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Quantum-Chemical Method for Determination of Effective Structure-Energy Parameters of Multiparticle Interaction in Solutions of Polar Substances

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Abstract—A new method is developed for the determination of equilibrium value of effective structure-energy parameter of multiparticle interaction (Onsager radius of a molecule) in solutions of polar compounds. The method is based on the results of quantum-chemical calculations of the dependence of an electric dipole moment of the studied molecule in the ground state on the dielectric properties of the individual solvents that are applied. Additinal data were obtained that confirmed an opinion that by its physical sense the Onsager radius of a molecule was a value close to van der Waals radius of the same molecule which can be found using known methods of quantum chemistry and structural chemistry for isolated molecules (gas phase). It was shown by an example of solutions of 4-dimethylaminochalcone and several phthalimide and *N*-methylphthalimide derivatives that the results of determination of Onsager and van der Waals radii of all the studied molecules using three independent methods are in good quantitative agreement confirming their validity.

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In recent decades many new scientific results were obtained confirming that continual approach (approximation) in the statistical theory of liquids and physics of liquid dielectrics is promising and fruitful for the study of regularities of the solvent effect on various physicochemical processes in liquid, viscous and solid solutions (for example, see [1–5] and publications cited therein). The key problem that should be overcome for successful application of this approach is the definition of valid values of equilibrium effective radius of intermolecular interactions (or Onsager radius of molecule of a dissolved substance) as generalized structure-energy parameters of multiparticle interactions in the studied systems. All this makes actual further efforts in the development of new (desirably independent) methods for finding these parameters, that is both of scientific and of practical significance.

Recently one of the authors of this publication has suggested [6] that for the determination of Onsager radius of a dissolved substance molecule (α_g) can successfully be applied the fundamental relation in the Onsager's reaction field theory [7] which as is known can be written as [1, 2, 6, 7]:

$$\mu_{g(S)} = \frac{\mu_{g(G)}}{1 - \dfrac{\alpha_g}{a_g^3}\left(\dfrac{2\varepsilon - 2}{2\varepsilon + 1}\right)}, \qquad (1)$$

where $\mu_{g(S)}$ and $\mu_{g(G)}$ are electric dipole moments of the studied molecule corresponding to its ground (g) energy state in the solution (S) and in a vacuum (G), α_g is the average polarizability of the molecule in this state, ε is the static dielectric constant of the solvent. After some simple transformations relation (1) can be written in the form:

$$a_g^3 = \frac{2\alpha_g\mu_{g(S)}}{(\mu_{g(S)} - \mu_{g(G)})}\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) \qquad (2)$$

That allows to find the required value a_g^3 from given α_g, $\mu_{g(S)}$ and $\mu_{g(G)}$, that is, from the dependence of dipole moment of a molecule on the dielectric properties of used individual solvents.

It was suggested in [6] that reliable enough information on the dependence $\mu_S = \mu_S(\varepsilon)$ can be obtained from the results of application of modern quantum-chemical theory of intermolecular forces to the study of steric charge distribution in real molecules

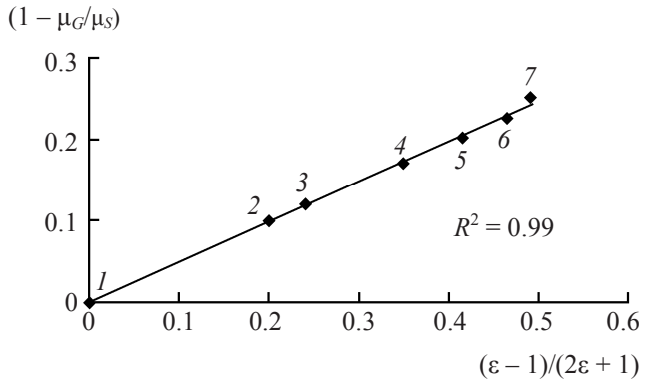

Fig. 1. Plot of expression (3) for 4-dimethylaminochalkone. Solvent: (*1*) vacuum, (*2*) heptane, (*3*) toluene, (*4*) ethyl ether, (*5*) THF, (*6*) acetone, and (*7*) water.

whose interaction with environment (solvent) can be described in the framework of the model of polarized continuum (e.g., see [4, 5] and publications cited therein). An example of successful application of such approach for finding $\mu_S = \mu_S(\varepsilon)$ dependence is [8] describing the study of solutions of 4-dimethylaminochalkone, one of the most effective luminescent probes used widely in the modern medical and biological investigations [9].

This article contains a development and extensive examination of the proposed in [6] method by an example of solutions of 4-dimethylaminochalkone and also amino-substituted phthalimide and *N*-methylphthalimide. From the analysis of expression (2) follows that for solution of the above task this expression is reasonable to transform into a form which we believe to be preferable: Whereas the expression (2) includes absolute values of the moments $\mu_{g(S)}$ and $\mu_{g(G)}$, Eq. (3) uses relative value $\mu_{g(S)}/\mu_{g(G)}$.

$$\left(1 - \frac{\mu_{g(G)}}{\mu_{g(S)}}\right) = \frac{2\alpha_g}{a_g^3} f(\varepsilon) = \frac{2\alpha_g}{a_g^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right), \qquad (3)$$

It is well known that errors in quantum-chemical calculations of physical values (including electric dipole moments of molecules) are much smaller when relative values are considered rather than absolute ones.

Now let us consider the results obtained in this work, starting with solutions of 4-dimethylaminochalkone. Fig. 1 shows the corresponding plot representing relation (3) and drawn using $\mu_{g(S)}$ and $\mu_{g(G)}$ values found by calculations in the [8] containing detailed information on the used methods of quantum-chemical calculations. Note a good linearity of this plot despite the fact that it is formed by the points corresponding to the solvents of very different chemical nature. With the value of polarizability of 4-dimethylaminochalkone molecule in the ground electronic state (α_g) calculated basing on the theory of molecular refraction [10] and the dipole moment in the ground state $\mu_{g(G)} = (5.5\pm0.5)D$ listed in [11] we found from the slope of the line in Fig. 1 the value of a_g^3, that turned out to be equal $a_g^3 = (135\pm25)$ Å^3 (see Table 1).

It is interesting to compare the obtained value with the results of an independent estimation of this value using the known semiempirical approach proposed by Lippert [12]. Remember that according to [12] the Onsager radius a_g can be found from the expression

$$a \cong 0.8\rho, \qquad (4)$$

where ρ is the radius of minimal sphere including the molecule of the explored substance. It is clear that this method being, as follows from practice, very effective, can be named structurally-chemical since it is based on building of a spatial model of the molecule with accounting for its chemical nature (bond lengths, bond angles, van der Waals radii of atoms, etc.). As shown in [11], the value calculated with formula (4) equals: $a_g^3 = (160\pm30)$ Å^3. Thus, the values of a_g^3 of 4-dimethylaminochalkone molecule found by two independent methods are in good quantitative agreement that attests their reliability.

The above data related to 4-dimethylaminochalkone molecule show that the used quantum-chemical and semiempirical structural-chemical methods for estimating the Onsager radius of this molecule provide sufficiently high accuracy in the evaluation of this parameter. Actually, at the average value $a_g = 5.3$ Å the error is within the limit (0.2–0.3) Å, (3–5)% of the calculated value. Besides, the results obtained confirm again the suggestion that the equilibrium value of effective structural-energy parameter of multiparticle interaction in solutions (or Onsager radius of the molecule of dissolved substance) by its physical sense is the value close to van der Waals radius of the same molecule. From this in turn follows a conclusion that as an independent additional method for estimating such a parameter one of the modern quantum-chemical methods can also be applied used for calculation of van der Waals radii of multiatomic organic molecules in gas phase, which we consider below.

With the above said in mind let us consider a group of mono- and disubstituted phthalimides (*N*-methyl-

Table 1. Results of quantum-chemical calculations of dipole moments $\mu_{g(S)}$ and $\mu_{g(G)}$ of the molecules of several amino-substituted phthalimides and *N*-methylphthalimides (D)

Solvent	Dipole moments							
	I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**
Vacuum	4.0	3.8	3.4	1.9	4.0	4.0	2.7	5.4
Heptane	4.6	4.2	3.9	2.2	4.3	4.4	3.2	6.1
Benzene	4.8	4.3	4.1	2.3	4.4	4.4	3.3	6.3
Chloroform	5.6	4.7	4.6	2.5	4.7	4.7	3.7	4.8
Ethanol	5.8	5.1	5.1	3.0	4.9	5.0	4.1	7.4
Acetone	5.9	5.1	5.2	2.8	5.0	4.9	4.0	7.3
Acetonitrile	6.2	5.1	5.3	3.0	4.9	5.0	4.1	7.3
Water	6.0	5.2	5.4	3.1	5.0	5.0	4.1	7.5

phthalimides). For these compounds the position of long-wave vibronic absorption and fluorescence bands are very sensitive to solvent effect, and this fact for a long period attracts attention of specialists on spectroscopy of intermolecular interactions (e.g., see [1, 2, 13]). As the objects for the study we selected the following compounds: 3-acetylaminophthalimide (3-AcAPh), 3-monomethylaminophthalimide (3-MMAPh), 3-dimethylaminophthalimide (3-DMAPh), 3-amino-*N*-methylphthalimide (3-ANMPh), 4-amino-*N*-methylphthalimide (4-ANMPh), 4-dimethylamino-*N*-methylphthalimide (4-DMANMPh), 3,6-diaminophthalimide (3,6-DAPh) and 3,6-tetramethyldiaminophthalimide (3,6-TMDAPh). In performing quantum-chemical calculations of $\mu_{g(S)}$ and $\mu_{g(G)}$ values of all the listed compounds we used data related to the following solvents: heptane, benzene, chloroform, ethanol, acetone, acetonitrile, and water.

The quantum-chemical calculation of the studied molecules was carried out by the non-stationary method of density functional [14] with B3LYP functional correlation potential [15, 16]. Basis set 6-311G(d,p) included polarizing functions for all the atoms. All calculations were performed using GAUSSIAN03 program package [17]. Optimization of geometric structure of the molecules was carried out with accounting for the effect of solvents by the method of self-consistent reaction field (SCRF) in the polarizable continuum model (PCM). The calculation was carried out for the following solvents: heptane, chloroform, benzene, acetone, acetonitrile, ethanol, water. We used standard parameters of the solvents embedded in the GAUSSIAN03 program.

The results obtained for all the studied phthalimide and *N*-methylphthalimide derivatives are listed in Table 2. Let us consider initially the data for isolated molecules (vacuum or gas phase). In practice the average standard experimental error at measuring electrical (dipole moments) and electrooptical (effective charges) parameters of molecules is about ±10% (e.g., see [1, 2, 13, 18]). It is doubtful that currently used theoretical methods for estimating the same values can provide the accuracy better than ±20%. If we took such error as the lowest estimate of the accuracy for the semiempirical and quantum-chemical methods of dipole moments calculation of multiatomic molecules, then a possibility appears to compare the related values obtained by two independent methods. The respective data for the mentioned phthalimide and *N*-methylphthalimide in gas phase are listed in Table 2. One can see that accounting for the above reasoning there is a good qualitative and a fair quantitative agreement between the compared values of dipole moments $\mu_{g(G)}$.

Table 2. Values of dipole moments $\mu_{g(G)}$ of free molecules of several amino-substituted phthalimides and *N*-methylphthalimides (D) obtained by different methods

Comp. no.	Method	
	Calculation according to valence scheme	Quantum-chemical calculation (Gaussian)
I	2.1±0.4	4.0±0.8
II	2.1±0.4	3.8±0.8
III	2.6±0.5	3.4±0.7
IV	2.4±0.5	1.9±0.4
V	2.7±0.5	4.0±0.8
VI	2.7±0.5	3.9±0.8
VII	3.5±0.7	2.7±0.5
VIII	3.5±0.7	5.4±1.1

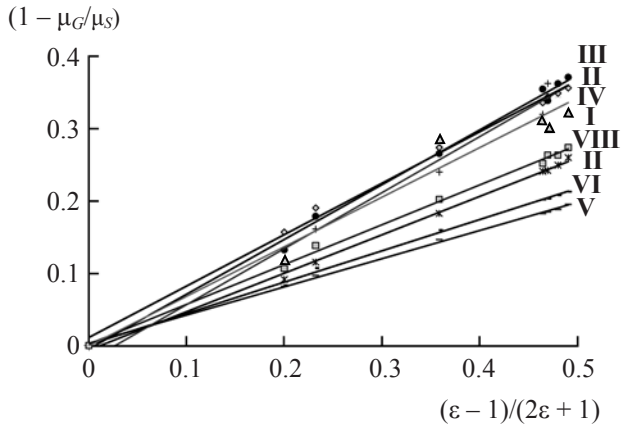

Fig. 2. Plot of expression (3) for several amino-substituted phthalimides and *N*-methylphthalimides. The solvents are listed in Table 1.

Now let us go back to Fig. 2 that gives a possibility by analogy with 4-dimethylaminochalkone (Fig. 1) to apply Eq. (3) for estimating the averaged over the solvents value of the cubed Onsager radius (a_g^3) for all the studied substituted phthalimides and *N*-methylphthalimides. The values of polarizability α_g required for such calculations, listed in Table 3, were calculated from the theory of molecular refraction. In the second column of Table 3 are given the values of a_g^3 parameter obtained from the slopes of the respective lines in Fig. 2. For comparison, in the last (third) column of Table 4 are listed the a_g^3 values for all the considered molecules found by the above-mentioned quantum-chemical method that allows calculation of van der Waals radii of molecules in gas phase. Analysis of the data in Table 4 shows that the a_g^3 values obtained by two independent quantum-chemical methods are in good qualitative agreement. Therefore it seems interesting to compare the data in Table 3 with the results of calculation of a_g^3 values by semiempirical Lippert's method [12, 13]. The respective data for the four substituted phthalimides and *N*-methylphthalimides are listed in Table 4 where in the second column are listed the a_g^3 values from [2] that have been found from the semiempirical relation (4), and in the third column the analogous values obtained by averaging the a_g^3 values calculated with two different quantum-chemical methods (see Table 3). The compared values are obviously in good quantitative agreement attesting adequacy of all three methods for estimating a_g^3 parameter applied in this work.

In conclusion we wish once again attract attention to the sufficiently high accuracy of estimatimg the equilibrium value of the effective structure-energy parameter of the multiparticle interaction in solutions (Onsager radius of the molecule of the solute) provided by application of all three above methods. Analysis of the data in Tables 3 and 4 shows that at the average values of a_g parameter for the whole set of the studied substituted phthalimides and *N*-methylphthalimides fall in the range from 3.7 to 5.0 Å, the error does not exceed the limit of (0.1–0.3) Å, only (2–6)% of the found value. It is reasonable to remember in this connection that the given reasons and estimations are well consistent with the results of studies [1–3] dedicated to the analysis and application of a wide range of experimental methods used for the evaluation of a_g^3 values for liquid systems of varied chemical nature.

It seems pertinent to emphasize the important circumstance that the materials in Table 2 as shown above allow to estimate not only the averaged over a

Table 3. Initial data and results of estimating average cubed Onsager (I) and van der Waals (II) radii of the molecules of several amino-substituted phthalimides and *N*-methylphthalimides obtained by various methods

Comp. no.	Polarizability, Å^3	Method	
		I (Gaussian)	II (Chem Draw)
I	18±1	50±10	40±10
II	26±1	100±20	95±20
III	18±1	50±10	55±10
IV	18±1	50±10	50±10
V	18±1	90±20	65±15
VI	20±1	90±20	65±15
VII	18±1	50±10	80±15
VIII	22±1	80±15	125±25

Table 4. Results of estimating cubed Onsager radius a_g^3 of the molecules of several amino-substituted phthalimides and *N*-methylphthalimides obtained by various methods (Å^3)

Comp. no.	Method	
	Semiempirical structural-chemical method [Eq. (4)]	Quantum-chemical method (B3LYP)
I	50±10	45±10
III	70±15	50±10
VII	70±15	65±15
VIII	90±20	100±20

series of solvents value of a^3_g parameter but also definite values for each studied solution. This opens principally new possibility of quantitative study of regularities in the process of solvation (including solvatochromism and solvatofluorochromism) based on more detailed analysis of interaction of a molecule of dissolved substance with environmental molecules with accounting for their structure and individual properties. We will attempt to realize these new possibilities in our further studies. By the way, some original results of such nature have been obtained in [19].

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