

REORGANIZATION ENERGY OF POLAR MEDIA IN INNER-SPHERE PROCESSES WITH COMPLEX CHARGE REDISTRIBUTION

Yu. I. Kharkats

UDC 541.13

The solvent reorganization energy, E_s , is an important parameter of the quantum theory of chemical reactions involving charge transfer or redistribution; it is an important factor for the activation energy of the processes. In the long-wave approximation, E_s is determined by the expression [1]

$$E_s = \frac{1}{8\pi} \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_{st}} \right) \int (\vec{D}_i - \vec{D}_f)^2 dv, \quad (1)$$

where ϵ_{st} and ϵ_{op} are the solvent's static and optical dielectric permittivity, $\vec{D}_i$ and $\vec{D}_f$ are the vectors of the electric induction set up in the solvent by the charge distributions in the initial and final state of the system. The integral in (1) is taken over the entire solvent volume. In [2-9], the energy of solvent reorganization in outer-sphere charge-transfer reactions has been calculated in terms of different models. In the case of inner-sphere charge transfer, which occurs in a wide range of chemical and biological processes, a calculation of reorganization energy has been possible in terms of the very simple model where the charge is transferred between two centers lying on a single diameter inside a spherical cavity placed into a dielectric medium [10].

In the present work we report the results of a calculation of solvent reorganization energy where the charges in the initial and final state are located in an arbitrary number of centers distributed in an arbitrary manner within the reactant. It is assumed that the reactant has the shape of a sphere of radius R with a dielectric permittivity ϵ_1 , and is placed into a polar medium with the dielectric permittivity ϵ_2 . Suppose that in the initial state, charges z_k^i ($1 \leq k \leq N$) are located in points $\vec{d}_k$ ($|\vec{d}_k| < R$), while in the final state the same points contain charges z_k^f (specifically, some of the z_k^i or z_k^f can become zero). Then the difference between the induction vectors set up in the solvent by the initial and final charge distribution can be written as

$$\vec{D}_i - \vec{D}_f = -\epsilon_2 \nabla (\varphi_i - \varphi_f), \quad (2)$$

where φ_i and φ_f are the potentials of the electric fields set up in the solvent by the charge distributions in the initial and final state.

Using the solution of the electrostatic problem of charge in spherical cavities [11] we shall write $\varphi_i - \varphi_f$ as

$$\varphi_i - \varphi_f = \sum_{k=1}^N \delta z_k \varphi_k, \quad (3)$$

$$\varphi_k = \sum_{n_k=0}^{\infty} \frac{2n_k+1}{n_k \epsilon_1 + (n_k+1) \epsilon_2} \frac{d_k^{n_k}}{r^{n_k+1}} P_{n_k}(\cos \theta_k). \quad (4)$$

Here φ_k is the potential created by a unit charge located in the point $\vec{d}_k$; r is the distance from the center of the sphere to an arbitrary point within the solvent; θ_k is the angle between vectors $\vec{d}_k$ and $\vec{r}$; $P_n(\cos \theta)$ are Legendre polynomials; $\delta z_k = z_k^i - z_k^f$; and $\sum_{k=1}^N \delta z_k = 0$.

Using (2) and (3) we can reduce (1) to

$$E_s = \frac{1}{8\pi} \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_2} \right) \epsilon_2^2 \sum_{k=1}^N \sum_{l=1}^N \delta z_k \delta z_l \int \nabla \varphi_k \nabla \varphi_l dv. \quad (5)$$

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from *Elektrokhimiya*, Vol. 15, No. 3, pp. 409-412, March, 1979. Original article submitted May 23, 1978.

Combining (8) and (9) we can reduce (5) to

$$E_s = \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_2} \right) \frac{1}{2R} \sum_{n=0}^{\infty} \frac{(2-1/(n+1))}{\left[1 + \frac{n\epsilon_1}{(n+1)\epsilon_2} \right]^2} \left\{ \sum_{k=1}^N (\delta z_k)^2 \left(\frac{d_k^2}{R^2} \right)^n + \right. \\ \left. + \sum_{k=1}^N \sum_{\substack{l=1 \\ l \neq k}}^N (\delta z_k) (\delta z_l) \left(\frac{d_k d_l}{R^2} \right)^n P_n(\cos \theta_{kl}) \right\}. \quad (12)$$

Considering that usually the dielectric permittivity of the reactants, $\epsilon_1 \sim 2$, is much lower than that of the polar solvent (for water $\epsilon_2 \sim 80$), one can neglect terms of the order of ϵ_1/ϵ_2 in the square brackets in (12). Summing over n we finally obtain

$$E_s = \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_2} \right) \frac{1}{2R} \left\{ \sum_{k=1}^N (\delta z_k)^2 \left[\frac{2R^2}{R^2 - d_k^2} + \frac{R^2}{d_k^2} \ln \frac{R^2 - d_k^2}{R^2} \right] + \right. \\ \left. + \sum_{k=1}^N \sum_{\substack{l=1 \\ l \neq k}}^N (\delta z_k) (\delta z_l) \left[\frac{2R^2}{\sqrt{R^4 + (d_k d_l)^2 - 2d_k d_l R^2 \cos \theta_{kl}}} - \right. \right. \\ \left. \left. - \frac{R^2}{d_k d_l} \ln \frac{d_k d_l - R^2 \cos \theta_{kl} + \sqrt{R^4 + (d_k d_l)^2 - 2d_k d_l R^2 \cos \theta_{kl}}}{R^2 (1 - \cos \theta_{kl})} \right] \right\}. \quad (13)$$

Expression (13) for the solvent reorganization energy serves as generalization of the result obtained in [10] for the case where charge transfer occurs between two centers located on a single diameter, and for $N = 2$ and $\cos \theta_{1,2} = \pm 1$ one can readily pass from (13) to relation (6) of [10].

The author thanks L. I. Krishtalik for conversations stimulating the realization of the present work, and for discussion of the results.

LITERATURE CITED

1. R. R. Dogonadze and A. M. Kuznetsov, in: Results [Itogi] of Science, Physical Chemistry. Kinetics, Vol. 2 [in Russian], VINITI, Moscow (1973).
2. R. A. Marcus, J. Chem. Phys., 24, 976 (1956).
3. Yu. I. Kharkats, *Élektrokhimiya*, 9, 881 (1973).
4. Yu. I. Kharkats, *Élektrokhimiya*, 10, 612 (1974).
5. Yu. I. Kharkats, *Élektrokhimiya*, 10, 1137 (1974).
6. Yu. I. Kharkats and G. M. Chonishvili, *Élektrokhimiya*, 11, 175 (1975).
7. N. Kestner, J. Logan, and J. Jortner, J. Phys. Chem., 78, 2148 (1974).
8. Yu. I. Kharkats, *Élektrokhimiya*, 12, 1284 (1976).
9. Yu. I. Kharkats, *Élektrokhimiya*, 14, 1721 (1978).
10. Yu. I. Kharkats, *Élektrokhimiya*, 12, 1866 (1976).
11. J. G. Kirkwood, J. Chem. Phys., 2, 351 (1934).
12. V. I. Smirnov, A Course of Higher Mathematics, Vol. 3, Pt. 2 [in Russian], Fizmatgiz, Moscow (1958), cited p. 496 [English translation: Pergamon Press, Oxford (1964)].