

LITERATURE CITED

1. J. S. Newman, *Electrochemical Systems*, Prentice-Hall, Englewood Cliffs, New Jersey (1973).
2. V. G. Levich, *Physicochemical Hydrodynamics*, 2nd edn., Prentice-Hall, Englewood Cliffs, New Jersey (1962).
3. J. Newman, *Ind. Eng. Chem. Fundam.*, **5**, 525 (1966).
4. V. V. Malaya and Ya. V. Durdin, *Élektrokhimiya*, **2**, 1354 (1966).
5. Yu. I. Kharkats, *Élektrokhimiya*, **14**, 1132 (1978).
6. J. Heyrovsky and J. Kuta, *Principles of Polarography*, Academic Press, New York (1966).
7. Yu. I. Kharkats, *Élektrokhimiya*, **14**, 1840 (1978).

EFFECT OF A DIELECTRIC INTERLAYER ON ELECTRODE KINETICS

Yu. I. Kharkats

UDC 541.138

The rate constants of electrochemical processes involving charged reactants and reaction products depend in an essential way both on the probability of access of the reactants to the electrode and on the rate of the elementary charge-transfer act itself [1]. For instance, in the case of very simple charge-transfer reactions without inner-sphere reorganization of the reactants, the rate constants can be written as

$$K = \frac{\omega_0}{2\pi} \kappa \exp \left[-\frac{U_i}{kT} - \frac{(E_s + \Delta I + U_i - U_f)^2}{4E_s kT} \right], \quad (1)$$

where ω_0 is the effective dielectric-relaxation frequency of the solvent, κ is the transmission coefficient, E_s is the solvent reorganization energy, ΔI is the free energy of the reaction, U_i and U_f are the work of transfer of reactants and reaction products from the interior of the solution to the discharge site, and T is temperature. Quantities κ , E_s , U_i , and U_f in the general case are functions of the distance from the electrode to the point of discharge, and can readily be calculated for the simplest models of reactants and medium. We stress that the dependence of E_s on the distance between reactant and electrode is highly essential for the discharge kinetics, and may be responsible for the fact that a "kinetic barrier" against reactant approach arises in addition to the "statistical barrier" [2]. This is due to the fact that E_s is proportional to $(1/\epsilon_{op} - 1/\epsilon_s) \approx 1/\epsilon_{op}$ while U_i is proportional to $1/\epsilon_s$, where ϵ_{op} , the dielectric permittivity at optical frequencies, is much smaller than ϵ_s , the static dielectric permittivity.

Attempts have been made in a number of papers to calculate the effect exerted by a thin layer next to the electrode where the dielectric permittivity is reduced, on the kinetics of electrochemical processes [3-8]. In this work, attention usually was focused on the way in which function U_i will change. But quantity E_s , which determines the activation energy in the normal reaction region and has an important influence on the effective distance of approach of the reactant to the electrode, should also undergo important changes when a layer with reduced dielectric permittivity is taken into account. In addition, in calculations of U_i which took an interlayer into account, the important effect of reactant resolution occurring during the approach to the electrode was disregarded.

In the present work, calculated values of E_s , U_i , and U_f are reported as functions of reactant-electrode distance and of the parameters governing the properties of the dielectric interlayer.

We shall adopt the following model of the system. Suppose that the interlayer is characterized by a dielectric permittivity ϵ_1 , and the remaining solvent volume by a dielectric permittivity ϵ_2 . The thickness of the dielectric interlayer will be called d . We shall examine the discharge possibility for an ion located at a distance h from the electrode. We shall describe the reactant as a sphere of radius a having charge z uniformly distributed over its surface (the model of Marcus [9]). It will be of interest to examine the two possibilities: $h < d$ (the ion is discharged within the interlayer [10]) and $h > d$ (ion discharge occurring from a region outside the interlayer) (Fig. 1).

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from *Élektrokhimiya*, Vol. 15, No. 2, pp. 246-249, February, 1979. Original article submitted March 22, 1978.

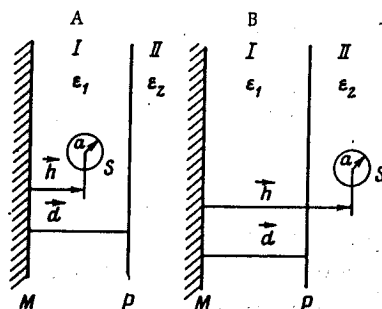


Fig. 1. Schemes showing where the ion undergoing discharge is located relative to the dielectric interlayer: A) for $a \leq h \leq d - a$, and B) for $h \geq d + a$.

The solvent reorganization energy in charge transfer reactions between ions and an electrode can be calculated, according to [1], via the relation

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

where $\vec{D}_i - \vec{D}_f$ is the change in the vector of induction occurring during charge transfer between the reactant and the electrode. Integration in (2) is extended over the entire solvent volume but excluding the reactant volume. In the interlayer model adopted, Eq. (2) becomes

$$E_s = \frac{1}{8\pi} \left(\frac{1}{\epsilon_{op1}} - \frac{1}{\epsilon_1} \right) \int_I (\vec{D}_i - \vec{D}_f)^2 dv + \frac{1}{8\pi} \left(\frac{1}{\epsilon_{op2}} - \frac{1}{\epsilon_2} \right) \int_{II} (\vec{D}_i - \vec{D}_f)^2 dv, \quad (3)$$

where I and II are the regions corresponding to the interlayer and the remaining part of the solvent, but excluding the reactant volume. Vector $\vec{D}_i - \vec{D}_f$ can be expressed in terms of the gradient of potential ϕ set up in the medium by the charge being transferred in the reaction; to calculate the latter one can use the method of image charges. We note that in the problem where a dielectric interlayer is present, the system of images yielding the spatial potential distribution is rather complex and made up of several successions of infinite arrays of charges alternating in sign. The potentials resulting in this case are the sums of contributions of point-charge potentials, and that obtained for the problem where the charge is located outside the interlayer, ϕ^{ext} , differs in form from that obtained when the charge is located inside the interlayer, ϕ^{int} . In addition, the expressions for potentials ϕ^{ext} and ϕ^{int} are of different forms in regions I and II

$$\phi_I^{ext} = \sum_{n=0}^{\infty} \frac{e\theta_1(-\lambda)^n}{\epsilon_1|\vec{r} - 2\vec{d}n|} - \sum_{n=0}^{\infty} \frac{e\theta_1(-\lambda)^n}{\epsilon_1|\vec{r} + 2\vec{h} + 2\vec{d}n|}, \quad (4)$$

$$\phi_{II}^{ext} = \frac{e}{\epsilon_2|\vec{r}|} - \frac{e\lambda}{\epsilon_2|\vec{r} + 2\vec{h} - 2\vec{d}|} - \sum_{n=0}^{\infty} \frac{e\theta_1\theta_2(-\lambda)^n}{\epsilon_2|\vec{r} + 2\vec{h} + 2\vec{d}(n-1)|}, \quad (5)$$

$$\phi_I^{int} = \frac{e}{\epsilon_1} \sum_{n=0}^{\infty} \left\{ (-\lambda)^n \left[\frac{1}{|\vec{r} + 2\vec{d}n|} + \frac{\lambda}{|\vec{r} + 2\vec{h} - 2\vec{d}(n+1)|} - \frac{1}{|\vec{r} + 2\vec{h} + 2\vec{d}n|} - \frac{\lambda}{|\vec{r} + 2\vec{d}(n+1)|} \right] \right\}, \quad (6)$$

$$\phi_{II}^{int} = \frac{e\theta_2}{\epsilon_2} \sum_{n=0}^{\infty} \frac{(-\lambda)^n}{|\vec{r} + 2\vec{d}n|} - \frac{e\theta_2}{\epsilon_2} \sum_{n=0}^{\infty} \frac{(-\lambda)^n}{|\vec{r} + 2\vec{h} + 2\vec{d}n|}. \quad (7)$$

Here $\theta_1 = 2\epsilon_1/(\epsilon_1 + \epsilon_2)$, $\theta_2 = 2\epsilon_2/(\epsilon_1 + \epsilon_2)$, $\lambda = (\epsilon_1 - \epsilon_2)/(\epsilon_1 + \epsilon_2)$, vector $\vec{r}$ issues from the point where the charge is located, and the location of vectors $\vec{d}$ and $\vec{h}$ is shown in Fig. 1.

The integrals contained in (3) are conveniently calculated by changing over to integration over the surface circumscribing the volume of the integration range [2, 11]. Thus, for external disposition of the ion undergoing discharge we have

$$\int_I (\vec{D}_i^{ext} - \vec{D}_f^{ext})^2 dv = \int_{M+P} \phi_I^{ext} \nabla \phi_I^{ext} d\vec{s} = I_I^{ext}(h), \quad (8)$$

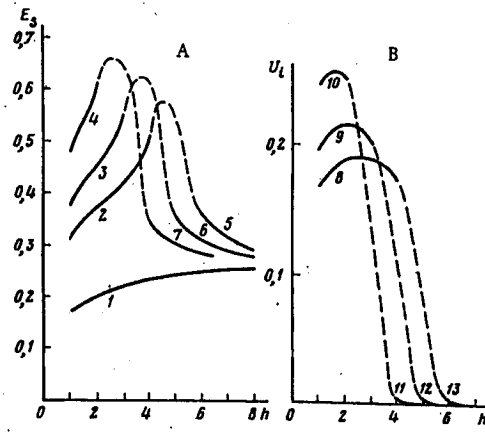


Fig. 2. The dependences $E_s(h)$ (A) and $U_i(h)$ (B) calculated for $a \leq h \leq d-a$ and $h \geq d+a$. The dashed lines show in a schematic way the variation of E_s and U_i are expressed in units of $e^2/\text{\AA}$. Values of the parameters used in the calculation: $a=1 \text{ \AA}$, $\epsilon_1=5$, $\epsilon_2=80$, $\epsilon_{0p1}=\epsilon_{0p2}=1.8$, $d=3$ (4, 7, 10, 11), $d=4$ (3, 6, 9, 12), $d=5 \text{ \AA}$ (2, 5, 8, 13), and $d=0$ (1). 1) E_s ; 2) to 4) E_s^{int} ; 5) to 7) E_s^{ext} ; 8) to 10) U_i^{int} ; and 11) to 13) U_i^{ext} .

where the electrode surface, M, and the plane P terminating the interlayer serve as the boundaries of the range on integration, while $\vec{ds}$ contains the vector of the external normal relative to region I. The integral over region II can be written, for this case, as

$$\int_{\text{II}} (\vec{D}_i^{\text{ext}} - \vec{D}_j^{\text{ext}})^2 dv = \int_{P+S}^{\text{ext}} \varphi_{\text{II}}^{\text{ext}} \nabla \varphi_{\text{II}}^{\text{ext}} \vec{ds} = I_{\text{II}}^{\text{ext}}(h). \quad (9)$$

Here P is the plane terminating the interlayer, while S is the surface of the ion; $\vec{ds}$ contains the vector of the normal to surfaces P and S that is external with respect to region II. For an ion located inside the interlayer, the integrals in (3) can be written as

$$\int_I (\vec{D}_i^{\text{int}} - \vec{D}_j^{\text{int}})^2 dv = \int_{M+P+S}^{\text{int}} \varphi_{\text{I}}^{\text{int}} \nabla \varphi_{\text{I}}^{\text{int}} \vec{ds} = I_{\text{I}}^{\text{int}}(h), \quad (10)$$

$$\int_{\text{II}} (\vec{D}_i^{\text{int}} - \vec{D}_j^{\text{int}})^2 dv = \int_P^{\text{int}} \varphi_{\text{II}}^{\text{int}} \nabla \varphi_{\text{II}}^{\text{int}} \vec{ds} = I_{\text{II}}^{\text{int}}(h). \quad (11)$$

Thus, with the aid of (8) to (11) we obtain for E_s^{ext} and E_s^{int}

$$E_s^{\text{ext,int}}(h) = \frac{1}{8\pi} \left(\frac{1}{\epsilon_{0p1}} - \frac{1}{\epsilon_1} \right) I_{\text{I}}^{\text{ext,int}}(h) + \frac{1}{8\pi} \left(\frac{1}{\epsilon_{0p2}} - \frac{1}{\epsilon_2} \right) I_{\text{II}}^{\text{ext,int}}(h). \quad (12)$$

Functions $U_i(h)$ and $U_f(h)$ are also expressed in terms of the integrals (8) to (11). Suppose that in the initial state the reactant has a charge z , and in the final state a charge $z \pm 1$. Then $U_f = U_i(z \pm 1)^2/z^2$, and U_i can be written as

$$U_i^{\text{ext,int}} = \frac{z^2}{8\pi\epsilon_1} I_{\text{I}}^{\text{ext,int}} + \frac{z^2}{8\pi\epsilon_2} I_{\text{II}}^{\text{ext,int}} - \frac{z^2 e^2}{2a\epsilon_2}. \quad (13)$$

We note that (13) includes the contribution from partial resolution of the reactant during its passage into the dielectric interlayer. Calculation of the integrals in (8) to (11) leads to the following results, after the reduction of similar terms:

$$I_{\text{I}}^{\text{ext}} = \pi e^2 \theta_i^z \sum_{n=0}^{\infty} (-\lambda)^n (n+1) \left[\frac{1}{h+d(n+1)} - \frac{1}{h+d(n+1)} \right]; \quad (14)$$

$$I_{II}^{exp} = \frac{4\pi e^2}{a} + \frac{\pi e^2}{h-d} (\lambda^2 - 2\lambda - 1) + \pi e^2 \theta_1^2 \theta_2^2 \sum_{n=0}^{\infty} \frac{(-\lambda)^n (n+1)}{h+d(n+1)} - 2\pi e^2 \theta_1 \theta_2 \sum_{n=0}^{\infty} \frac{(-\lambda)^n (1-\lambda)/(h+dn)}{h+d(n+1)}; \quad (15)$$

$$I_I^{int} = \frac{4\pi e^2}{a} - \frac{2\pi e^2}{h} + \pi e^2 \sum_{n=0}^{\infty} \frac{(-\lambda)^{n-1} [n(\lambda-1)(1-\lambda^2) - \lambda(\lambda^2 + 2\lambda - 1)]}{h+d(n+1)} +$$

$$+ \pi e^2 \sum_{n=0}^{\infty} \frac{(-\lambda)^n [\lambda^2(n+1) + 2\lambda - n - 1]}{-h+d(n+1)} + 2\pi e^2 \sum_{n=0}^{\infty} \frac{(-\lambda)^n [-\lambda^2(n+1) - 2\lambda + n + 1]}{d(n+1)}; \quad (16)$$

$$I_{II}^{int} = \pi e^2 \theta_2^2 \sum_{n=0}^{\infty} \frac{(-\lambda)^n (n+1)}{d(n+1) - h} + \pi e^2 \theta_2^2 \sum_{n=0}^{\infty} \frac{(-\lambda)^n (n+1)}{d(n+1) + h} - 2\pi e^2 \theta_2^2 / d(1+\lambda). \quad (17)$$

Thus, relations (12) to (17) yield the solution to the desired problem, and can be used to determine in which way the exponential factor in (1) is changing with the distance h between reactants and electrode in the problem involving a dielectric interlayer. Dependences $E_S(h)$ and $U_I(h)$ calculated for a number of values of the system parameters are presented in Fig. 2. It follows from this figure that E_S increases as the reactant approaches the interlayer, and then decreases as the ion approaches the electrode. We note that in the absence of a dielectric interlayer, E_S decreases monotonically as the reactant approaches the electrode. Function U_I is increasing sharply as the ion approaches the interlayer, and has a shallow maximum within the interlayer. Thus, the above calculations show that in the expression (1) for the rate constant of charge transfer, the dependence $E_S(h)$ found in the presence of a dielectric interlayer gives rise to an additional repulsive barrier against penetration of the ion to the electrode, which at small distances changes to effective attraction.

The author expresses his gratitude to M. A. Vorotyntsev, R. R. Dogonadze, L. I. Krishtalik, and A. M. Kuznetsov for useful discussions, and to É. M. Itskovich for help in the numerical calculations.

LITERATURE CITED

1. R. R. Dogonadze and A. M. Kuznetsov, Progress in Science, Physical Chemistry. Kinetics, Vol. 2 [in Russian], VINITI, Moscow (1973).
2. Yu. I. Kharkats, Élektrokhimiya, 12, 592 (1976).
3. V. G. Levich, V. A. Kir'yanov, and V. S. Krylov, Dokl. Akad. Nauk SSSR, 155, 662 (1964).
4. V. A. Kir'yanov, V. A. Kuznetsov, and B. B. Damaskin, Élektrokhimiya, 3, 12 (1967).
5. V. A. Kir'yanov and V. S. Krylov, Élektrokhimiya, 6, 1595 (1970).
6. V. S. Krylov, Élektrokhimiya, 12, 331 (1976).
7. V. S. Krylov, W. R. Fawcett (Fosett), and V. A. Kir'yanov, Élektrokhimiya, 12, 424 (1976).
8. V. S. Krylov, J. Res. Inst. Catal. Hokkaido Univ., 22, 114 (1974).
9. R. A. Marcus, J. Chem. Phys., 24, 966 (1956).
10. L. I. Krishtalik, Progress in Science, Electrochemistry, Vol. 12 [in Russian], VINITI, Moscow (1977), p. 5.
11. Yu. I. Kharkats, Élektrokhimiya, 12, 1370 (1976).