SELECTION OF DIELECTRIC-CONSTANT VALUES FOR CALCULATION OF COMPLEX MOLECULAR SYSTEMS

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We have determined the errors associated with introduction of the effective dielectric constant into calculations for complex molecular systems. Appropriate numerical results were obtained for certain amides.

One of the most problematical factors in studying transfer processes and a number of the equilibrium properties of systems consisting of sets of molecules with electrical multipole moments or of mixtures of such molecules with ions (as occurs, e.g., in electrolytes) is evaluation of the electrostatic interaction between the charged atoms and functional groups. The main difficulty in this respect is determination of the errors resulting from introduction of a certain atomic point-charge distribution (from the standpoint of model adequacy and partial-charge magnitude) and selection of the dielectric constant ε. The role of the latter factor is considered in the present article.

It must first be noted that the introduction of some "universal" value of ε for all pairs of interacting atoms or functional groups means that it is averaged over different situations, since the value of ε for different pairs of atoms depends on their short-range environment. However, the use of an ε averaged over a macroscopic system for evaluation of particle interactions at a microscopic distance, although done (e.g., in the Debye–Huckel theory of electrolytes), is in no way justified. Nevertheless, the errors resulting from this procedure can be estimated. If we assume that, with a given value of ε_m, the pair-additive approximation gives the best results, the error introduced by the deviation of ε from ε_m can be characterized by the mean square error in calculation of the system energy:

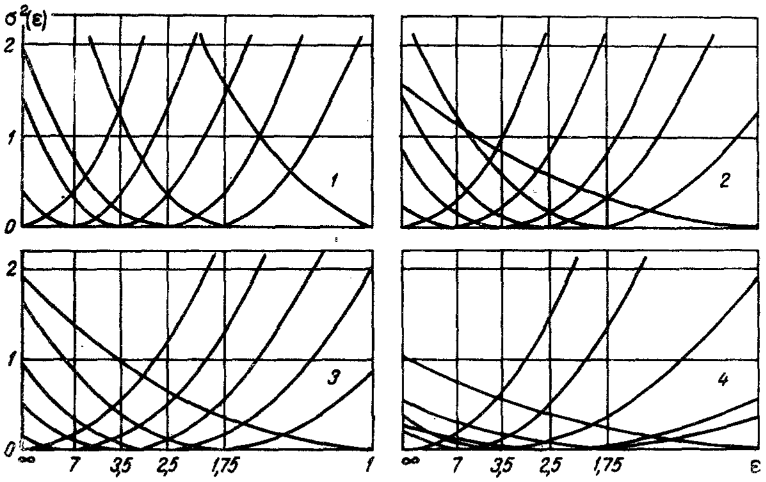

Fig. 1. Mean square error in conformation energy of fragments 1-4 as a function of ε_m at different ε.

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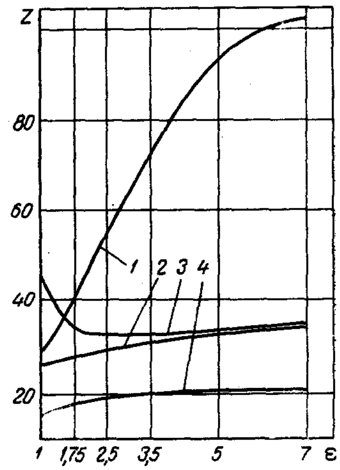


Fig. 2. Statistical sums of fragments 1-4 as a function of ε.

$$\sigma^2 = \frac{\int\limits_{U(\Phi)<P} [U(\varepsilon_m) - U(\varepsilon)]^2 d\Phi}{\int\limits_{U(\Phi)<P} d\Phi}. \tag{1}$$

The restriction of the integration region in the phase space is due to the fact that the sterically permitted regions are of great interest.

Actually, however, the quantity ε_m is not constant but is characterized by a certain distribution $P(\varepsilon)$. This distribution must obviously depend on the distance l between the interacting atoms and, at the limit, where $l \to \infty$, becomes $\delta(\varepsilon - \varepsilon_m^\sim)$, where $\varepsilon_m^\sim$ is some "macroscopic" value of the dielectric constant. The relationship between $\varepsilon_m^\sim$ and ε_m that provides the smallest error in calculations of this type can be described in the following manner.

As is well known [1], the dielectric constant of a heterogeneous volume (in this case, a cylinder of length l) is described by the relationship

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{\varepsilon} = \frac{1}{l} \frac{4\pi}{kT} \sum_{i=1}^{k} \overline{m_i m_i^*} n_i, \tag{2}$$

where m_i^* is the average volumetric dipole moment produced by the dipole moment m_i of a functional group of the i-th type, n_i is the number of such groups, $\overline{m_i m_i}^*$ is the average product $m_i m_i^*$, T is the temperature in °K, and k is the Boltzmann constant.

If the probabilities that different functional groups will be found in a certain interatomic volume are equal and independent, the incidences of these groups are distributed exponentially. The distribution for the quantity $(\varepsilon - 1)(2\varepsilon + 1)/\varepsilon$ is then found in terms of the corresponding exponents (with an accuracy down to the constant multiplier)

$$f\left[\frac{(\varepsilon - 1)(2\varepsilon + 1)}{\varepsilon}\right] = \frac{\beta_1 l}{\overline{m_1 m_1^*}} \exp\left(-\frac{\beta_1 l}{\overline{m_1 m_1^*}} n_1\right) * \cdots * \frac{\beta_{kl} l}{\overline{m_{kl} m_{kl}^*}}$$

$$\times \exp\left(-\frac{\beta_{kl} l}{\overline{m_{kl} m_{kl}^*}} n_{kl}\right) = \sum_{i=1}^{kl} c_i \exp\left(-\frac{\beta_i l n_i}{\overline{m_i m_i^*}}\right), \tag{3}$$

where c_i are coefficients that depend solely on $\beta_i l/\overline{m_i m_i}^*$.

A distribution of type (3) is similar to the well-known Γ-distribution and reverts to it when $\beta_1/\overline{m_1 m_1}^* = \ldots = \beta_{kl}/\overline{m_{kl} m_{kl}}^* = \beta$. Thus, the distribution for $\varepsilon - 1$ acquires the form

$$P(\varepsilon - 1) = \int\limits_0^\infty \frac{(\beta l)^{\alpha l}}{\Gamma(\alpha l)} \left(2 + \frac{1}{\varepsilon^2}\right)$$

$$\times \left(\frac{(\varepsilon - 1)(2\varepsilon + 1)}{\varepsilon}\right)^{\alpha l - 1} \exp\left(-\beta l \frac{(\varepsilon - 1)(2\varepsilon + 1)}{\varepsilon}\right) d\varepsilon. \tag{4}$$

Using the notation $z = [(\varepsilon - 1)(2\varepsilon + 1)]/\varepsilon$, we obtain

$$\varepsilon - 1 = \frac{-(3 - z) + \sqrt{(3 - z)^2 + 8z}}{4}. \tag{5}$$

Equation (5) can be approximated as follows:

$$(\varepsilon - 1) = -\frac{3}{4} + \frac{z}{4} + \frac{1}{4}\left(1 + z + 2t \sum_{i=1}^{k} e^{-a_i z}\right). \tag{6}$$

The average value of $\varepsilon-1$ is

$$\overline{(\varepsilon-1)}=\frac{1}{2}\int\limits_0^\infty\frac{(\beta l)^{\alpha l}}{\Gamma(\alpha l)}\left(z-1+t\sum_{i=1}^{k}e^{-a_i z}\right)z^{\alpha l-1}e^{-\beta l z}\,dz$$

$$=\frac{1}{2}\left(\frac{\alpha}{\beta}-1+t\sum_{i=1}^{k}\left(\frac{\beta l}{\beta l+a_i}\right)^{\alpha l}\right). \tag{7}$$

As l increases, this quantity tends toward

$$(\varepsilon_{\tilde{m}}-1)=\frac{1}{2}\left(\frac{\alpha}{\beta}-1+t\sum_{i=1}^{k}e^{-a_i\frac{\alpha}{\beta}}\right). \tag{8}$$

Here it is important to note that the corresponding macroscopic value is somewhat smaller than $\overline{(\varepsilon-1)}$ at small l.

Similarly,

$$\int\limits_0^\infty\frac{(\beta l)^{\alpha l}}{\Gamma(\alpha l)}\left[U(\varepsilon_m)-U(\varepsilon)\right]^2 z^{\alpha l-1}e^{-\beta l z}\,dz$$

$$=\left[\frac{1}{\varepsilon_m}-t\sum_{i=1}^{k}\left(\frac{\beta l}{\beta l+a_i}\right)^{\alpha l}\right]^2. \tag{9}$$

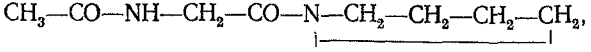
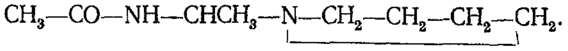
The optimum value of ε_m is defined by the equation

$$\frac{1}{\varepsilon_m}=t\sum_{i=1}^{k}\left(\frac{\beta l}{\beta l+a_i}\right)^{\alpha l}. \tag{10}$$

It should be noted that ε_m is smaller than $\varepsilon_{\tilde{m}}$; however, this difference is comparatively small, since small distances (less than 2.5 Å) are excluded by steric repulsion.

The above considerations are valid for complex molecules with integral degrees of freedom as well; it is specifically possible to obtain useful quantitative estimates with their aid. In this case, the phase space of the system is the space of internal-rotation angles.

We will give below some numerical results obtained for the amides:

1) $CH_3—CO—NH—CH_2—CO—NH—CH_3$,
2) $CH_3—CO—NH—CHCH_3—CO—NH—CH_3$,
3) 
$CH_3—CO—NH—CH_2—CO—N—CH_2—CH_2—CH_2—CH_2$,
4) 
$CH_3—CO—NH—CHCH_3—N—CH_2—CH_2—CH_2—CH_2$.

The nonvalence intramolecular interactions were taken into account with the aid of the Bakenheim –Slater potentials; the calculation procedure was described previously [2].

According to measurements made by a number of authors, the macroscopic dielectric permeability of amides is about 3.5 [3, 4]. Figure 1 shows the function $\sigma^2(\varepsilon_m)$ for different values of ε. The data in this figure indicate that there is a relatively small error in calculating the conformational energy of the fragments in question with a rather broad range of variation in ε near ε_m. Actually, assuming that the quantities $U(\varepsilon_m)-U(\varepsilon)$ have a normal distribution, it can be asserted that the error in a calculation made with $\varepsilon = 3.5$ does not exceed 0.5 kcal/mole for a 90% sterically permitted region in the phase space, provided that ε_m falls into the following ranges: 3.0-6.0 (fragment 1), 2.5-6.5 (fragment 2), 2.0-7.0 (fragment 3), or 2.0-12.0 (fragment 4).

Comparison of these data with the statistical sums of fragments 1-4 (Fig. 2) shows that the error in the selection of ε has the greatest effect for fragments with high mobility, primarily fragment 1.

Returning to Eq. (10), it must be noted that variation of ε_m over the range 2.5-4.0 [5] should have no material influence on the calculated results. Thus, the difference between ε_m and $\varepsilon_{\tilde{m}} = 4.0$ for an average interatomic distance of 5 Å is about 1%. The scattering of the distribution in Eq. (9) is characterized by a certainty interval of 0.1 for the range 0-10.0 in this case.

Use of the macroscopic value of ε in molecular calculations thus provides the smallest error in estimating electrostatic interactions.

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