COLLOID CHEMISTRY
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Permittivity at Infinite Frequency

Yu. A. Lyubimov

Faculty of Physics, Moscow State University, Leninskie gory, Moscow, 119992 Russia
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Abstract—A method independently developed by Boyer-Donzelot and Levin for determining the permittivity at infinite frequency ε_∞ on the basis of the concept of polarizability additivity of interatomic bonds is considered. The ε_∞ values calculated for various chemical compounds are compared.

PHYSICAL MEANING AND METHODS FOR DETERMINING THE DIELECTRIC PERMITTIVITY AT INFINITE FREQUENCY

The classical static and dynamic theories of electric polarization implicate a parameter known as the permittivity at infinite frequency ε_∞ [1–4]. This parameter is a measure of deformational electric polarization, which arises due to displacements of positive and negative charges in the molecule (atom) from their equilibrium positions under the action of an external field.

Note, however, that it is difficult to reliably measure the contribution from deformational polarization. What is more, various authors at different times treated the notion of ε_∞ far differently. For example, Cole [5] defined ε_∞ as "the dielectric constant at infinite frequency that reflects only induced polarization." Imanov [6] proposed to determine ε_∞ from molecular refraction with a 30% correction for atomic polarization, an ill-founded approach without regard for the individual characteristics of the substance. Lindenberg [7] recommended to calculate ε_s from the static permittivity and the dipole moment μ_0 in vacuum.

Thus, most of the above methods for determining ε_∞ are of phenomenological character, not based on sound physical concepts. In addition, such approaches ignore the specifics of the structure and properties of substances.

Since the 1950s, the determination of ε_∞ by extrapolating the permittivity measured at various frequencies to infinite frequency has come into wide use [8]. This method is based on the Debye dispersion theory. Despite being widely accepted, this method cannot be considered flawless for a number of reasons. First, any extrapolation, especially over a wide range, entails significant uncertainties; second, the method employs the Debye dispersion relationships, which take into account only the orientational mechanism of polarization relaxation, without regard for other possible contributions, for example, from molecular librations and from interactions of translational and rotational degrees of freedom of the molecules.

In fact, it is these simplifications that raise doubts as to whether it is possible to assign the same *physical meaning* to ε_∞ in the theory of the dielectric constant in the far IR region and in the relationships describing relaxation processes (the Debye formulas and analogous expressions) [9]. We will take a further look at whether it is admissible to determine ε_∞ by extrapolation and will compare results obtained by this procedure with predictions of other methods for calculating ε_∞.

CALCULATION OF ε_∞ ON THE BASIS OF THE BOND POLARIZABILITY ADDITIVITY METHOD PROPOSED BY BOYER-DONZELOT

In 1970, Boyer-Donzelot (France) [10–13] proposed a method for calculating ε_∞ on the basis of the molar deformational polarizabilities (MDPs) of bonds, or molar bond polarizabilities for short (in cm^3/mol). The MDP of the bond between of atoms A and B (identical or different) can be calculated from the molar polarizability of a nonpolar compound containing atoms A and B. All the bonds (single, double, or triple) between atoms A and B can be assumed to be identical to one another. This assumption can be realized by selecting a suitable compound with known structural formula, type of molecular orbitals, bond lengths, etc. In this case, the MDP of the A–B bond can be calculated by dividing the molar polarizability (P_M) of the compound by the number of such bonds in its molecule.

Next, it was postulated that the MDP of a polar compound can be calculated by adding the MDPs of all its bonds, determined as described above. Clearly, this procedure implies that all properties of the interatomic bonds in the compound for which P_M is determined are identical to the properties of the bonds in the compounds used to calculate the required MDPs. In addition, it is assumed that P_M is the sum of the polarizabilities of the individual interatomic bonds of the compound. It is obvious that both these assumptions are fulfilled only approximately. Indeed, the properties of a

bond are determined not only by the natures of the atoms it binds but also by the effect produced by neighboring bonds. Changes in the positions of the bonds and their geometry result in more or less significant violations of the validity of the first assumption.

The assumption that the molecular polarizability is an additive quantity is also approximate; it proved to be unsuitable for describing the molecular refraction of some compounds. It is evident that the difference between the measured and calculated values of P_M is greater, the larger the distinctions between the structures of the molecules used to calculate the DBPs and the molecule for which P_M is calculated based on these DBPs. Within the framework of the considered methods of estimating P_M for a compound on the basis of the MDPs of its interatomic bond (see below), this problem is solved by selecting compounds with similar structures. It is desirable, of course, to take a closer look at this issue.

Let us now consider the calculation scheme. In [10], calculations are started with the determination of the MDPs for the $C_{sp^3}-C_{sp^3}$ and $C_{sp^3}-H$ bonds from experimental data on the properties of normal alkanes, for which (excluding the lowest one or two homologues) the following relationships are valid:

$$P_{C_nH_{2n+2}} = (n-1)P_{C_{sp^3}-C_{sp^3}} + (2n+2)P_{C_{sp^3}-H}$$

$$(n = 3, 4, 5 \ldots).$$

Using, for example, the P_M values for hexane (29.9 cm^3/mol) and heptane (34.5 cm^3/mol), one can obtain

$$\Delta P = 4.6 \text{ cm}^3/\text{mol} = P_{C_{sp^3}-C_{sp^3}} + 2P_{C_{sp^3}-H},$$

whence

$$P_{C_{sp^3}-C_{sp^3}} = 4.6 \text{ cm}^3/\text{mol} - 2P_{C_{sp^3}-H}.$$

Substituting this value into the expression for the polarizability of *n*-hexane yields $P_{C_{sp^3}-H} = 1.72$ cm^3/mol and $P_{C_{sp^3}-C_{sp^3}} = 1.16$ cm^3/mol. Next, the MDP of the $C_{sp^3}-C_{sp^2}$ bond for the alkene homologous series was determined. Based on Boyer-Donzelot's assumption that the lengths of the $C_{sp^3}-C_{sp^3}$ $C_{sp^3}-C_{sp^2}$ bonds are identical (the consequences of this approximation are discussed below), 1.54 Å for both, we assigned them the same value of DBP, 1.16 cm^3/mol. Then, using two members of the ethylene series, ethylene ($P_M = 10.72$ cm^3/mol) and *trans*-3-hexene ($P_M = 30.19$ cm^3/mol), we obtained (in a similar manner) the following expression for ethylene

$$P_M = 4P_{C_{sp^2}-H} + P_{C=C},$$

and *trans*-3-hexene

$$P_M = P_{C=C} + 2P_{C_{sp^2}-H} + 2P_{C_{sp}-C_{sp^2}} + 2P_{C_{sp^2}} + 10P_{C_{sp^3}-H}.$$

Solving this system, we obtained the MDPs of the $C_{sp^3}-C_{sp^2}$ and $C_{sp^2}-H$ bonds:

$$P_{C_{sp_2}=C_{sp_2}} = 5.98 \text{ cm}^3/\text{mol} \text{ and } P_{C_{sp^2}-H} = 1.18 \text{ cm}^3/\text{mol}.$$

For the $C_{sp^2}-C_{sp^2}$ bond in dimethyl-2,3-butadiene ($P_M = 31.0$ cm^3/mol), we obtained

$$P_{C_{sp^2}-C_{sp^2}} = 1.66 \text{ cm}^3/\text{mol}.$$

The MDP of the bonds in the benzene rings was calculated using the values of P_M for benzene ($P_M = 26.64$ cm^3/mol) and *p*-xylene ($P_M = 36.6$ cm^3/mol): $P_{C_{ar}-H} = 1.48$ cm^3/mol and $P_{C_{ar}-C_{ar}} = 2.94$ cm^3/mol. For the rest of the carbon–carbon and carbon–hydrogen bonds, calculations were performed in a similar way (Tables 1 and 2). The same calculation scheme was used in [10] to determine the MDP values for the carbon–halogen bonds (Table 1 in [10]).

In [13], this method for calculating the MDP was extended to simple bonds of carbon atoms with boron, nitrogen, mercury, and thallium atoms, with special attention paid to carbon–nitrogen bonds [12, 13].

LEVIN BOND POLARIZABILITY ADDITIVITY METHOD

The approach developed by Levin [15, 16] is generally similar to that proposed by Boyer-Donzelot; however, some important details differ. First of all, the Levin model *ignores distinctions between the states of hybridization of carbon atoms*; therefore, the deformational components of the polarizability of simple C–C bonds are postulated to be identical to those in the compound for which ε_∞ is determined. Clearly, the values of the molecular mass and density at the corresponding temperature are required.

The papers by Boyer-Donzelot [10–13] contain numerous data on the polarizability of single, aromatic (in the benzene ring), double, and triple bonds. Analogous data are reported in the articles by Levin, [15, 16] (Table 1). The insignificant discrepancies observed can be accounted for by distinctions in the initial tabulated values of the permittivity and density and, possibly, in the methods of data processing.

REFINEMENT OF THE METHOD FOR CALCULATING THE BOND POLARIZABILITIES

As can be seen from Table 1, the DBP values calculated by the two version of the bond polarizability additivity method differ significantly. This may result in differences between the values of P_M and ε_∞ for some

Table 1. Molar deformational polarizabilities (in cm^3/mol) of various C–C bonds as determined from the data of (I) [10–13] and (II) [15, 16] and (III) our calculations

Bond	I	II	III	Substance
$C_{sp^3}–C_{sp^3}$	1.16		1.18 ± 0.02	n-Hexane (P_M = 29.9)
$C_{sp^3}–C_{sp^2}$	1.16		1.18 ± 0.02	[10]
$C_{sp^2}–C_{sp^2}$	1.66		1.60 ± 0.5	Conjugated dienes
$C_{sp^3}–C_{sp}$	1.74	1.22	–	the same
$C_{sp^2}–C_{sp}$	1.93		–	"
$C_{sp}–C_{sp}$	2.28		–	"
$C_{sp^3}–C_{ar}$	1.30		1.18 ± 0.02	"
$C_{ar}–C_{ar}$	2.94	2.74	3.19 ± 0.04	Benzene (P_M = 26.64)
C=C	5.98	5.00	6.0 ± 0.2	Ethylene, $trans$-3-hexane (P_M = 10.72; P_M = 30.19)
C≡C	9.41	10.40	–	Di-n-butylacetylene (P_M = 50.81)

Note: The indicated nonpolar substance were used in [10–13] to determine the MDPs of C–C bonds; for conjugated dienes, the calculations were based on the assumption that the MDP of the bond increases linearly with decreasing the bond length; P_M, in cm^3/mol.

organic compounds. For example, the values of P_M for chloroethane calculated from the data presented in [10–13] and [15, 16] were found to be 17.08 and 16.76 cm^3/mol, respectively.

Unfortunately, the authors of [10–13, 15, 16] did not reported the error limits for the DBP; therefore, it is impossible to evaluate the discrepancies in P_M values and to select the most reliable ones. A comparison of the experimental and calculated values of P_M for a number of organic compounds presented in [16] showed that they differ by no more than 4%.

Clearly, neighboring bonds and molecules affect the MDP of a given bond. From this point of view, the method proposed in [10–13] seems to be more advantageous than that developed in [15–16], since the former is based on a more detailed classification of bonds.

A drawback of the Boyer-Donzelot method is that it provides no possibility of calculating the polarizability of all bonds from experimental data on the polarizability of organic compounds. Therefore, it was necessary to postulate that the MDP of the bond increases linearly with decreasing the bond length. This assumption underlies, for example, the calculation of the MDP of the $C_{sp^3}–C_{ar}$ bond. More specifically, based on the assumption that the lengths and, hence, MDPs of the $C_{sp^3}–C_{sp^3}$ and $C_{sp^3}–C_{sp^2}$ bonds are equal, the MDP of the $C_{sp^2}–C_{sp^2}$ bond is determined, after which the relationship between the lengths and MDPs of the $C_{sp^3}–C_{sp^3}$ and $C_{sp^2}–C_{sp^2}$ bonds is used to calculate the MDP of the $C_{sp^3}–C_{ar}$ bond. A serious shortcoming of this approach is that the lengths of both the $C_{sp^3}–C_{sp^3}$

and $C_{sp^3}–C_{sp^2}$ bonds are set equal to 1.54 Å, while, according to [17], the correct values are 1.534 ± 0.004 and 1.508 ± 0.004 Å, respectively. In addition, Boyer-Donzelot's hypothesis that the MDP of a bond increases linearly with decreasing bond length seems doubtful, as follows from the polarizability versus bond length dependence for carbon–carbon bonds plotted based on the calculations performed in [15, 16] and from our calculations (in which this hypothesis is not used).

This prompted us to try to refine the method for determining the MDP, by introducing, in particular, the procedure for estimating the root-mean-square errors in the calculated MDP values. The method was tested by comparing its predictions with reliable experimental data [18]. We used the classification of bonds proposed in [10–13]. However, we made no use of the hypothesis about the MDP of a bond increasing linearly with decreasing bond length. Since the differences between the lengths of the $C_{sp^3}–C_{sp^3}$, $C_{sp^3}–C_{sp^2}$, and $C_{sp^3}–C_{ar}$ are small, so are, we believe, the possible differences in their MDPs (figure), i.e.,

$$P_{C_{sp^3}–C_{sp^3}} = P_{C_{sp^3}–C_{sp^2}} = P_{C_{sp^3}–C_{ar}}.$$

Note that, in Boyer-Donzelot's calculations, $P_{C_{sp^3}–C_{sp^3}} = P_{C_{sp^3}–C_{sp^2}} = 1.16$ cm^3/mol and $P_{C_{sp^3}–C_{ar}} = 1.30$ cm^3/mol.

The MDPs of the $C_{sp^3}–C_{sp^3}$ and $C_{sp^3}–H$ bonds were calculated from the experimental values of P_M for alkanes; therefore, the results are strongly dependent on the MDPs of these bonds. The calculations performed

Table 2. Molar deformational polarizabilities (in cm^3/mol) of carbon atoms with other atoms

Bond	I	II	III	Substance
C_{sp^3}–H	0.30		–	Di-*n*-butylacetylene (P_M = 50.81 and 9.41)
C_{sp^2}–H	1.18	1.70	1.18 ± 0.06	Ethylene and *trans*-3-hexene
C_{sp^2}–H	1.72		1.715 ± 0.009	*n*-Hexane and *n*-heptane (P_M = 29.9 and 34.5)
C_{ar}–H	1.48		1.32 ± 0.04	Benzene and durene (P_M = 26.64 and 46.56)
C_{sp^3}–O	2.10	2.15	2.13 ± 0.03	*p*-Dioxane (P_M = 24.5)
C=O		7.46	–	Hexamethylene (P_M = 41.0)
C_{sp^3}–N	1.70	1.72	–	Pyrazine (P_M = 24.5)
C_{ar}–N	3.18	3.06	–	Furaronitrile (P_M = 29.8)
C≡N	8.80	9.50		
C_{sp^3}–F	2.64	2.48	2.63 ± 0.02	*n*-Perfluoroheptane (P_M = 49.2)
C_{ar}–F	2.52	2.48	2.3 ± 0.2	1,4-Difluorobenzene (P_M = 28.6)
C_{sp^3}–Cl	7.32	7.04	7.35 ± 0.04	Hexachloroethane (P_M = 45.1)
C_{sp^2}–Cl	7.32	7.04	6.23 ± 0.07	*trans*-5-Decene (P_M = 23.0)
C_{ar}–Cl	6.92	7.04	6.7 ± 0.2	1,4-Difluorobenzene (P_M = 37.4)
C_{sp^3}–Br	11.97	9.93	–	*trans*-1,4-Dibromocyclohexane (P_M = 48.1)
C_{sp^3}–I	17.3	15.0	–	*trans*-1,4-Dibromocyclohexane (P_M = 58.8)
C_{sp^3}–S	4.68	4.69	–	Dithiane (P_M = 34.8)

Note: For notations, see Table 1.

in [10–13] were based on the data of [19] for *n*-hexane and *n*-heptane, which now seem obsolete. Therefore, when calculating the MDPs of the C_{sp^3}–C_{sp^3} and C_{sp^3}–H bonds, we largely used the most reliable data on normal alkanes (for details, see [18]).

It is known that, in the homologous series of alkanes, starting from at least propane, P_M increases by a constant value in passing to every subsequent member:

$$a = P_{C_{sp^3}-C_{sp^3}} + 2P_{C_{sp^3}-H},$$

i.e., the MDP is a linear function of the number of carbon atoms *n* in the alkane molecule:

$$P_M(n) = an + b \quad (n = 3, 4, 5, \ldots).$$

This allowed us to processes MDP values for alkanes by using the least-squares method.

Note that, although the data in [16] were also processed by means of the least-squares method, the density values used there were borrowed from handbooks, not original papers; in addition, some reliable data, for example, [20, 21], were not taken into consideration.

We used all reliable experimental values of P_M for each *n*-alkane from C_5H_{12} to $C_{16}H_{34}$ (for detailed bibli-

ography, see [18]). Processing the entire set of collected data by using the least-squares method, we determined the regression coefficients ($a = 4.611 ± 0.009$ and $b = 2.25 ± 0.04$) and, based on it, the MDPs of the C_{sp^3}–C_{sp^3} and C_{sp^2}–H bonds and the root-mean-square errors of these quantities.

The same scheme (see [18]) was used to calculate the MDPs of C=C and some other bonds (Tables 1, 2). The MDPs for the C=C aromatic bonds in the benzene ring and C_{ar}–H bonds in aromatic compounds were obtained based on experimental values of P_M for benzene and *p*-xylene. In our calculations, we used a larger number of reliable and high-precision measurements of MDPs. This allowed us, we hope, to minimize random errors and to obtain $P_M = 26.63 ± 0.01$ cm^3/mol for benzene and $P_M = 36.65 ± 0.03$ cm^3/mol for *p*-xylene.

When calculating the MDPs of carbon–halogen and C–O bonds, we used the same classification as for the C–H bond. Thus, in our calculations, the MDPs of the bonds depended on the hybridization state of the carbon atom. The MDPs of various carbon–carbon bonds reported by different authors are summarized in Table 1. Analogous data for carbon–hydrogen bonds with various hybridizations of the carbon atom and the MDPs of

the bonds of the carbon atom with some other atoms are listed in Table 2.

Note that, we did not calculate MDP values for some bonds (Tables 1, 2) because of lack or insufficient accuracy of the required data. If necessary, such data can be borrowed from [10–13].

The obtained MDPs of bonds were tested by comparing the P_M values for nonpolar substances calculated from these MDPs to the P_M values for the same substances calculated by the Clausius–Mossotti formula from measured density ρ and static permittivity ε_s. In doing so, we used the most reliable published data for which the errors are known (Table 3). Such a comparison shows that the polarizabilities of individual bonds, independent of the nature of the neighboring molecules and changes in the intermolecular interactions, are invariants; in addition, it provides a possibility to test whether the MDPs are additive quantities. For better perception, the values in Table 3 are intentionally presented with extra decimal places. For substances for which averaging is unjustified, two experimental values are given.

As can be seen from Table 3, the values of P_M determined from the data reported in [15, 16] are lower than the experimental values and the values obtained in the other two calculations, especially for aromatic hydrocarbons. This observation is indicative of drawbacks of the method proposed in [15, 16], in which the simplified classification of bonds is used. In this case, the most significant discrepancies are observed in the MDP values for C–H (as well as C–Cl, C–F, etc.) bonds rather than in the MDP values of C–C bonds. Indeed, as can be seen from Tables 1 and 2, the discrepancies in the MDP values for the C_{ar}–C_{sp^3} bond, and even for the C=C bond, do not exceed 10–15%, while the relative deviations of the MDP values for the C_{ar}–H bond calculated in [15, 16] from those calculated by the other two method are as high as 25–30%.

Thus, a comparison of the values of P_M for a number of organic compounds calculated in [10–13] and [15, 16] led us to conclude that the calculation method proposed by Boyer-Donzelot is more accurate that the method developed by Levin. When the values of P_M for nonpolar organic compounds were determined based on our data, the deviation of the calculated values of P_M differed from the experimental was within the root-mean-square error limits or did not exceed 2%. The values of P_M and ε_∞ for fluoroderivatives of methane should be calculated using the MDP values for the corresponding bonds presented in [15, 16].

METHOD FOR DETERMINING
ATOMIC POLARIZATIONS

In some cases, the available experimental data are insufficient to reliably determine the required polarizabilities of the bonds or there are no suitable nonpolar substance for such determinations. In addition, in some
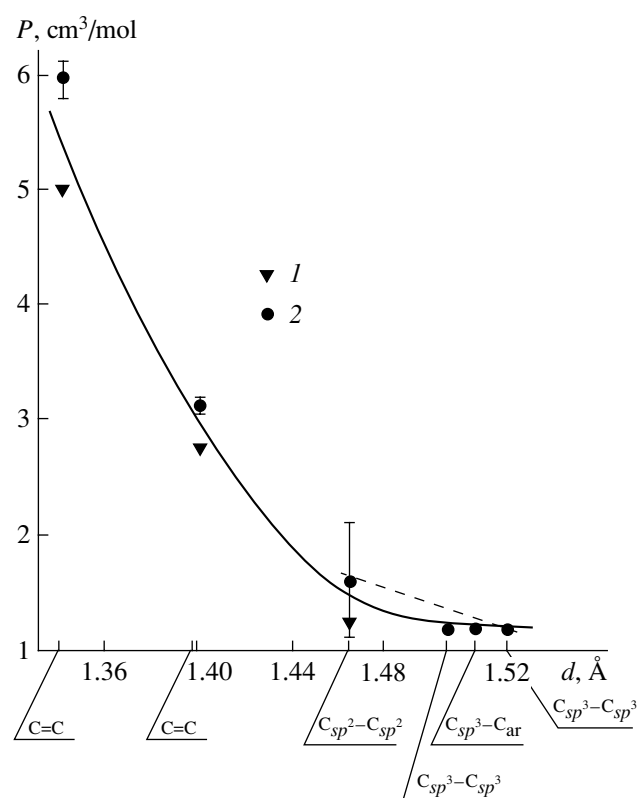
Dependence of the molar polarizabilities of various carbon–carbon bonds: (*1*) [15, 16] and (*2*) present work.

cases, it is more convenient to use atomic polarizability (AP) rather than bond polarizabilities.

By analogy with atomic refraction [22], one can suggest a method for determining the atomic polarizability.[1] This became possible due to the development of techniques for accurate measurements of the dielectric constant of a number of liquids along the coexistence curve, including liquefied hydrogen, oxygen, nitrogen, methane, ethane, etc. [23–28].

The atomic polarizability of a simple substance can in principle be calculated by the Clausius–Mossotti formula. Note, however, that, for a number of substances, such sulfur, silicon, and carbon, this is difficult, if not impossible.

The determination of the AP of hydrogen from measurements in liquid hydrogen is complicated by the temperature dependence of the liquid hydrogen density being poorly known [23]. Therefore, the molar AP (MAP) of hydrogen was determined from the molecular polarizability of gaseous hydrogen reported in [29] (at 20°C) with a correction for the modern value of the molecular mass of hydrogen; as a result, we obtained $P_H = 1.033$ cm^3/mol.

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[1] The atomic polarizability is the fraction of the deformational polarizability corresponding to the given atom.

Table 3. Comparison of the calculated and measured values of the molar polarizabilities P_M (cm³/mol) of nonpolar substances

Substance	Experiment	Calculated from [10–13]	Calculated from [15, 16]	Our calculations
Methane	6.52 ± 0.03	6.88	6.80	6.86 ± 0.04
Ethane	11.21 ± 0.03	11.48	11.42	11.47 ± 0.06
Isopentane	25.5 ± 0.1	25.28'	25.28	25.30 ± 0.13
Cyclohexane	27.49 ± 0.03	27.60	27.72	27.66 ± 0.16
Ethylene	10.71 ± 0.04	10.70	11.80	10.72 ± 0.3
trans-3-Hexene	31.3 ± 0.1	30.18	30.28	30.23 ± 0.26
trans-4-Octene	39.62 ± 0.08	39.38	39.52	39.45 ± 0.3
trans-5-Decene	48.7 ± 0.1	48.58	48.76	48.67 ± 0.33
Benzene	26.63 ± 0.01	26.52	26.64	26.64 ± 0.34
p-Xylene	36.65 ± 0.03	36.20	35.88	36.65 ± 0.3
1,3,5-Trimethylbenzene	41.6 ± 0.2	41.04	40.50	41.66 ± 0.3
Diphenyl	52.0 ± 0.2	51.67	51.10	51.82 ± 0.6
1,3,5-Triethylbenzene	55.5 ± 0.2	55.26	54.36	55.49 ± 0.3
Hexamethylbenzene	55.8 ± 0.4	56.40	54.40	56.67 ± 03
CCl₄	28.17 ± 0.04	29.28	28.16	29.40 ± 0.16
Perchlorobutane	77.0 ± 0.4	76.68	74.06	77.04 ± 0.4
1.4-Dichlorobenzene	37.4 ± 0.3	37.40	37.32	37.4 ± 0.5
1,3,5-Trichlorobenzene	42.8 ± 0.3	42.84	42.66	42.78 ± 0.7
Hexachlorobenzene	57.3 ± 0.3	59.16	58.68	58.92 ± 1.2
Tetrafluoromethane	10.15 ± 0.06	10.56	9.92	10.52 ± 0.08
Hexafluoroethane	17.0 ± 0.3	17.00	16.10	16.96 ± 0.1
Octafluorocyclobutane	26.0 ± 0.5	25.76	24.72	25.76 ± 0.2

The determination of the AP of carbon, with consideration given to the bond it forms, is similar to the determination of the corresponding atomic refraction [30]. The MAP values for a carbon atom that forms simple C–H bonds (in saturated hydrocarbons) changes in passing to every consecutive member of the homologous series of normal alkanes, tending to a constant value of $P_{C-} = 2.593$ cm³/mol, which was used in the subsequent calculations.

Table 4. Atomic polarizabilities of some elements P_{at} (cm³/mol)

Atom	P_{at}	Substance
H	1.033	Gaseous hydrogen [34]
C–	2.593	Average data for butane, pentane, and heptane [31–33, 36–38]
C$_{ar}$	3.415	Benzene [39]
C=	3.320	Ethylene [40]
O	1.977	Oxygen [41]
N	2.20	Nitrogen [42]
Cl	6.0	Chlorine [43]

Note: The substances and published data used in calculations are specified.

The MAP values for carbon atoms involved in aromatic or double bonds were calculated using the molar polarizabilities of liquid benzene and ethylene and the MAP of hydrogen. The MAP of carbon atoms forming triple bonds was determined from the MDP of acetylene. The MAPs of oxygen and nitrogen were determined from the MDPs of these substances in the liquid state [25, 26] (with the introduction of corrections for the temperature dependence of the Clausius–Mossotti function).

Note that these atomic polarizabilities can be determined with the use of other nonpolar substances, but the results can differ from the above values due to the possible effects of the quadrupole moments of the molecules, anisotropy in their polarizabilities, etc. Our calculated MAP values for some elements typical of organic compounds are summarized in Table 4.

To test the MAP values obtained, we used them to calculate the values of P_M for a number of nonpolar compounds and compared them to the corresponding experimental data and to the P_M values for the same compounds calculated by us from the MDPs of the molecule's interatomic bonds (Table 5). Table 5 also contains relative deviations (in %) from the experimental values of P_M.

Table 5. Comparison of the molar polarizabilities P_M (cm³/mol) of various compounds (I) measured experimentally and calculated from (II) the MDPs of the molecule bonds and (III) atomic polarizabilities

Substance	I	II	III	δ_{MDP}, %	δ_{AP}, %
Methane	6.52 ± 0.03	6.86 ± 0.04	6.73	5.2	3.1
Ethane	11.21 ± 0.03	11.47 ± 0.06	11.38	2.3	1.6
Propane	16.07	16.08	16.04	0.06	0.2
n-Pentane	25.3	25.28	25.36	0.8	0.2
Isopentane	25.5 ± 0.1	25.30 ± 0.13	25.36	0.8	0.5
n-Decane	48.4	48.32	47.66	0.2	1.5
Cyclohexane	27.49 ± 0.03	27.66 ± 0.16	27.95	0.6	1.7
trans-3-Hexane	30.1 ± 0.1	30.23 ± 0.26	28.68	3.4	8.3
trans-Octane	39.62 ± 0.08	39.45 ± 0.3	38.0	0.4	4.1
trans-Decene	48.7 ± 0.1	48.67 ± 0.33	47.32	0.06	2.7
p-Xylene	36.65 ± 0.03	36.65 ± 0.3	36.01	0.0	1.7
1,3,5-Trimethylbenzene	41.6 ± 0.2	41.66 ± 0.3	41.70	0.1	0.2
1,3,5-Triethylbenzene	55.5 ± 0.2	55.49 ± 0.3	54.64	0.02	1.5
Hexamethylbenzene	55.8 ± 0.4	55.67 ± 0.3	54.64	1.6	2.1
Perchlorobutane	77.0 ± 0.4	77.0 ± 0.4	70.37	0.05	8.6
1.4-Dichlorobenzene	37.4 ± 0.3	37.4 ± 0.5	36.62	0.0	2.1
1,3,5-Trichlorobenzene	42.8 ± 0.3	42.8 ± 0.8	41.6	0.05	2.7
Hexachlorobenzene	57.3 ± 0.3	58.9 ± 1.2	56.5	2.8	1.4

Note: The data for propane, *n*-pentane, and *n*-decane were borrowed from [10]; the absolute values of the relative deviations δ from the experimental data are given.

As can be seen, in most cases, the deviations of the P_M values calculated using the MAPs from the corresponding experimental values are comparable to the analogous deviations obtained using the refined method for determining the DMPs of the molecule interatomic bonds. This means that the method for determining P_M from MAP values can be used in practical calculations. In some cases, its accuracy can be improved by using special procedures for averaging experimental data from which MAP values are determined and by introducing corrections for temperature changes into the Clausius–Mossotti formula. Such corrections are necessary in order to extend P_M values determined at low temperatures to a wider temperature range.

DETERMINATION OF ε_∞ FOR WATER

The methods of calculating ε_∞ within the framework of the bond polarizability additivity method were considered above. Unfortunately, the absence of accepted methods for determining the polarizability of the O–H bond makes it difficult to calculate the deformational component of the permittivity of hydroxyl-containing compounds (water, alcohols, etc.). We suggested to determine the polarizability of the O–H bond from the molar polarizability of *p*-dihydroxybenzene, a nonpolar compound; as a result, the MDP of water was found to

be P_{H_2O} = 8.5 cm³/mol, a value close to the molar polarizability of ice.

This results suggests that ε_∞ (H₂O) can be determined independently. Indeed, at sufficiently low temperatures, the dielectric polarizability of polar substances is completely governed by the deformational polarization mechanism, since the process of orientational polarization is "frozen." Measurements can be performed with ordinary and heavy ice within 2–270 K [32, 33]. The absence of dielectric losses at a frequency of 1 MHz suggests that measured ε_∞ values represent only deformational polarization. The molar polarizability was calculated from ε_∞ by the Clausius–Mossotti formula. The value obtained was in close agreement with that calculated using the bond polarizability additivity method in conjunction with the polarizability data for *p*-dihydroxybenzene (see above).

Given the importance of the physicochemical (including dielectric) properties of ordinary and heavy water, we compared the temperature dependences of ε_∞ calculated by the bond additivity polarizability methods, by using the atomic polarizabilities, and from low-temperature measurements of the permittivity of ice (Table 6).

Table 6. Temperature dependence of ε_∞ for water

t, °C	[10–13]	[15, 16]	[18]	[28, 29]	[43]
0	4.02	4.17	3.68	3.34	5.68
5	4.02	4.17	3.68	3.34	5.69
10	4.02	4.17	3.68	3.34	5.54
20	4.01	4.16	3.67	3.34	5.62
25	4.00	4.15	3.67	3.33	5.16
30	4.00	4.15	3.66	3.33	4.89
40	3.98	4.12	3.64	3.31	3.91
50	3.95	4.10	3.62	3.30	4.00
60	3.92	4.07	3.60	3.27	4.19

CLAUSIUS–MOSSOTTI FORMULA AND THE LIMITS OF ITS APPLICABILITY

The Clausius–Mossotti formula [1–4],

$$\frac{\varepsilon - 1}{\varepsilon + 2}\frac{M}{\rho} = P_{\mathrm{M}}.$$

(M, ε, and ρ are the molecular mass, relative permittivity, and density, respectively), is considered to be a good approximation for nonpolar substances.

It was demonstrated, both experimentally and theoretically, that the deviations of values calculated by this formula from experimental data become progressively larger with increasing density (see, e.g., [2, 4]). However, when used at moderate densities over a limited temperature range (several tens of degrees), it yields satisfactory results. At any rate, the uncertainties are of the same order of magnitude as the errors in the density and relative permittivity.

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