which practically always holds for solid and liquid bodies and for gases near the critical temperature on the saturation line.

To verify the theory proposed in this work, we calculate p and ε_s for ice, water, and its vapor on the saturation line, and liquid ammonia and chlorine on the saturation line. To determine p and e_s of water in different states of aggregation, we used $p^0 = 1.834 \cdot 10^{18}$ cgs units and $a = 1{,}444 \cdot 10^{-24}$ cgs units [14]. The values of the internal energy of interaction for different substances and their calculation procedure are given in [16, 17]. To determine the values of the internal interaction energy of supercooled water in $\mathrm{J \cdot mol^{-1}}$, we used the approximate solution

$$\hat{U}_{\mathrm{sup.w}} = \hat{U}_{\mathrm{w}} + 50.2\,\Delta T = 42.786 + 50.2\,(273.15 - T)\,,$$

which assumes that $\Delta\hat{U}/\Delta T$ in the interval of the melting point T_m (−35°C) is the same as in water in the interval 0–100°C [16]. The values of the internal interaction energy in ice *Ih* were found using reference values of $H^0(T) - H^0(0)$ and the value of the internal interaction energy of ice at the melting point ($48{,}800\ \mathrm{J \cdot mol^{-1}}$, $\hat{u} = 0.810362 \cdot 10^{-12}$ erg).

Simultaneous solution of Eqs. (12) and (1) with the proviso that $\langle\cos\theta\rangle = l(x)$ enables us to obtain an expression for determining the values of the dipole moment in the condensed state. For water and ammonia molecules (the symmetry C_{nv}) we can write this expression as

$$p^4 l^2(x) - p^3 p^0 l^2(x) - 2p^2 \alpha\hat{u} l^2(x) - 2p\beta_1 \hat{u}^2 l(x) - \frac{8}{6}\beta_2 \hat{u}^3 = 0\,. \tag{19}$$

The values of molecular hyperpolarizability are found from Eq. (1) by alternately substituting two values of p and F, the values of p being determined by formula (8) with the use of the most reliable experimental data

TABLE 1. Average Values of p and ε_s of a Water Molecule in Ice Ih and in Supercooled Water

T, K	p, D, according to [19]		ε_s (water)		ε_s, (ice)		ε_s, (ice) [20]
	ice	water	I	II	I	II	Experiment; $-t$, °C
273,15	3,015	2,827	87,74	88	91,74	94,0	91,5; 0,0
268,15	3,020	2,834	89,71	90,4	93,9	95,8	–
263,15	3,026	2,842	91,43	92,9	96,2	97,6	96; 10,8
258,15	3,031	2,849	93,75	95,4	98,5	99,65	–
253,15	3,037	2,857	95,40	98,0	100,9	101,7	97,4; 20,9
243,15	3,048	2,872	99,70	103,5	106,0	106,1	100; 32,0
238,15	3,053	2,879	101,9	106,3 ± 2	108,7	108,5	–
230,15	3,059	–	–	–	113,2	112,5	104; 44,7
220,15	3,069	–	–	–	119,2	118,0	114; 56,8
200,15	3,085	–	–	–	133,1	130,7	133; 65,8
180,15	3,100	–	–	–	149,6	146,7	–
160,15	3,114	–	–	–	170,2	167,5	–
133,15	3,130	–	–	–	207,4	207,8	–
123,15	3,136	–	–	–	225,4	228,6	–

Notes: 1) I is the calculated values, II is the smoothed experimental ones. 2) The smoothed experimental values are obtained using the formulas $\varepsilon_s^{\perp} - \varepsilon_\infty = C_\perp/T$, $\varepsilon_s^{\parallel} - \varepsilon_\infty = C_\parallel(T - T_0)^{-1}$, and $\varepsilon_s = e_\perp + \varepsilon_\parallel)/3$ where C = $2.37\cdot10^4$ K, C = $2.25\cdot10^4$ K, and T_0 = 46 K [11, 12]. 3) $\varepsilon_0 = 3.10$ [20]. 4) The experimental values of the supercooled water are smoothed using the coefficient $(\Delta\ln\varepsilon_s)/\Delta T =$ K^{-1}.

TABLE 2. Calculated and Experimental Values of ε_s for Water on Saturation Line

T, K	p, D		ε_s			$l(x)$	
	vapor	water	experiment	calculation	calculation (vapor)	water	vapor
273,15	–	2,827	88	87,74	–	0,974147	–
283,15	–	2,812	83,80	83,67	–	0,972915	–
293,15	–	2,797	80,20	79,79	–	0,971658	–
313,15	–	2,768	73,10	72,60	–	0,969063	–
333,15	–	2,738	66,50	66,09	–	0,966353	–
353,15	–	2,709	60,60	60,21	–	0,963520	–
373,15	–	2,680	55,30	54,92	–	0,960551	–
393,15	–	2,651	50,50	50,12	–	0,957434	–
413,15	–	2,621	46,00	45,71	–	0,954153	–
433,15	–	2,592	41,90	41,71	–	0,950687	–
453,15	–	2,562	38,10	38,02	–	0,947012	–
473,15	1,86	2,531	34,50	34,60	1,07	0,943098	0,4
493,15	1,864	2,500	31,35	31,44	1,11	0,938904	0,45
533,15	1,890	2,436	25,30	25,68	1,26	0,929440	0,56
573,15	1,920	2,366	19,65	20,43	1,59	0,917515	0,65
593,15	1,938	2,326	16,90	17,86	1,87	0,910629	0,698
613,15	1,963	2,282	14,10	15,22	2,32	0,901629	0,742
623,15	1,979	2,256	–	13,80	2,66	0,896355	0,765
633,15	2,001	2,227	11,20	12,20	3,18	0,889462	0,790
638,15	2,018	2,208	–	11,21	3,60	0,884860	0,8046
643,15	2,043	2,182	9,74	9,87	4,28	0,878184	0,8226
647,27	2,117	2,117	–	6,75	6,75	0,857755	0,857755

on ε_s. The values of F are found from formula (12). The values of hyperpolarizability for the water and ammonia molecules are as follows:

$$H_2O:\ \beta_1 = -8.1857\cdot10^{-30}\ \text{cgs. units},\quad \beta_2 = 59.5794\cdot10^{-36}\ \text{cgs units};$$

TABLE 3. Calculated and Experimental Values of ε_s for Liquid Ammonia on Saturation Line

T, K	p, D	ε_s		$\varepsilon_{s.sm}$	P_m, cm$^3\cdot$ mol^{-1}	
		calculation	experiment [22]		(11)	(15)
195,45	1,582	30,25	25	29,75	226,2	226,2
213,15	1,574	26,70	26,7 [23]	26,70	204,4	204,4
223,15	1,570	24,95	22,7	25,12	193,8	193,6
239,8	1,565	22,41	22,38	22,69	178,3	178,2
260	1,562	19,81	–	20,05	162,8	162,7
288	1,562	16,83	16,9	16,90	145,5	145,5
298	1,565	15,92	15,9	15,90	140,5	140,5
350	1,583	11,77	–	–	119,5	119,4
390	1,600	8,47	–	–	106,1	106,1
400	1,608	7,27	–	–	103,3	103,3
405,6	1,617	5,14	–	–	100,0	100,0

Notes: 1) The average polarizability and the constant dipole moment of an ammonia molecule are equal to $2.4\cdot10^{-24}$ and $1.46\cdot10^{-4}$ egs units [22]. 2) The smoothed experimental values ε_{ssm} were found using the coefficient $(\Delta\ln\varepsilon_s)/\Delta T = -6.109\cdot10^{-3}$ K^{-1} and $\varepsilon_s = 15.9$.

TABLE 4. Calculated and Experimental Values of ε_s for Liquid Chlorine on Saturation Line ($a = 4.60\cdot10^{-24}$ cgs units [22], $p^0 = 0$, $l(x) = 1$, $\beta_2 = -33.3668\cdot10^{-36}$, $\beta_4 = 213.0331\cdot10^{-48}$ cgs units, the Symmetry of a Chlorine Molecule $D_{\infty h}$)

T, K	p, D	ε_s		$\Delta\varepsilon_s/\varepsilon_s$, %
		calculation	experiment [22]	
183,15	0,5162	2,918	–	–
207,15	0,4894	2,464	2,147	14,8
213,15	0,4841	2,386	2,150	11,0
239,95	0,4562	2,047	2,048	−0,05
253,15	0,443	1,914	2,030	−5,7
283,15	0,4968	1,97	1,97	0,0

$$\mathrm{NH_3}:\ \beta_1 = -\ 18.3242\cdot10^{-30}\ \text{cgs units}\,,\quad \beta_2 = 58.1219\cdot10^{-36}\ \text{cgs units}\,.$$

The calculation results are tabulated. Analyzing the data of Tables 1-3, we see that the calculated values of p and ε_s for ice, water and its vapor, and liquid ammonia are in good agreement with experiment [18-21]. From Tables 1 and 2 it is evident that the values of the dipole moment of a water molecule in supercooled water are larger than in water on the saturation line and smaller than Ih in ice. From Table 2 it follows that with decreasing density of the saturated vapor $p \to p^0$, which is actually observed since the saturated vapor near T_m is close to ideal in state. It is pertinent to note that the experimental values of the dipole moment of a water molecule in ice and in water are (2.88 ± 0.3)D and (2.5 ± 0.7)D respectively [15]. Analysis of the calculated values of p in liquid ammonia demonstrates that the values of the dipole moment of an ammonia molecule in the liquid state exceed slightly the value of p^0. This result is attributable to the presence in the ammonia molecule of three dipoles of the N-H bonds arranged at an angle of 107° relative to each other. It is clear that rotations of the ammonia molecules in space do not result in a substantial change in the molecular configurations or in the occurrence of significant orientation polarizability. Calculation of the values of ε_s for liquid chlorine shows that the dependence $\varepsilon_s = f(T)$ is quite reasonable and is, in principle, consistent with experiment. The calculated values of the dipole moment of a chlorine molecule in the liquid state are approximately twice its reference value [22]. In our opinion, this is due to the wrong theoretical expression from which the reference value of the dipole moment of the chlorine molecule was determined.

Conclusion. The proposed theory enables us to determine the parameters of the dielectric polarization mechanism for a substance: the average value of dielectric permittivity of a substance, the dipole moment of molecules in the associated state, the total polarizability and hyperpolarizabilities of a molecule, and the strength of the internal electric field. It can prove useful in studying many problems of the theory of solutions. The validity of the theory is verified by experiment and by the fact that the values of molar polarization found using the apparatus of the theory proposed coincide with the corresponding values calculated from the known phenomenological relations.

NOTATION

ε_s, static dielectric permittivity; ε_∞, high-frequency dielectric permittivity; $\varepsilon_s^{\perp}$, permittivity perpendicular to the axis C; $\varepsilon_s^{\parallel}$, permittivity in the direction of the axis C; a, average molecular polarizability; χ, dielectric susceptibility; β_i, molecular hyperpolarizability; p^0, constant dipole moment of a molecule; p, dipole moment of a molecule in condensed state; p_{add}, additional dipole moment of a molecule; P, polarization of a substance; P_{m}, molar polarization; k, Boltzmann constant; T, Kelvin temperature; t, Celsius temperature; θ, angle between the vectors $\overline{p}^0$ and $\overline{F}$; F, internal electric field strength; $\hat{U}$, internal interaction energy, $\mathrm{J \cdot mol^{-1}}$; $\hat{u}$, internal interaction energy per molecule; N_0, Avogadro number; V_0, molar volume; a_{t}, total molecular polarizability; $H^0(T)$, enthalpy as a function of temperature; $l(x)$, Langevin function; n, molecular concentration.

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