

CALCULATION OF SOLVENT REORGANIZATION ENERGY IN CHARGE TRANSFER REACTIONS IN POLAR MEDIA

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The solvent reorganization energy in processes accompanied by charge transfer or charge redistribution in the reactants usually is calculated via the relation [1]

$$E_s = (C/8\pi) \int (\vec{D}_i - \vec{D}_f)^2 dv, \quad (1)$$

where $C = 1/\epsilon_{op} - 1/\epsilon_s$, ϵ_{op} and ϵ_s are the optical and static dielectric permittivities of the solvent, and $\vec{D}_i$ and $\vec{D}_f$ are the electric induction vectors corresponding to the initial and final charge distribution in the system.

Recently the opinion was put forward that instead of $\vec{D}_{i,f}$ one must write $\vec{G}_{i,f}$ (the field in vacuum) in relation (1) [2]. The relation between $\vec{D}$ and $\vec{G}$ in various models was discussed in [3].

In [4], the solvent reorganization energy was calculated for charge transfer in a spherical cavity, and the reorganization energy E_s^D obtained when using vectors $\vec{D}_{i,f}$ was compared with the energy E_s^G obtained when using the electric field in vacuum and a dielectric constant in the cavity of $\epsilon_i = 1$. Quantity E_s^D/E_s^G assumes values of 2.25 and 4 for certain limiting cases discussed in [4], which correspond to different arrangements of the charges undergoing redistribution inside the cavity.

Another problem where E_s^D and E_s^G can be calculated accurately is that of charge transfer in a cavity having the shape of an elongated ellipsoid of revolution. The expression for E_s^G in charge transfer between the foci of the ellipsoid which corresponds to the case of $\epsilon_i = 1$ was recently obtained in [5], and is of the form

$$E_s^G = \frac{2Ce^2}{R} \left[\frac{\lambda_0^2 + 1}{2\lambda_0(\lambda_0^2 - 1)} - \frac{\lambda_0^2 - 1}{4\lambda_0^2} \ln \frac{\lambda_0 + 1}{\lambda_0 - 1} \right], \quad (2)$$

where R is the distance between the foci of the ellipsoid, $\lambda_0 = (2a/R) > 1$, and a is the major semiaxis of the ellipsoid. The expression for E_s^D corresponding to charge transfer between centers located on the ellipsoid's axis is readily obtained from the exact solution of the electrostatic problem which was found by Westheimer and Kirkwood [6]:

$$E_s^D = \frac{2C}{R} \sum_{n=0}^{\infty} \frac{(1 + 1/2n) \left(\sum_k e_k^i P_n(\mu_k^i) - \sum_k e_k^f P_n(\mu_k^f) \right)^2}{P_n^2(\lambda_0) [Q_{n-1}(\lambda_0)/Q_n(\lambda_0) - \lambda_0]} \left[1 - \frac{\epsilon_i P_n'(\lambda_0) Q_n(\lambda_0)}{\epsilon_s P_n(\lambda_0) Q_n'(\lambda_0)} \right]^{-2}, \quad (3)$$

where ϵ_i is the dielectric permittivity of the cavity, P_n and Q_n are Legendre functions of the first and second kind, $\mu_k = 2(r_1^k - r_2^k)/R$ is the coordinate of charge e_k on the ellipsoid's axis, r_1^k and r_2^k are the distances from the center of location of charge e_k to the ellipsoid's foci, and indices i and f refer to the initial and final charge distribution.*

*Relation (3) was obtained independently by É. D. German.

Let us compare expressions (3) and (2) in the case where charge transfer is accomplished between the foci of the ellipsoid ($\mu_1 = 1$, $\mu_2 = -1$). We assume for simplicity that $\varepsilon_i \ll \varepsilon_s$; then we have, from (3),

$$E_s^D = \frac{2Ce^2}{R} \sum_{n=0}^{\infty} \frac{(1 + 1/2n)[1 - (-1)^n]^2}{P_n^2(\lambda_0)[Q_{n-1}(\lambda_0)/Q_n(\lambda_0) - \lambda_0]} \quad (4)$$

and the ratio $E_s^D/E_s^{G_1}$ defined by (4) and (2) only depends on the parameter λ_0 . Calculations show that $E_s^D/E_s^{G_1}$ for λ_0 -values close to reality are substantially different from unity. Thus, for λ_0 of 1.25, 1.4, 1.5, 1.6, and 1.75, the ratio $E_s^D/E_s^{G_1}$ is found to be 1.73, 1.82, 1.86, 1.91, and 1.96, respectively.

It will also be of interest to compare E_s^D with values of reorganization energy $E_s^{G_i}$ obtained when using the electric field in vacuum and ε_i -values different from unity. As an example, consider charge transfer between the foci of the ellipsoid with $\varepsilon_s = 37$ (the solvent, acetonitrile), $\varepsilon_i = 3$, and λ_0 -values of 1.25 and 1.5. Setting $\varepsilon_i/\varepsilon_s$ in (3) equal to 3 and 1 for the calculation of $E_s^{G_i}$ and $E_s^{G_1}$ we obtain

$$\begin{aligned} E_s^D/E_s^{G_i} &= 1.64; & E_s^D/E_s^{G_1} &= 3.46, & \text{for } \lambda_0 &= 1.25; \\ E_s^D/E_s^{G_i} &= 1.76; & E_s^D/E_s^{G_1} &= 4.10, & \text{for } \lambda_0 &= 1.5. \end{aligned}$$

Thus, a calculation of E_s^D rather than E_s^G leads to substantially exaggerated values of the reorganization energy, both in the spherical-cavity model and in the ellipsoidal-cavity model (these differences are more substantial the larger ε_i relative to unity). The difference between E_s^D and E_s^G is less important for charge transfer calculated in terms of the Marcus model [7, 8].

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