ORIENTING FIELD AND DIPOLE POLARIZATION

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Despite numerous theoretical and experimental studies, the question of the relation between the dielectric constant of a liquid ε and the dipole moment μ of its molecules has not yet received a satisfactory solution.

The well-known Debye formula, which is often written in the form

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

where n is the refractive index and N is the number of molecules in 1 cm^3, contains an internal contradiction, namely that the right-hand side can in principle take any positive value, whereas the left-hand side is bounded by unity.

In Onsager' s theory this contradiction is removed. But it suffers from a number of other shortcomings, which arise from the fact that this theory is based on a model molecular picture of the polarization of a dielectric. One cannot expect much from such a theory ([1]). Numerous attempts to refine the theory have not led to any substantial improvement.

The unsatisfactory state of the theory of dielectrics is manifested, among other things, in the fact that when pure liquids are studied, Onsager' s theory is used, whereas when solutions are studied, Debye' s theory is used. It would be desirable to have a unified theory that would make it possible to describe equally well the polarization of both pure liquids and solutions.

The principal merit of Onsager' s theory is that it convincingly showed for the first time that the field which produces the orientation of dipoles cannot be taken to be the Mosotti field

$$F_{\text{Mos}} = \frac{\varepsilon + 2}{3} E, \tag{2}$$

as is done in Debye' s theory, but that the orienting field must be assumed to be weaker than that field. But what is the true magnitude of the orienting field?

How is this field related to the Mosotti field? These questions found no answer in Onsager' s theory.

In Onsager' s theory the field of a spherical cavity is taken as the acting field. But if one takes into account the optical polarization of the dipole in an external field, then for the Onsager acting field one obtains the expression

$$F_{\text{Ons}} = \frac{\varepsilon(n^2+2)}{2\varepsilon + n^2}E. \tag{3}$$

It is not difficult to see that such a field cannot have universal significance. It depends only very weakly on ε. At values of ε above 10 it practically does not depend on ε and is close to the value $\frac{n^2+2}{2}E$. Hence it follows that Onsager' s theory can lay claim to a satisfactory description of dielectric polarization only for comparatively not very strongly polar liquids.

In choosing the acting field in a dielectric, one should be guided by one important condition: this field must lead to the correct value of the polarization energy of the dielectric. If we write two formulas for the dipole moment of a unit volume,

$$P = \frac{\varepsilon - 1}{4\pi}E = aNF$$

and multiply both by $E/2$, then we obtain two expressions for the density of the polarization energy

$$U = \frac{\varepsilon - 1}{8\pi}E^2, \tag{4}$$

$$U = aN\frac{FE}{2}. \tag{5}$$

If in the second formula the Mossotti field (2) is substituted for F, then in the case of a nonpolar substance the two formulas (4), (5) give coinciding results. If the same is done for a polar substance, replacing a by $\mu^2/3kT$, it turns out that in many cases formula (5) gives an energy approximately 1.5-3 times greater than the true thermodynamic quantity determined by formula (4).

The situation can be corrected in only one way: the Mossotti field (2) must be replaced by such a field that the correct value of the polarization energy is obtained. This field must be weaker than the Mossotti field (2), but stronger than the simply applied external field E, since if F in formula (5) is replaced by E, one obtains an energy that always proves to be smaller than the thermodynamic quantity.

For the time being let us use the following considerations. We have established that the orienting field F is weaker than $\dfrac{\varepsilon+2}{3}E$, but stronger than E; in other words, the factor $\frac{\varepsilon+2}{3}$, taken to the first power, gives too large a value, and to the zeroth power too small a value. The idea arises to take it to the power 1/2, i.e., to take for F the expression

$$F = \sqrt{\frac{\varepsilon+2}{3}}\,E. \tag{6}$$

We do not give here a more substantiated theoretical derivation, following from the picture of relaxation dispersion of polar liquids, from which, among other things, it follows that field (6) is strictly valid only for liquids with rigid dipoles, for which $n^2 = 1$. In the case of ordinary liquids it is valid when $\varepsilon \gg n^2$.

Consideration of another limiting case, when $\varepsilon \simeq n^2$, presents no difficulty. This includes very weakly polar liquids, such as toluene, and strongly diluted solutions of a polar substance in a nonpolar solvent. In this case, when the external field is switched on, optical polarization first arises practically instantaneously, and only then is dipole polarization created, which is established over some time τ. Since the dipole polarization is very weak, the orientation of the dipoles occurs practically in the Lorentz field. Therefore, in this limiting case, for the orienting field we shall have

$$F = \frac{n^2+2}{3}E. \tag{7}$$

Consideration of the two limiting cases makes it possible to pass to the general case. It is obvious that in the general case the field must consist of two terms, taking into account, respectively, the first and second limiting cases. It is also clear that the expression for the field must have such a form that for $n^2 = 1$ it passes into formula (6), and for $\varepsilon = n^2$ it passes into (7).

In passing from a polar liquid with rigid dipoles, for which formula (6) is valid, to a dipole liquid with deformable molecules, it is necessary everywhere to replace $\varepsilon - 1$ by $\varepsilon - n^2$ and ε by $\varepsilon - n^2 + 1$. Therefore, for the first term of the orienting field, instead of (6), we shall have

$$F = \sqrt{\frac{\varepsilon - n^2 + 3}{3}}\,E. \tag{8}$$

The orienting field F is the sum of two fields: the external field E and the additional field E_{add}, due to the polarization of the dielectric. Formula (8) takes both fields into account. Therefore, in the second term for F, the external field E must be excluded, since it has already been taken into account by the first term. Consequently, for the second term, instead of (7), one should write

$$F - E = \frac{n^2-1}{3}E. \tag{9}$$

Thus, in the general case, for the orienting field it is necessary to write the sum of (8) and (9)

$$F = \frac{n^2 - 1}{3} E + \sqrt{\frac{\varepsilon - n^2 + 3}{3}} E. \tag{10}$$

It is easy to see that formula (10) fully satisfies the conditions of limiting transitions: at $n^2 = 1$ it passes into (6), and at $\varepsilon - n^2$ into (7).

To find the expression relating ε and μ, it is sufficient to write two relations

$$P_\mathrm{d} = \frac{\varepsilon - n^2}{4\pi} E,$$

$$P_\mathrm{d} = \frac{\mu^2 N}{3kT} \left[\frac{n^2 - 1}{3} + \sqrt{\frac{\varepsilon - n^2 + 3}{3}} \right] E, \tag{11}$$

whence, after some transformations, we find for the molecular dipole polarization

$$\mathfrak{P}_\mathrm{d} = \frac{\varepsilon - n^2}{n^2 - 1 + \sqrt{3(\varepsilon - n^2 + 3)}} \frac{M}{\rho} = \frac{4}{3} \pi N_A \frac{\mu^2}{3kT}. \tag{12}$$

It should be noted that here n^2 should be understood as the dielectric permittivity at the boundary between the regions of electric and optical waves, $n^2 = \varepsilon_\infty$.

Before proceeding to a comparison of the theory with experiment, it should be recalled that this entire theory, like Debye' s theory, applies to liquids in which the molecules can orient themselves in the field as freely as in a gas. Consequently, all strongly associated liquids, such as alcohols and fatty acids, in which association occurs through intermolecular hydrogen bonding, must be excluded from consideration. Perhaps very strongly polar liquids should also be excluded, whose molecules have a very large dipole moment. In such liquids, a considerable orientational dipole interaction is possible, which also hinders the free orientation of molecules in the field. Apparently, this kind of interaction exists in acetonitrile, nitrobenzene, and other similar liquids, the molecules of which have a very large dipole moment ($\mu \approx 4$ debye).

Table 1 gives the results of calculations of the dipole moments of a number of molecules from the polarization of the liquid according to formula (12), on the basis of literature data ([2–7]). The table contains both organic and inorganic substances. Only nonassociated liquids are included in it, not counting formamide and water. Substances with very large dipole moments are also excluded. Only those substances are given for which dipole moments determined from vapor polarization are known ([8,9]). These are mainly fluorides, chlorides, bromides, and iodides.

Table 1

Dipole moments of a series of molecules, determined from the polarization of liquids by formula (12)

Polar liquid	$t°$, C	ε	ε_∞	ρ	$\mu \cdot 10^{18}$	$\mu \cdot 10^{18}$ (vapor)	Polar liquid	$t°$, C	ε	ε_∞	ρ	$\mu \cdot 10^{18}$	$\mu \cdot 10^{18}$ (vapor)
Hydrogen chloride	−15	6,32	1,80	1,02	1,10	1,08	*o*-Chlorotoluene	20	4,45	2,40	1,082	1,48	1,55
Hydrogen bromide	−81,2	7,11	2,56	2,80	0,80	0,80	Bromomethane	0	10,6	2,20	1,732	1,71	1,75
Hydrogen sulfide	−61	8,04	2,59	0,967	1,00	1,00	Bromoethane	25	9,2	2,20	1,452	1,96	2,02
Toluene	20	2,391	2,240	0,867	0,42	0,37	Bromopropane	25	8,09	2,22	1,343	2,04	2,08
Ethylbenzene	20	2,412	2,240	0,867	0,48	0,59	Bromobutane	25	6,93	2,22	1,270	2,04	2,12
o-Xylene	20	2,568	2,265	0,880	0,63	0,62	Bromopentane	25	5,33	2,21	1,136	2,10	2,15
Pyridine	25	12,3	2,30	0,978	2,29	2,20	Bromobenzene	25	5,39	2,46	1,488	1,63	1,70
Fluorobenzene	21	5,44	2,33	1,023	1,59	1,60	Iodomethane	20	7,00	2,47	2,279	1,48	1,62
o-Fluorotoluene	30	4,22	2,30	0,998	1,43	1,35	Iodoethane	25	7,69	2,42	1,925	1,81	1,87
m-Fluorotoluene	30	5,42	2,30	0,988	1,76	1,85	Iodopropane	20	7,00	2,38	1,749	1,87	1,97
Chloromethane	−20	12,6	2,05	0,98	1,74	1,85	Iodobutane	25	6,12	2,37	1,607	1,90	2,08
Chloropropane	20	7,7	2,08	0,892	1,96	2,04	1-Iodo-3-methylbutane	19	5,6	2,34	1,520	1,90	1,98
Chlorobutane	25	7,24	2,10	0,884	2,09	2,10	Iodobenzene	75	4,87	2,64	1,750	1,63	1,70
Chloropentane	11	6,6	2,13	0,892	2,06	2,12	Formamide	20	110	4,2	1,133	3,03	3,22
Chlorobenzene	25	5,63	2,35	1,100	1,70	1,73	Water	20	80,36	3,00	0,998	1,95	1,84

The dipole moments determined from the polarization of a liquid by means of formula (12) are given in the next-to-last column. The last column gives the dipole moments of the molecules in vapor. A comparison of the two columns of numbers shows, in most cases, such agreement that one may speak of coincidence. With the exception of three or four cases, the two series of numbers agree to within 4–5%. Better agreement can hardly be expected, if all possible errors in determining the value of μ in the liquid and in the vapor are taken into account.

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Note: Figure translations are in progress. See original paper for figures.