

Reorganization energy of electron transfer in polar liquids. Dependence on reactant size, temperature and pressure

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The solvent reorganization energy of outer sphere electron transfer in polar liquids is derived in a molecular treatment. The reorganization energy is shown to be the sum of two contributions: the reorganization energy of reorientation of liquid permanent dipoles and the energy of reorganization of the liquid density. Reorientation of the dipoles gives the main contribution to the solvent reorganization energy, whereas reorganization of the density contributes mainly to the activation entropy which is positive in the normal and negative in the inverted regions of electron transfer. The reorganization energy of the liquid density contains an explicit temperature dependence which causes the non-Arrhenius temperature dependence of the rate constant. Entropy, enthalpy and volume of activation are found for several solvents.

1. Introduction

Since the outstanding work of Marcus [1] one knows that the free energy of activation of electron transfer (ET) in condensed matter is determined by the reorganization energy E_r , which is equal to the work expended for changing a configuration of the nuclear subsystem of reactants and a medium from the state of reactants to the product state. Usually one distinguishes [2,3] two contributions to E_r : the intramolecular (inner-sphere) reorganization energy of the reactants (donor and acceptor) and the solvent reorganization energy. Combined (intramolecular and solvent) contributions to E_r also exist [4,5] because of coupling of the donor–acceptor motion with the medium. The intramolecular reorganization energy of the reactants is connected with changes in lengths of bonds within a donor and an acceptor as a result of ET. It was repeatedly calculated for classical [6,7] as well as quantum [8–10] vibrational modes. The solvent reorganization energy for reactions in polar liquids according to the Marcus model [1–3] is equal to the work for the reorientation of the permanent molecular dipoles of a liquid from the initial to the final equilibrium configuration.

Essential efforts have been made recently into determination of the pre-exponent of the ET rate constant, including dynamic effects of solvents with one [11–14] and several [13,15–17] relaxation times, effects of dynamics of intramolecular vibrations on the preexponent value [18,19] and multi-exponential ET [19,20]. In contrast to this the expression of Marcus [1] for the ET activation energy remained unrevised and is widely used for systems with classical nuclear modes. It was obtained [1] in the framework of a rather simple model, where the solvent was considered as a dielectric continuum in which the reactants occupy spherical cavities. The theory was further extended to the nonspherical reactants [21] and to donor–acceptor complexes in the form of an ellipsoidal cavity in a dielectric continuum [22–24]. The applicability of the continuum approximation to ET reactions remains, however, questionable because the sizes of the solvent molecules are often comparable with those of the donor and acceptor. This limitation of the theory was overcome in the context of the dynamic mean spherical approximation (MSA) [25–27] and in the interaction-site approximation [28], where the finite size of the solvent molecules has been taken into account. The polar liquid response becomes nonlocal

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because of correlations between the solvent molecules, which was allowed for phenomenologically in nonlocal electrostatics [29,30].

In the above enumerated [1–30] theories of ET in polar liquids electronic transitions are assumed to accomplish due to thermal fluctuations of orientations of the permanent liquid dipoles. They are based on a solid-like model of a solvent in which molecules do not perform a translational motion. In real liquids, however, translations of the molecules cause density fluctuations near the donor–acceptor complex for pure solvents [31,32] and composition fluctuations for mixtures [33,34]. It became apparent recently [35,36] that translations of solvent molecules nearest to a solute significantly affect the relaxation of a polar liquid. The influence of the solvent translational motion on the activation energy of ET, in contrast, has not received any attention. In the previous work [32] a molecular theory of ET reactions in dipolar liquids of hard nonpolarizable spheres with permanent dipole moments has been proposed. It takes into account both orientational and density fluctuations of the solvent. The present work extends this concept to polar liquids with polarizable molecules. The general expression for the solvent reorganization energy of outer-sphere ET is derived. The contributions from orientational and density fluctuations to the total reorganization energy as well as temperature and pressure dependencies of the reorganization energy are analyzed.

2. Free energy of activation

As a result of diffusional approach of a donor and an acceptor in a polar liquid the precursor complex ($i=1$) is formed. It is transformed to the successor complex ($i=2$) due to ET. The induction of the donor–acceptor complex $D_i(\mathbf{r})$ affects the molecular dipole moments μ_j and polarizes solvent molecules. In the present work the solvent will be treated as a liquid of hard spheres with diameter σ and permanent dipole moment μ . The induced polarization $P_e(\mathbf{r})$ will be taken into account in the continuum approximation. Consequently, we will proceed from the model of dipolar liquid in the dielectric continuum with dielectric constant ϵ_∞ . Using the Felderhof functional [37,38] the free energy of the donor–acceptor complex and the polar liquid in the adopted model can be determined as

$$G_i = G_{0i} + G_e^{(i)}[P_e] - \sum_j \mu_j \cdot D_i(\mathbf{r}_j) + \sum_j \varphi(\mathbf{r}_j) + \frac{1}{2} \sum_{j \neq k} \Phi(\mathbf{r}_{jk}) - \frac{1}{2} \sum_{j \neq k} \mu_j \cdot \mathbf{T}_{jk} \cdot \mu_k, \quad (1)$$

where the tensor \mathbf{T}_{jk} has the form

$$\mathbf{T}_{jk} = (3\hat{r}_{jk}\hat{r}_{jk} - \mathbf{1})/r_{jk}^3, \quad \hat{r}_{jk} = \mathbf{r}_{jk}/r_{jk}, \quad \mathbf{r}_{jk} = \mathbf{r}_j - \mathbf{r}_k,$$

\mathbf{r}_j is the coordinate of the j th solvent molecule, $j=1, \dots, N$; G_{0i} is the free energy of the donor–acceptor complex in vacuum, $\Phi(\mathbf{r}_{jk})$ is the potential energy of repulse of hard spheres, $\varphi(\mathbf{r}_j)$ is the potential energy of the short-range solute–solvent interaction. The free energy $G_e^{(i)}[P_e]$ in eq. (1) describes the induced medium polarization $P_e(\mathbf{r})$ and its interaction with permanent dipoles and with the electric field of the donor–acceptor complex,

$$G_e^{(i)}[P_e] = \frac{2\pi\epsilon_\infty}{\epsilon_\infty - 1} \int [P_e(\mathbf{r})]^2 d\mathbf{r} - \int P_e(\mathbf{r}) \cdot D_i(\mathbf{r}) d\mathbf{r} - \sum_j \mu_j \cdot \int \hat{\mathbf{T}}(\mathbf{r}_j - \mathbf{r}) \cdot P_e(\mathbf{r}) d\mathbf{r}. \quad (2)$$

The tensor of dipole–dipole interaction $\hat{\mathbf{T}}(\mathbf{r}_j - \mathbf{r})$ in eq. (2) should be determined separately to exclude the singularity at $\mathbf{r}_j = \mathbf{r}$. Usually [39,40] it is cut as

$$\begin{aligned} \hat{\mathbf{T}}(\mathbf{r}_j - \mathbf{r}) &= \mathbf{T}_1(\mathbf{r}_j - \mathbf{r}) = \mathbf{T}(\mathbf{r}_j - \mathbf{r}), & |\mathbf{r}_j - \mathbf{r}| \geq a, \\ &= \mathbf{0}, & |\mathbf{r}_j - \mathbf{r}| < a, \end{aligned} \quad (3)$$

where a is a cutoff parameter. The limit $a \rightarrow 0$ corresponds to the mean-field approximation, where Nienhuis and Deutch determined [41] $\hat{\mathbf{T}}(\mathbf{r}_j - \mathbf{r})$ in the form

$$\tilde{\mathbf{T}}(\mathbf{r}_j - \mathbf{r}) = \mathbf{T}(\mathbf{r}_j - \mathbf{r}) - \frac{4}{3}\pi \delta(\mathbf{r}_j - \mathbf{r}) . \quad (4)$$

Hoye and Stell [42], however, showed that different mean-field approximations can be embraced for $\tilde{\mathbf{T}}(\mathbf{r}_j - \mathbf{r})$ in the form

$$\tilde{\mathbf{T}}(\mathbf{r}_j - \mathbf{r}) = \mathbf{T}_1(\mathbf{r}_j - \mathbf{r}) - \Theta(1/a^3)\theta(a - |\mathbf{r}_j - \mathbf{r}|) \quad (5)$$

by an appropriate choice of the parameter Θ . The value $\Theta=0$ corresponds to the definition (3) and $\Theta=1$ gives eq. (4) for $a \rightarrow 0$.

According to the fundamental idea of Pekar [43] and Marcus [1] (current works on this subject are presented in refs. [44–46]) the electronic polarization of the liquid $\mathbf{P}_e(\mathbf{r})$ follows adiabatically the transferred electronic density. Orientational and translational motions of molecules, in contrast, are considered as inertial degrees of freedom, fluctuations of which cause radiationless transitions. From this point of view the use of the equilibrium dielectric constant ϵ_∞ in eq. (2) is not correct, as ϵ_∞ is the equilibrium quantity being a result of averaging [47] both over inertialess orientations of induced dipoles and over inertial coordinates of the molecules. We shall, however, assume the contribution of averaging over the molecular coordinates to ϵ_∞ to be negligible and use $G_e^{(i)}[\mathbf{P}_e]$ in the form (2). An analogous assumption is made in all theories of ET and dynamic solvation [25,48,49]. Then, the free energy of the donor–acceptor complex and the liquid in the initial and final states can be obtained by the functional integration over $\mathbf{P}_e(\mathbf{r})$,

$$\exp(-\beta E_i) = \left(\frac{2\epsilon_\infty}{\epsilon_\infty - 1} \right)^{1/2} \int \exp(-\beta G_i) \mathcal{D}\mathbf{P}_e(\mathbf{r}) , \quad (6)$$

where $\beta = 1/k_B T$, k_B is the Boltzmann constant. Eq. (6) gives

$$\begin{aligned} E_i = E_{0i} - \sum_j \mu_j \cdot \left(\mathbf{D}_i(\mathbf{r}_j) + \frac{\epsilon_\infty - 1}{4\pi\epsilon_\infty} \int \tilde{\mathbf{T}}(\mathbf{r}_j - \mathbf{r}) \cdot \mathbf{D}_i(\mathbf{r}) d\mathbf{r} \right) + \sum_j \varphi(r_j) + \frac{1}{2} \sum_{j \neq k} \Phi(r_{jk}) \\ - \frac{1}{2} \sum_{j \neq k} \mu_j \cdot \left(\mathbf{T}_{jk} + \frac{\epsilon_\infty - 1}{4\pi\epsilon_\infty} \int \tilde{\mathbf{T}}(\mathbf{r}_j - \mathbf{r}) \tilde{\mathbf{T}}(\mathbf{r} - \mathbf{r}_k) d\mathbf{r} \right) \cdot \mu_k , \end{aligned} \quad (7)$$

$$E_{0i} = G_{0i} - \frac{\epsilon_\infty - 1}{8\pi\epsilon_\infty} \int \mathbf{D}_i(\mathbf{r})^2 d\mathbf{r} - \frac{\epsilon_\infty - 1}{8\pi\epsilon_\infty} \sum_j \mu_j \cdot \left(\int \tilde{\mathbf{T}}(\mathbf{r}_j - \mathbf{r}) \tilde{\mathbf{T}}(\mathbf{r} - \mathbf{r}_j) d\mathbf{r} \right) \cdot \mu_j .$$

Using $\tilde{\mathbf{T}}(\mathbf{r}_j - \mathbf{r})$ in form (5) we have from eq. (7)

$$E_i = E_{0i} - q \sum_j \mu_j \cdot \mathbf{D}_i(\mathbf{r}_j) + \sum_j \varphi(r_j) + \frac{1}{2} \sum_{j \neq k} \Phi(r_{jk}) - \frac{1}{2} p \sum_{j \neq k} \mu_j \cdot \mathbf{T}_{jk} \cdot \mu_k , \quad (8)$$

where

$$q = \frac{\epsilon_\infty(1 - \Theta) + (2 + \Theta)}{3\epsilon_\infty} , \quad p = \frac{2\epsilon_\infty(1 - \Theta) + (1 + 2\Theta)}{3\epsilon_\infty} .$$

At $\Theta=0$ we have $q = (\epsilon_\infty + 2)/3\epsilon_\infty$ and the second term in eq. (8) corresponds to the local Lorentz field, acting upon a dipole in a nonpolar medium. The dielectric constant ϵ_∞ is related to the polarizability α and the liquid density n by the expression [50]

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{y_e}{1 + \Theta y_e} , \quad y_e = \frac{4}{3}\pi n \alpha . \quad (9)$$

The value $\Theta=0$ corresponds to the Lorentz–Lorenz equation, i.e. to the approximation of totally uncorrelated positions of the molecules [39]. At $\Theta=1$, $\epsilon_\infty = 1 + 4\pi n \alpha$. This formula describes the dielectric constant of gases

[39] and is inapplicable for liquids. Correlations in positions of molecules were partially taken into account by Wertheim [52] by summation of chain diagrams. This result can be obtained if one substitutes in eq. (9)

$$\theta = \theta_w = \frac{-3 + q(2\zeta) + 2q(-\zeta)}{q(2\zeta) - q(-\zeta)}, \quad (10)$$

where

$$q(x) = (1 + 2x)^2 / (1 - x)^4, \quad (11)$$

$$\epsilon_\infty = q(2\zeta) / q(-\zeta). \quad (12)$$

The difference of the free energies (8) of the donor–acceptor complex and the liquid in the final and initial states is usually considered [11,12,32] as the ET reaction coordinate

$$X = \Delta E_0 - q \sum_j \mu_j \cdot \Delta \mathbf{D}(\mathbf{r}_j),$$

where $\Delta E_0 = E_{02} - E_{01}$, $\Delta \mathbf{D} = \mathbf{D}_2 - \mathbf{D}_1$. The diabatic free energy surfaces over the reaction coordinate X are determined in the form

$$\exp[-\beta F_i(X)] = (1/Q) \text{Sp}[\delta(X - E_2 + E_1) \exp(-\beta E_i)],$$

$$Q = \text{Sp}[\exp(-\beta U_s)], \quad U_s = -\frac{\rho}{2} \sum_{j \neq k} \mu_j \cdot \mathbf{T}_{jk} \cdot \mu_k + \frac{1}{2} \sum_{j \neq k} \Phi(r_{jk}),$$

where the trace is taken over the coordinates and orientations of the liquid molecules. Making an expansion over the Mayer functions of the solute–solvent interaction

$$f_i(j) = \exp\{-\beta \phi(r_j) + \mu_j q \cdot [\beta \mathbf{D}_i(\mathbf{r}_j) + i z \Delta \mathbf{D}(\mathbf{r}_j)]\} - 1$$

in the equation

$$\exp[-\beta F_i(X)] = \frac{1}{Q} \int_{-\infty}^{\infty} \frac{dz}{2\pi} \exp[iz(X - \Delta E_0)] \text{Sp}\left[\exp\left(izq \sum_j \mu_j \cdot \Delta \mathbf{D}(\mathbf{r}_j) - \beta E_i\right)\right],$$

we obtain [32]

$$\exp[-\beta F_i(X)] = \int_{-\infty}^{\infty} \frac{dz}{2\pi} \exp[iz(X - \Delta E_0) + \tilde{G}_i(z) - \beta E_{0i}],$$

$$\tilde{G}_i(z) = n \int f_i(1) d\Gamma_1 + \frac{n^2}{2} \int \int f_i(1) f_i(2) h(12) d\Gamma_1 d\Gamma_2,$$

where $(j) \equiv (\mathbf{r}_j, \mathbf{s}_j)$, $\mathbf{s}_j = \mu_j / \mu$, $d\Gamma_j = d\mathbf{r}_j d\Omega / 4\pi$, $h(12)$ is the pair correlation function of the pure solvent. In the Gaussian approximation we have

$$\beta F_i(X) = \beta E_{0i} - \tilde{G}_i(0) + \frac{(X + X_{0i} - \Delta E_0)^2}{2\sigma_{m,i}^2}, \quad (13)$$

where

$$X_{0i} = qn \int \mu_1 \cdot \Delta \mathbf{D}(\mathbf{r}_1) g_{0i}(1) d\Gamma_1 \left(1 + n \int h(12) f_{0i}(2) d\Gamma_2\right), \quad (14)$$

$$\sigma_{m,i}^2 = q^2 n \int [\boldsymbol{\mu}_1 \cdot \Delta \mathbf{D}(\mathbf{r}_1)]^2 g_{0i}(1) d\Gamma_1 \left(1 + n \int h(12) f_{0i}(2) d\Gamma_2 \right) + q^2 n^2 \int \boldsymbol{\mu}_1 \cdot \Delta \mathbf{D}(\mathbf{r}_1) g_{0i}(1) d\Gamma_1 \int h(12) \boldsymbol{\mu}_2 \cdot \Delta \mathbf{D}(\mathbf{r}_2) g_{0i}(2) d\Gamma_2, \quad (15)$$

$$f_{0i}(1) = \exp[-\beta\varphi(r_1) + \beta q \boldsymbol{\mu}_1 \cdot \mathbf{D}_i(\mathbf{r}_1)] - 1, \quad g_{0i} = f_{0i} + 1.$$

The Gaussian approximation (13) is correct when the dispersion $\sigma_{m,i}$ is essentially less than the distance over the coordinate X from the bottom of the free energy surface to the top of the barrier at the interaction point $F_1(X) = F_2(X)$. If in the expressions for $\sigma_{m,i}^2$ and $\Delta X = X_{02} - X_{01}$ the expansion over $\beta q \boldsymbol{\mu} \cdot \mathbf{D}_i$ is limited only by the first nonvanishing terms, the free energies of activation of the forward (ΔF_{12}) and back (ΔF_{21}) reactions take the familiar form [1–3]

$$\Delta F_{12} = \frac{(E_r + \Delta F_0)^2}{4E_r}, \quad \Delta F_{21} = \frac{(E_r - \Delta F_0)^2}{4E_r}, \quad (16)$$

where $\Delta F_0 = \Delta E_0 - [\tilde{G}_2(0) - \tilde{G}_1(0)]/\beta$ and the solvent reorganization energy $E_r = \beta \sigma_{m,i}^2/2$ is determined by

$$E_r = \frac{1}{2} \beta q^2 n \int [\boldsymbol{\mu}_1 \cdot \Delta \mathbf{D}(\mathbf{r}_1)]^2 g_0(1) d\Gamma_1 \left(1 + n \int h(12) f_0(2) d\Gamma_2 \right) + \frac{1}{2} \beta q^2 n^2 \int \boldsymbol{\mu}_1 \cdot \Delta \mathbf{D}(\mathbf{r}_1) g_0(1) d\Gamma_1 \int h(12) \boldsymbol{\mu}_2 \cdot \Delta \mathbf{D}(\mathbf{r}_2) g_0(2) d\Gamma_2. \quad (17)$$

In eq. (17) the functions

$$f_0(r) = \exp[-\beta\varphi(r)] - 1, \quad g_0(r) = f_0(r) + 1$$

for the donor and acceptor being hard spheres of radii R_d and R_a with coordinates \mathbf{r}_d and \mathbf{r}_a at distances $R \geq R_a + R_d$, $\mathbf{R} = \mathbf{r}_a - \mathbf{r}_d$ have the form

$$f_0(r) = -\theta(R_1 - r) - \theta(R_2 - |\mathbf{r} - \mathbf{R}|), \quad R_1 = R_d + \sigma/2, \quad R_2 = R_a + \sigma/2. \quad (18)$$

The correlation function $h(12)$ in eq. (17) can be expanded [53] in terms of the angular functions

$$A(12) = \mathbf{s}_1 \cdot \mathbf{s}_2, \quad D(12) = 3(\mathbf{s}_1 \cdot \hat{\mathbf{r}}_{12})(\mathbf{s}_2 \cdot \hat{\mathbf{r}}_{12}) - \mathbf{s}_1 \cdot \mathbf{s}_2$$

as

$$h(12) = h^s(r_{12}) + h^A(r_{12})A(12) + h^D(r_{12})D(12), \quad (19)$$

where $h^s(r_{12})$ is the correlation function for the liquid of hard spheres. Using eqs. (18) and (19) we have

$$E_r = E_p + E_d, \quad (20)$$

$$E_p = \frac{\beta q^2 \mu^2 n}{6} \int_V [\Delta \mathbf{D}(\mathbf{r}_1)]^2 d\mathbf{r}_1 + \frac{\beta q^2 \mu^2 n^2}{18} \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 \{ h^A(r_{12}) \Delta \mathbf{D}(\mathbf{r}_1) \cdot \Delta \mathbf{D}(\mathbf{r}_2) + h^D(r_{12}) [3(\Delta \mathbf{D}(\mathbf{r}_1) \cdot \hat{\mathbf{r}}_{12})(\hat{\mathbf{r}}_{12} \cdot \Delta \mathbf{D}(\mathbf{r}_2)) - \Delta \mathbf{D}(\mathbf{r}_1) \cdot \Delta \mathbf{D}(\mathbf{r}_2)] \}, \quad (21)$$

$$E_d = -\frac{\beta q^2 \mu^2 n^2}{6} \int_V [\Delta \mathbf{D}(\mathbf{r}_1)]^2 d\mathbf{r}_1 \int_{V_0} h^s(r_{12}) d\mathbf{r}_2, \quad (22)$$

where the integration is carried out over the volumes

$$V: \quad r \geq R_1, \quad |r - R| \geq R_2,$$

$$V_0: \quad r < R_1, \quad |r - R| < R_2.$$

For outer-sphere ET (e is the electron charge)

$$\Delta D(r) = e \nabla \left(\frac{1}{|r - R|} - \frac{1}{r} \right),$$

and eq. (21) reduces to

$$E_p = \frac{\beta q^2 \mu^2 n}{6} \int \Delta \tilde{D}(k) \cdot \Delta \tilde{D}(-k) m^+(k) \frac{dk}{(2\pi)^3}. \quad (23)$$

The Fourier transform

$$\Delta \tilde{D}(k) = \int_V \Delta D(r) \exp(ik \cdot r) dr$$

has the form

$$\Delta \tilde{D}(k) = \frac{4\pi i e k}{k} [j_0(kR_1) - \exp(ik \cdot R) j_0(kR_2)], \quad (24)$$

where $j_n(x)$ is the spherical Bessel function. In eq. (23) the function

$$m^+(k) = 1 + \frac{1}{3} n \tilde{h}^+(k), \quad \tilde{h}^+(k) = \tilde{h}^A(k) + 2\tilde{h}^D(k)$$

is analogous in form to the structure factor of a liquid,

$$\tilde{h}^A(k) = 4\pi \int_0^\infty h^A(r) j_0(kr) r^2 dr, \quad \tilde{h}^D(k) = -4\pi \int_0^\infty h^D(r) j_2(kr) r^2 dr.$$

For a dipolar liquid the medium polarization $P(r)$ is related to the external field $E(r)$ in the linear response approximation by the expression [42]

$$4\pi k \cdot \tilde{P}(k) = \frac{4}{3} \pi \beta n \mu^2 m^+(k) k \cdot \tilde{E}(k).$$

The function $m^+(k)$, consequently, determines the longitudinal linear response of the liquid permanent dipoles.

The total reorganization energy E_r , as can be seen from eq. (20), is the sum of two contributions E_p and E_d . The reorganization energy E_p is caused by reorientations of the liquid permanent dipoles, whereas the reorganization energy E_d is connected with a change in coordinates of the solvent molecules, i.e. with the reorganization of the liquid density near the donor–acceptor complex due to ET. These two contributions to E_r appear to be uncoupled because of different symmetry of long-range dipole–dipole and short-angle repulsive interactions. The appearance of E_d is the result of inclusion of translational motion of the molecules in the framework of the molecular treatment. It should be noted that the importance of the allowance for translational motion in a liquid when calculating the ET free energy of activation was pointed out for the first time in refs. [33,34], where ET in a liquid with point defects was considered.

3. Reorganization energy E_p

The energy of reorientation of the permanent dipoles (23) can be found when the correlation function $\tilde{h}^+(k)$ is known. For a dipolar liquid an exact solution has been obtained [53] in the framework of the MSA. According to the Baxter factorization [54] it determines $m^+(k)$ in the form

$$m^+(k) = [Q^+(k)Q^+(-k)]^{-1}, \quad (25)$$

where

$$Q^+(k) = 1 - 24\xi \int_0^1 \exp(ik\sigma r) q^+(r) dr, \quad q^+(r) = \frac{1}{2}a(r^2 - 1) + b(r - 1), \quad (26)$$

$$a = \frac{1 + 4\xi}{(1 - 2\xi)^2}, \quad b = -\frac{3\xi}{(1 - 2\xi)^2}. \quad (27)$$

For a dipolar liquid the parameter ξ in eq. (27) is expressed through the solvent dielectric constant ϵ_s via a relation analogous to eq. (12). In the accepted model, however, the dipolar liquid resides in the dielectric continuum with dielectric constant ϵ_∞ . Therefore, the relation between ξ and the dielectric properties of the solvent has to be considered separately. This relation can be found from the energy of interaction of probe charges 1 and 2 being at a macroscopic distance. The interaction energy Φ_{12} in accord with ref. [40] is determined by the diagram

$$\beta\Phi_{12} = \begin{array}{ccccccc} \circ & \text{---} & \circ & + & \circ & \text{---} & \bullet \\ 1 & 2 & 1 & 3 & 2 & 1 & 3 \end{array} \wedge \wedge \begin{array}{cc} \bullet & \circ \\ 4 & 2 \end{array}.$$

where $\circ\text{---}\circ = \beta \times$ direct interaction between charges, $\circ\text{---}\bullet = \beta \times$ charge-dipole interaction, $\wedge\wedge = h(34)$, the black dots 3 and 4 over which the integration is carried out each give a factor n . It should be taken into account that the averaging over the induced medium polarization has already been made and the interactions are screened. Thus, the Fourier transforms of the interactions at small k have the form

$$\circ\text{---}\circ = 4\pi\beta/\epsilon_\infty k^2, \quad \circ\text{---}\bullet = \beta(4\pi i q \mu/k) \hat{k} \cdot s.$$

Consequently,

$$\frac{4\pi}{k^2\epsilon} = \frac{4\pi}{k^2\epsilon_\infty} - \frac{16\pi^2\beta q^2\mu^2 n}{3k^2} - \frac{16\pi^2\beta q^2\mu^2 n^2}{k^2} \int \hat{k} \cdot s_3 h(34) s_4 \cdot \hat{k} \frac{d\Omega_3}{4\pi} \frac{d\Omega_4}{4\pi}. \quad (28)$$

From eq. (28) at $k \rightarrow 0$ we have

$$c_0 = q^2 y [3 + n\tilde{h}^+(0)], \quad (29)$$

where $c_0 = 1/\epsilon_\infty - 1/\epsilon_s$ is the Pekar factor,

$$y = \frac{4}{3}\pi\beta\mu^2 n. \quad (30)$$

Repeating the calculations of Wertheim [53] it is easy to obtain y in eq. (30) and $\tilde{h}^+(0)$ in eq. (29),

$$3py = q(2\xi) - q(-\xi), \quad n\tilde{h}^+(0) = 3[1/q(2\xi) - 1], \quad (31)$$

where $q(x)$ is determined by eq. (11). From eqs. (29)–(31) we obtain the relation

$$c_0 = (q^2/p)[1 - q(-\xi)/q(2\xi)], \quad (32)$$

which determines the parameter ξ in eq. (27) and, consequently, the function $m^+(k)$.

From eqs. (23) and (24) we have

$$E_p = \frac{3\gamma q^2 e^2}{2\pi\sigma} \int_{-\infty}^{\infty} [j_0(\kappa\tilde{R}_1)^2 + j_0(\kappa\tilde{R}_2)^2 - 2j_0(\kappa\tilde{R}_1)j_0(\kappa\tilde{R}_2)j_0(\kappa\tilde{R})] m^+(\kappa) d\kappa, \quad (33)$$

where $\kappa = k\sigma$, $\tilde{R}_1 = R_1/\sigma$, $\tilde{R}_2 = R_2/\sigma$, $\tilde{R} = R/\sigma$. The integral (33) can be calculated numerically or analytically

when using an approximation for $m^+(k)$. As in the previous paper [32], we shall use the simplest Pade approximation

$$m_p^+(\kappa) = \frac{1 + \kappa^2 b^2}{a^2 + \kappa^2 b^2}, \quad (34)$$

which permits an analytical expression for E_p to be obtained. As a result the reorganization energy is given by

$$E_p = c_0 e^2 g, \quad (35)$$

where the parameter g is different for contact ($R_d + R_a \leq R < R_1 + R_2$) and solvent-separated ($R_1 + R_2 \leq R$) ET. For contact ET

$$g = \frac{R^2 + (R_1 - R_2)^2}{4RR_1R_2} + \frac{\psi(2R_1/A_p)}{2R_1} + \frac{\psi(2R_2/A_p)}{2R_2} + \frac{A_p^2(a^2 - 1)}{2RR_1R_2} \{ \cosh[(R_1 - R_2)/A_p] \exp(-R/A_p) + \sinh(R/A_p) \exp[-(R_1 + R_2)/A_p] - 1 \}, \quad (36)$$

where

$$\psi(x) = \frac{a^2 - 1}{x} (1 - e^{-x}), \quad (37)$$

$$A_p = 3\sigma\xi / (1 + 4\xi). \quad (38)$$

For solvent-separated ET

$$g = \frac{1}{2R_1} [1 + \psi(2R_1/A_p)] + \frac{1}{2R_2} [1 + \psi(2R_2/A_p)] - \frac{1}{R} \left(1 + \frac{A_p^2(a^2 - 1)}{R_1R_2} \sinh(R_1/A_p) \sinh(R_2/A_p) \exp(-R/A_p) \right). \quad (39)$$

In the continuum limit $\sigma \rightarrow 0$ eqs. (36) and (39) reduce to the well-known result [1–3]

$$E_r^{(0)} = e^2 c_0 g^{(0)}, \quad g^{(0)} = 1/2R_1 + 1/2R_2 - 1/R, \quad R \geq R_a + R_d. \quad (40)$$

As it has already been pointed out previously [32], if instead of the approximation (34) $m^+(k)$ is taken in the form

$$m_0^+(\kappa) = (a^2 + b^2 k^2)^{-1}$$

we have for the solvent-separated ET ($R_a = R_d$) the expression

$$g = \frac{1}{R_1} \left(1 - \frac{A_p}{2R_1} [1 - \exp(-2R_1/A_p)] \right) - \frac{1}{R} \left(1 - \frac{A_p^2}{2R_1^2} [\cosh(2R_1/A_p) - 1] \exp(-R/A_p) \right), \quad (41)$$

analogous to the result of nonlocal electrostatics [29,30]. In eq. (41), however, in contrast to refs. [29,30], R_1 instead of R_d is involved and the length parameter A_p is not an empirical value, but is determined by eq. (38). It has repeatedly been pointed out [55–57] that the equations of nonlocal electrostatics with $A_p \sim \sigma$ essentially underestimate the solvent reorganization energy. This is the result of a wrong approximation of $m^+(k)$ ($m^+(k) \rightarrow 1$, whereas $m_0^+(k) \rightarrow 0$ at $k \rightarrow \infty$) and the use [29,58] of overestimated values of the length A_p [32].

The solvent molecular structure in ET reactions and the problem of dynamic solvation was also taken into account in the context of the MSA for ion-dipolar systems. The Born solvation energy of a separate ion calculated by Chen, Mitchell and Ninham [59] has been used by Wolynes [48] to determine the dynamic response

function of a polar liquid. In this approach the energy of reorientation of dipoles for the reaction with $R_a = R_d$, $R = 2R_d$ can be written [25] as

$$E_p^{(1)} = \frac{e^2}{2R_d} \left(\frac{1 - 1/\epsilon_s}{1 + \Delta(0)} - \frac{1 - 1/\epsilon_\infty}{1 + \Delta(\infty)} \right), \quad (42)$$

where

$$\Delta(\infty) = \frac{\sigma}{2R_d} \frac{1 - 2\zeta}{1 + 4\zeta}, \quad \Delta(0) = \frac{\sigma}{2R_d} \frac{1 - 2\zeta'}{1 + 4\zeta'}, \quad (43)$$

the parameters ζ and ζ' are determined, correspondingly, by eqs. (11), (12) and by the relation

$$\epsilon_s = \frac{(1 + 4\zeta')^2 (1 + \zeta')^4}{(1 - 2\zeta')^6}.$$

Expression (42) is rather apparent, since the solvation energy was determined [25] only for separate ions. The approximation

$$E_p^{(2)} = e^2 \left(\frac{1}{R_d} - \frac{1}{R} \right) \left(\frac{1 - 1/\epsilon_s}{1 + \Delta(0)} - (1 - 1/\epsilon_\infty) \right) \quad (44)$$

has been proposed [26,27] to take into account the finite distance between the donor and acceptor. The geometrical structure of the donor-acceptor complex has also been allowed for adequately in the context of the interaction-site approximation [28]. These results, however, will not be considered here, because of the different model of the solvent (dipolar dumbbells) and the condition $\epsilon_\infty = 1$ has been accepted in ref. [28].

Eq. (35) shows that in the framework of the present theory, as in the continuum limit, the energy of reorientation of the permanent dipole E_p is proportional to the Pekar factor c_0 which is independent of the choice of the parameter Θ in eqs. (5) and (8). The length A_p , on the other hand, depends on Θ through the parameter ζ , determined by eq. (32). This dependence is, however, weak (see figs. 1a and 1b) and for calculations the values $\Theta = 0$ or $\Theta = \Theta_w$ can be taken. The solvent reorganization energy E_p in dimethylformamide is plotted in figs. 1a and 1b versus the reduced reactant size R_d/σ ($R_a = R_d$) according to eqs. (33), (35)–(38), (40), (42)–(44). As is seen from the figures, the Pade approximation (34) gives a good agreement (especially for solvent-sepa-

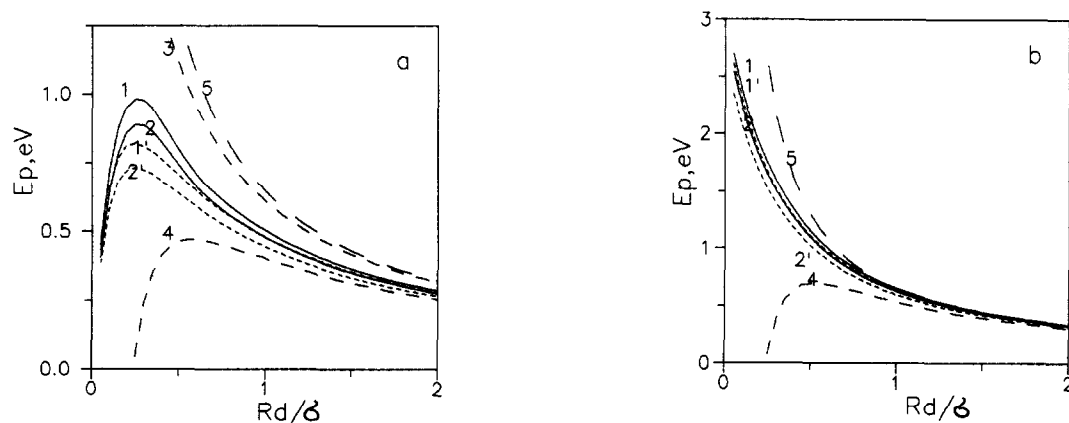


Fig. 1. Reorganization energy E_p versus R_d/σ for (a) contact ($R_a = R_d$, $R = 2R_d$) and (b) solvent-separated ($R = 2R_d + \sigma$) ET in dimethylformamide. (1) Eq. (33), $\Theta = \Theta_w$; (2) eq. (33), $\Theta = 0$; (1') eqs. (35), (36), $\Theta = \Theta_w$; (2') eqs. (35), (36), $\Theta = 0$; (3) eq. (42); (4) eq. (44); (5) eq. (40).

rated ET) between numerical calculations following eq. (33) and the analytical result (35)–(38). The energy E_p calculated in accordance with the present theory for contact ET proves to be between the values of the dynamic MSA (42), (43) and the approximation (44). The area of application of eq. (44) is, however, limited, as $E_p^{(2)}$ becomes negative with the decrease of R_d/σ .

4. Reorganization energy E_d

The reorganization energy of the liquid density E_d is determined by eq. (22) which for outer-sphere ET can be rewritten in bipolar coordinates as

$$E_d = \frac{3e^2q^2y}{2\sigma} \sum_{i=1}^2 s_i(\tilde{R}), \quad (45)$$

where $\tilde{R} = R/\sigma$,

$$s_i(\tilde{R}) = -12\eta \int_{\tilde{R}_i}^{\tilde{R}} \frac{dx}{x^3} \int_0^{\tilde{R}_i} y dy \int_{x-y}^{x+y} h^*(t) t dt, \quad (46)$$

$\tilde{R}_i = R_i/\sigma$, $\eta = \pi n \sigma^3/6$ is the packing parameter. The function $s_i(\tilde{R})$ can be determined by using the exact solution by Baxter [54] for a hard sphere liquid which determines the Fourier transform of the correlation function $\tilde{h}^*(k)$. Then it is easy to obtain

$$s_i(\tilde{R}) = \frac{1}{\pi} \int_{-\infty}^{\infty} \left(1 - \frac{1}{Q(\kappa)Q(-\kappa)}\right) F(\kappa\tilde{R}_i, \kappa\tilde{R}) d\kappa, \quad (47)$$

where

$$F(x, y) = (\sin x - x \cos x) \int_x^y \frac{dt}{t^3} \sin t, \quad (48)$$

and the function $Q(k)$ is determined by the relation

$$Q(\kappa) = 1 - 12\eta \int_0^1 [a_1(r^2 - 1)/2 + b_1(r - 1)] \exp(ikr) dr, \quad (49)$$

$$a_1 = \frac{1+2\eta}{(1-\eta)^2}, \quad b_1 = -\frac{3\eta/2}{(1-\eta)^2}.$$

In the previous work [32] the integral (47) was calculated by using the simplest Pade approximation

$$1 - [Q(\kappa)Q(-\kappa)]^{-1} = \frac{a_1^2 - 1}{a_1^2 + b_1^2 \kappa^2}, \quad (50)$$

which yields

$$s_i(\tilde{R}) = \frac{a_1^2 - 1}{|a_1 b_1|} \left(\frac{R_i}{\Lambda_d} \cosh \frac{R_i}{\Lambda_d} - \sinh \frac{R_i}{\Lambda_d} \right) \left(\frac{E_3(R_i/\Lambda_d)}{(R_i/\Lambda_d)^2} - \frac{E_3(R/\Lambda_d)}{(R/\Lambda_d)^2} \right), \quad (51)$$

where $R \geq R_i$,

$$A_d = \frac{3\sigma\eta}{2+4\eta}, \quad E_n(x) = \int_1^\infty \frac{dt}{t^n} e^{-xt}.$$

As it was shown previously [32] and is seen from fig. 2, the approximation (50) and eq. (51) give a rather crude evaluation of the integral (47), which is the result of the strongly oscillatory character of $\tilde{h}^s(k)$. To increase the accuracy of the calculation of E_d a Pade approximation $\sim k^4$ for $\tilde{h}^s(k)$ can be used. It yields

$$[Q(\kappa)Q(-\kappa)]^{-1} = \frac{1-b_3\kappa^2+b_0^2\kappa^4}{a_1^2-b_2\kappa^2+b_0^2\kappa^4}, \quad (52)$$

where

$$b_0 = \frac{\eta}{10} \frac{4+\eta/2}{(1-\eta)^2}, \quad b_2 = 2b_0a_1 - b_1^2,$$

and the coefficient b_3 from the condition of finiteness of the integral

$$\int \tilde{h}^s(k) dk \quad (53)$$

should be chosen as $b_3 = b_2$. Thus we have

$$-n\tilde{h}^s(k) = \frac{a_1^2 - 1}{a_1^2 - b_2\kappa^2 + b_0^2\kappa^4}, \quad (54)$$

from which it is easy to obtain

$$s_i(\tilde{R}) = \frac{a_1^2 - 1}{2b_0^2\gamma_d\alpha_d} \operatorname{Im} \left\{ \left(\tilde{R}_i \cosh \tilde{\kappa}\tilde{R}_i - \frac{1}{\tilde{\kappa}} \sinh \tilde{\kappa}\tilde{R}_i \right) \left(\frac{E_3(\tilde{\kappa}\tilde{R}_i)}{(\tilde{\kappa}\tilde{R}_i)^2} - \frac{E_3(\tilde{\kappa}\tilde{R})}{(\tilde{\kappa}\tilde{R})^2} \right) \right\}, \quad (55)$$

where

$$\tilde{\kappa} = \alpha_d - i\gamma_d, \quad (56)$$

$$\alpha_d = 15/(8+\eta), \quad (57)$$

$$\gamma_d = \sqrt{4b_0a_1 - b_1^2}/2b_0. \quad (58)$$

The dependence of E_d on R_d/σ in accordance with eqs. (55)–(58) as well as the solution (51) and the numer-

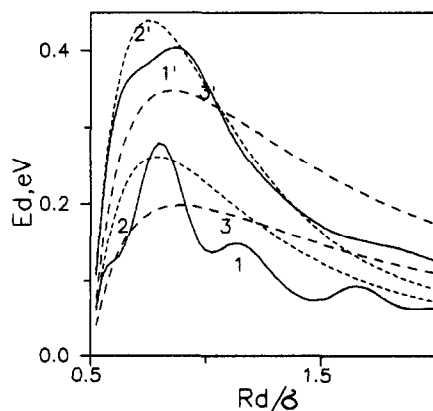


Fig. 2. Plot of the reorganization energy E_d of contact ($R_s = R_d$, $R = 2R_d$) ET versus R_d/σ in dimethylformamide (1, 2, 3) and methanol (1', 2', 3'). Calculations are made in accordance with eq. (47) (1, 1'), eq. (51) (3, 3') and eq. (55) (2, 2').

ical result (47) are plotted in fig. 2. The solution (55) gives a better agreement with the numerical integration (47), but both the approximations (50) and (52) do not yield the oscillations of E_d versus R_d . An exact analytical solution for E_d can be obtained in the Wertheim [60] representation for the binary distribution function of a hard sphere liquid. Following refs. [60,61] eq. (46) can be represented in the form

$$s_i(\tilde{R}) = 8\eta\tilde{R}_i^3 \left(\frac{1}{\tilde{R}_i} - \frac{1}{\tilde{R}} \right) - \frac{1}{\pi i} \int_{c-i\infty}^{c+i\infty} \mathcal{F}(s) d_i(s) ds, \quad (59)$$

$$d_i(s) = (s\tilde{R}_i \cosh s\tilde{R}_i - \sinh s\tilde{R}_i) \int_{s\tilde{R}_i}^{s\tilde{R}} \frac{dx}{x^3} e^x, \quad (60)$$

where

$$\mathcal{F}(s) = \frac{12\eta L(s)}{12\eta L(s) + S(s)e^s}, \quad (61)$$

$$L(s) = (1 + \eta/2)s + 1 + 2\eta,$$

$$S(s) = (1 - \eta)^2 s^3 + 6\eta(1 - \eta)s^2 + 18\eta^2 s - 12\eta(1 + 2\eta).$$

To obtain a closed relation for $s_i(\tilde{R})$ the denominator in eq. (61) is explained over $12\eta L(s)/S(s)e^s$, with the integration contour providing the condition $|S(s)| > |12\eta L(s)e^{-s}|$. At $\tilde{R} - \tilde{R}_i < 1$ the summand proportional to $\exp[s(x - \tilde{R}_i - 1)]$ in eq. (59) gives a zero contribution to the integral. Consequently, under such a condition

$$s_i(\tilde{R}) = 8\eta\tilde{R}_i^3 \left(\frac{1}{\tilde{R}_i} - \frac{1}{\tilde{R}} \right) + \sum_{n \geq 1} S_n(\tilde{R}_i, \tilde{R}) \theta(\tilde{R} + \tilde{R}_i - n), \quad (62)$$

where

$$S_n(\tilde{R}_i, \tilde{R}) = - \left(\frac{1}{\tilde{R}_i} - \frac{1}{\tilde{R}} \right) + \frac{(-12\eta)^n}{(n-1)!} \sum_{l=0}^2 \lim_{s \rightarrow s_l} \frac{d^{n-1}}{ds^{n-1}} \left[(s - s_l)^n \left(\frac{L(s)}{S(s)} \right)^n (s\tilde{R}_i - 1) \exp[s(\tilde{R}_i - n)] \int_{s\tilde{R}_i}^{s\tilde{R}} \frac{dx}{x^3} e^x \right]. \quad (63)$$

In eq. (63) s_l are the roots of $S(s) = 0$ which are determined as

$$s_l = \frac{2\eta}{1-\eta} (-1 + x_+ j^l + x_- j'^l), \quad j = \exp(2\pi i/3),$$

$$x_+ = \sqrt[3]{\sqrt{f^2 + 1/8} + f}, \quad x_- = -\sqrt[3]{\sqrt{f^2 + 1/8} - f},$$

$$f = (3 + 3\eta - \eta^2)/4\eta^2.$$

The function $s_i(\tilde{R})$ in the explicit form for $\tilde{R} + \tilde{R}_i < 3$ is calculated in the Appendix. For contact electron exchange ($R_a = R_d$, $R = 2R_d$) the former condition means $1/2 \leq R_d/\sigma \leq 5/6$. Values of $s_i(\tilde{R})$ for arbitrary $\tilde{R} \geq \tilde{R}_i$ can be obtained by subsequent calculation of the summands in eq. (62).

5. Reactant size dependence

As is seen from figs. 1 and 2 the reorganization energies E_p and E_d depend on the reduced reactant size R_d/σ in a similar manner. Both the functions for contact ET change from zero, pass through a maximum and then decrease with R_d/σ . It is seen from fig. 2 and eq. (46) that $E_d = 0$ for $R < R_i$, $i = 1, 2$. For contact electron exchange ($R_a = R_d$, $R = 2R_d$) this condition means that $E_d = 0$ for $R_d \leq \sigma/2$, $R \leq \sigma$, i.e. when the donor–acceptor

distance is less than the solvent diameter. In this case the different shifts of the donor and acceptor electronic levels necessary for ET cannot be created by the density fluctuations and $E_d=0$. In figs. 3a and 3b the dependence of the total reorganization energy $E_r=E_p+E_d$ together with the dependencies of E_p and E_d on R_d/σ are plotted for the contact electron exchange reaction in dimethylformamide and methanol. At $R_d/\sigma > 1$ the values of E_r calculated in the framework of the present theory are close to $E_r^{(0)}$ (eq. (40)) corresponding to the continuum limit. The maxima of E_p and E_d appear to be separated, which result in a nonmonotonic dependence of E_r on R_d/σ . The length parameters A_p and A_d in eqs. (36), (39) and (51) are smaller than the solvent molecule diameter σ : for the ordinary values $\xi=0.1$, $\eta=0.5$ we have $A_p=0.2\sigma$, $A_d=0.4\sigma$. The common use of the Lorentzian form for the Fourier transform of the linear response function assumes that A_p and A_d should correspond to the correlation lengths of the corresponding fluctuations. The use of $A_p \approx \sigma$ in nonlocal electrostatics [29,30,55] was one of the reasons for underestimating the E_p values. To study this problem let us consider the asymptotic behavior of the correlation functions $h^s(r)$ and $h^+(r)$. The quadratic approximations (34) and (50) are inadequate in this case, since they cannot provide the finiteness of the integral (53). Therefore, we use the approximation (54) which yields

$$-nh^s(r) \propto \frac{1}{r} \exp(-r/\lambda_d) \sin \gamma_d r, \quad -nh^+(r) \propto \frac{1}{r} \exp(-r/\lambda_p) \sin \gamma_p r, \quad (64)$$

where

$$\lambda_p = (8+2\xi)\sigma/15, \quad \lambda_d = (8+\eta)\sigma/15,$$

γ_d is determined by eq. (58) and γ_p is given by the same relation upon the change $\eta \rightarrow 2\xi$. The asymptotic of the correlation function of a liquid in the form (63) is quite general [62] and λ_p , λ_d instead of A_p , A_d should be considered as the correlation lengths. For $\xi=0.1$, $\eta=0.5$ we have $\lambda_p=0.5\sigma$, $\lambda_d=0.6\sigma$.

6. Temperature dependence

The free energy of ET is determined experimentally from the temperature dependence of the reaction rate constant. The reorganization energy E_r and the free energy difference ΔF_0 are generally temperature dependent and care is needed when determining the entropy

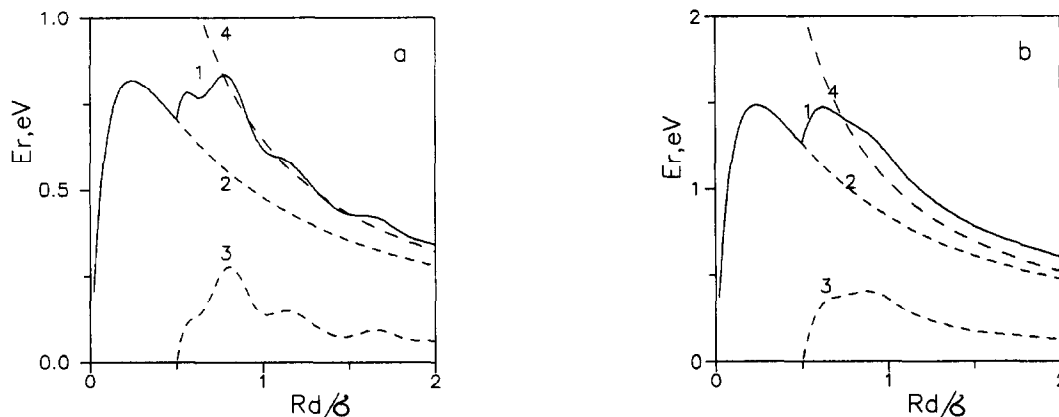


Fig. 3. Plot of the ET reorganization energy in dimethylformamide (a) and methanol (b) versus R_d/σ : (1) E_r ; (2) E_p ; (3) E_d ; (4) $E_r^{(0)}$ (eq. (40)).

$$\Delta S_{12} = - \frac{\partial \Delta F_{12}}{\partial T} \quad (65)$$

and enthalpy

$$\Delta H_{12} = \Delta F_{12} + T \Delta S_{12} \quad (66)$$

of activation. From eqs. (16), (20) the activation entropy is represented as

$$\Delta S_{12} = \Delta S_r + \Delta S^0,$$

where

$$\Delta S_r = \Delta S_p + \Delta S_d = \frac{1}{4} \left(\frac{\partial E_p}{\partial T} + \frac{\partial E_d}{\partial T} \right) \left(\frac{\Delta F_0^2}{E_r^2} - 1 \right)$$

is the activation entropy due to the dependence of E_r on T ,

$$\Delta S^0 = \frac{1}{2} \left(1 + \frac{\Delta F_0}{E_r} \right) \Delta S_0, \quad \Delta S_0 = - \frac{\partial \Delta F_0}{\partial T},$$

is the activation entropy, caused by the standard entropy of a redox system ΔS_0 . The dependence of the energy of reorientation of the permanent dipoles on temperature is implicit and results from the change of the dielectric constants ϵ_∞ and ϵ_s with temperature. Therefore, from eq. (35) we have

$$\frac{\Delta S_p}{k_B} = - \frac{\beta E_p}{4} \left(- \frac{T}{c_0 \epsilon_\infty^2} \frac{\partial \epsilon_\infty}{\partial T} + \frac{T}{c_0 \epsilon_s^2} \frac{\partial \epsilon_s}{\partial T} + \frac{T}{g} \frac{\partial g}{\partial T} \right) \left(\frac{\Delta F_0^2}{E_r^2} - 1 \right). \quad (67)$$

The reorganization energy E_d , in contrast, apart from an implicit temperature dependence through $\eta(T)$ and $\epsilon_\infty(T)$ depends on the temperature explicitly, since in accordance with eq. (30) $y \propto \beta$.

We shall use in this and in the next sections for the parameter Θ , determined in section 3, the value $\Theta=0$, which yields

$$q = (\epsilon_\infty + 2)/3\epsilon_\infty, \quad p = (2\epsilon_\infty + 1)/3\epsilon_\infty. \quad (68)$$

Taking into account eqs. (68) and (45) it is easy to obtain

$$\frac{\partial E_d}{\partial T} = -E_d \left(\frac{1}{T} + \chi_p + \frac{4}{\epsilon_\infty(\epsilon_\infty + 2)} \frac{\partial \epsilon_\infty}{\partial T} \right) - \frac{3e^2 q^2 y}{2\sigma} \chi_p \eta \sum_{i=1}^2 \frac{\partial s_i}{\partial \eta}, \quad (69)$$

where

$$\chi_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

is the solvent thermal expansibility. We have from eq. (59)

$$\frac{\partial s_i}{\partial \eta} = \frac{s_i}{\eta} + \frac{1}{\pi i \eta} \int_{c-i\infty}^{c+i\infty} \mathcal{F}(s)^2 d_i(s) ds. \quad (70)$$

Calculations show that the main contribution to eq. (70) is given by the first term and, consequently,

$$\frac{\Delta S_d}{k_B} = - \frac{\beta E_d}{4} \left(1 + 2T\chi_p + \frac{4T}{\epsilon_\infty(\epsilon_\infty + 2)} \frac{\partial \epsilon_\infty}{\partial T} \right) \left(\frac{\Delta F_0^2}{E_r^2} - 1 \right). \quad (71)$$

In table 2 the reorganization energies E_p and E_d , the activation entropies ΔS_p , ΔS_d , the free energy ΔF_{12} and

enthalpy ΔH_{12} of activation are listed for the resonant ($\Delta F_0=0$, $R_d=R_a$) contact ($R=2R_d$) ET reaction. The quantities are calculated for five solvents, the parameters of which are given in table 1. The free energy of activation of ET in the continuum limit is indicated for comparison. As is seen from table 2 the energy of reorientation of the permanent dipoles E_p contributes mainly to E_r , whereas the activation entropy is essentially determined by the translational motion (density fluctuations) of the solvent molecules. In eq. (67) all three summands are of the same order and should be taken into account when calculating ΔS_p . For the entropy ΔS_d the main contribution gives the explicit dependence on temperature (the first summand in brackets of eq. (71)) and, consequently, for resonant ET it is easy to obtain the very simple relation

$$\Delta H_{12}^{(d)} = \frac{E_d}{4} + T \Delta S_d \approx \frac{E_d}{2} = 2\Delta F_{12}^{(d)}. \quad (72)$$

In heterogeneous ET kinetics the enthalpy of activation often [63–65] proves to be approximately twice as large as the Marcus free energy of activation. This fact is usually explained by neglecting the image interaction of the reactant with the electrode. The reasons for this assumption, however, are not clear. If in heterogeneous ET the density fluctuations are of main importance, eq. (72) can yield an alternative explanation of the observed phenomenon. It is seen from eqs. (67) and (71) that the activation entropies ΔS_p and ΔS_d are proportional to the corresponding reorganization energies. This can be the reason for the observed [66] isokinetic relationship between the activation enthalpy and the pre-exponential factor.

The value of the activation entropy depends on the energy gap. For the entropy ΔS_r it should be expected that $\Delta S_r > 0$ in the normal region ($|\Delta F_0| < E_r$) and $\Delta S_r < 0$ in the inverted region ($|\Delta F_0| > E_r$) of ET. It was shown in the previous paper [32] that the negative value of ΔS_r can cause a negative activation enthalpy for highly exothermic ET reactions.

Table 1
Solvent parameters at 298 K

No.	Solvent	ϵ_∞	ϵ_s	$\partial\epsilon_\infty/\partial T$ (10^{-3} K^{-1})	$\partial\epsilon_s/\partial T$ (K^{-1})	σ (Å)	η	χ_p (10^{-3} K^{-1})
1	1,2-dichlorethane	2.08	10.4	−1.47	−0.056	5.01	0.468	1.156
2	pyridine	2.27	12.3	−1.66	−0.032	5.13	0.526	1.012
3	acetone	1.84	20.7	−1.36	−0.098	4.76	0.470	1.423
4	propionitrile	1.86	27.2	−1.23	−0.120	4.77	0.483	1.326
5	methanol	1.76	32.7	−1.09	−0.197	3.71	0.404	1.182
6	dimethylformamide	2.04	36.7	−1.31	−0.178	5.17	0.575	1.009

Table 2
Activation parameters of outer-sphere self-exchange reaction ($R_d=R_a$, $R=2R_d$, $R_d=4 \text{ Å}$, $\Delta F_0=0$)

No.	E_p (eV)	E_d (eV)	$\Delta S_p/k_B$	$\Delta S_d/k_B$	ΔF_{12} (eV)	ΔH_{12} (eV)	$E_t^{(0)}/4$ (eV)
1	0.330	0.109	−1.53	1.57	0.110	0.111	0.173
2	0.306	0.108	−0.55	1.47	0.103	0.127	0.162
3	0.568	0.242	−1.10	3.87	0.202	0.272	0.223
4	0.620	0.278	−0.84	4.29	0.224	0.313	0.226
5	0.794	0.311	−2.12	4.56	0.276	0.339	0.242
6	0.563	0.269	−0.62	3.69	0.208	0.287	0.208

7. Pressure dependence

The dependence of the ET rate constant k_{ET} on pressure gives an additional coordinate which permits to obtain the kinetic characteristics of ET. Such measurements are essentially important when determining the solvent contribution to ET, since in the usually used range of pressure (0.1–200 MPa) it influences intermolecular solute–solvent and solvent–solvent distances and interactions. From the rate constant pressure dependence one can find the activation volume [67]

$$\Delta V^\ddagger = -k_B T (\partial \ln k_{\text{ET}} / \partial P)_T,$$

which can be written in the form

$$\Delta V^\ddagger = \Delta V_A^\ddagger + \Delta V_r^\ddagger + \Delta V_i^\ddagger. \quad (73)$$

In eq. (73)

$$\Delta V_A^\ddagger = -k_B T (\partial \ln A / \partial P)_T$$

allows for the dependence of the rate constant pre-exponent A on pressure, the term ΔV_r^\ddagger is due to the variation of the solvent reorganization energy with pressure, and ΔV_i^\ddagger contains contributions from the intramolecular reorganization energy, Coulomb and Debye–Hückel terms [68]. The last term in eq. (72) is ordinarily small [69] in comparison with ΔV_r^\ddagger . For self-exchange ET we have

$$\Delta V_r^\ddagger = \Delta V_p^\ddagger + \Delta V_d^\ddagger = \frac{1}{4} \left(\frac{\partial E_p}{\partial P} \right)_T + \frac{1}{4} \left(\frac{\partial E_d}{\partial P} \right)_T.$$

Using eq. (9) at $\Theta=0$ from relations (45), (70) it is easy to obtain for ΔV_d^\ddagger the simple expression

$$\Delta V_d^\ddagger = (q/2) E_d \chi_T, \quad (74)$$

where

$$\chi_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

is the solvent isothermal compressibility. The change of E_p with pressure is connected with the dependence of the dielectric constants on the liquid density. From eq. (35) ΔV_p^\ddagger has the form

$$\Delta V_p^\ddagger = \frac{E_p}{4} \left[\frac{1}{c_0} \left(\frac{\partial c_0}{\partial P} \right)_T + \frac{1}{g} \left(\frac{\partial g}{\partial P} \right)_T \right]. \quad (75)$$

Taking into account the relation ($\Theta=0$)

$$\left(\frac{\partial \epsilon_\infty}{\partial P} \right)_T = \frac{(\epsilon_\infty - 1)(\epsilon_\infty + 2)}{3} \chi_T$$

we obtain

$$\frac{1}{c_0} \left(\frac{\partial c_0}{\partial P} \right)_T = -\frac{(\epsilon_\infty - 1)(7\epsilon_\infty + 2)}{3\epsilon_\infty(2\epsilon_\infty + 1)} \chi_T + \frac{4q(-\xi)}{q(2\xi) - q(-\xi)} \left(\frac{3}{1-2\xi} + \frac{1}{1+\xi} + \frac{2}{1+4\xi} \right) \left(\frac{\partial \xi}{\partial P} \right)_T. \quad (76)$$

The derivative $(\partial \xi / \partial P)_T$ can be found from relation (31), which yields

$$\chi_T \left(1 - \frac{(\epsilon_\infty - 1)(\epsilon_\infty + 2)}{3\epsilon_\infty(2\epsilon_\infty + 1)} \right) = \frac{\partial \ln [q(2\xi) - q(-\xi)]}{\partial \xi} \left(\frac{\partial \xi}{\partial P} \right)_T. \quad (77)$$

The value of the derivative $\partial \ln g / \partial P$ can be easily obtained from eqs. (36) and (77).

The values of $(\partial \ln c_0 / \partial P)_T$, $(\partial \ln g / \partial P)_T$ and ΔV_p^\ddagger , ΔV_d^\ddagger calculated in accordance with eqs. (74)–(76) are presented in table 3 (the solvent parameters are taken from ref. [70]). The value of ΔV_d^\ddagger is positive, since the liquid density increases with pressure. The value of ΔV_p^\ddagger is determined by the competition of two terms $(\partial \ln c_0 / \partial P)_T$ and $(\partial \ln g / \partial P)_T$ which have opposite signs. It is seen from table 3 that $\Delta V_p^\ddagger > 0$. Although in some cases the activation volume is positive [71], usually [72] $\Delta V^\ddagger < 0$. The positive value of ΔV_p^\ddagger can be the result of the use of the MSA to calculate $(\partial \ln c_0 / \partial P)_T$ and $(\partial \ln g / \partial P)_T$ which gives a poor description of the liquid dielectric properties. To obtain more exact values of ΔV_p^\ddagger empirical data for the pressure dependence of the dielectric constants [69] should be used, as was done in the previous section when calculating the activation entropy.

8. Discussion

The present molecular theory of outer-sphere ET reactions in polar liquids permits to determine the solvent reorganization energy on the basis of four solvent parameters (the dielectric constants ϵ_∞ and ϵ_s , the packing parameter η and the solvent molecule diameter σ) and the reactant geometrical sizes (donor R_d and acceptor R_a radii, the donor–acceptor distance R). Thus, in comparison with the widely used continuum model [1–3] the theory includes two additional solvent parameters η and σ . A consistent calculation of the solvent reorganization energy demands the allowance for orientational, as well as translational motion of the liquid molecules. In section 2 a general expression for the solvent reorganization energy through the pure liquid correlation function was obtained. Because of the different symmetries of short-range solvent–solvent and dipole–dipole interactions the reorganization energy E_r is broken into two summands: the energy of reorientation of the permanent dipoles E_p and the reorganization energy of the liquid density near the reactants E_d . The reorganization energy E_d can be calculated exactly in the context of the Percus–Yevick equation for the hard-sphere liquid, whereas E_p is found in the framework of the MSA. The reorganization energy E_p , found in this work, has a value which falls between the value of the dynamic MSA [5,48,49] ($R_a = R_d$, $R = 2R_d$) and that found by Fawcett and Blum [26]. The allowance for the finite size of solvent molecules causes some peculiarities of E_p and E_d . The analytical expression for E_p proves to be different for contact ($R_a + R_d + \sigma > R$) and solvent-separated ($R_a + R_d + \sigma \leq R$) ET. These two cases correspond to different physical situations, observed experimentally [73]. The reorganization energy E_d is equal to zero at $R < R_a + \sigma/2$, $R < R_d + \sigma/2$. For $R_a = R_d$ this means that the density fluctuations cannot cause ET at a donor–acceptor distance less than the solvent molecule diameter. Because of this result the maxima of the functions $E_p(R_d)$ and $E_d(R_d)$ appear to be separated. As a consequence the dependence $E_r(R_d)$ is nonmonotonic and generally contains oscillations.

To determine the entropy and volume of activation apart from the above indicated solvent parameters the derivatives $(\partial \epsilon_\infty / \partial T)_P$, $(\partial \epsilon_s / \partial T)_P$, $(\partial \epsilon_\infty / \partial P)_T$, $(\partial \epsilon_s / \partial P)_T$ should be known. The reorganization energy E_d con-

Table 3
Activation volumes of self-exchange ET

No.	χ_T (10^{-10} Pa^{-1})	$(\partial c_0 / \partial P) / c_0$ (10^{-10} Pa^{-1})	$(\partial g / \partial P) / g$ (10^{-10} Pa^{-1})	ΔV_p^\ddagger ($\text{cm}^3 \text{ mol}^{-1}$)	ΔV_d^\ddagger ($\text{cm}^3 \text{ mol}^{-1}$)
1	7.8	−2.01	2.92	0.71	2.68
2	5.5	−1.68	2.07	0.79	1.79
3	12.55	−3.98	7.90	5.14	10.18
4	8.7	−3.01	5.93	4.13	8.08
5	11.95	−4.02	7.95	7.15	12.75
6	6.2	−2.46	4.30	2.28	5.32

tains an explicit temperature dependence ($E_d \sim 1/T$) which results in a non-Arrhenius temperature dependence of the rate constant [32]. The ET activation entropy is determined mainly by this explicit temperature dependence of E_d . Therefore, one can approximately write

$$\Delta S_r/k_B \approx -(\beta E_d/4)(\Delta F_0^2/E_r^2 - 1).$$

Consequently, the ET activation entropy arises mostly due to translational rather than orientational motion of the liquid molecules. The positive contribution of the density fluctuations to the volume of activation exceed also that of orientational fluctuations. It is seen from table 2 and figs. 3a and 3b that the free energies of activation calculated in the framework of the present (for large enough reactants) and Marcus theories are in striking accord. Discrepancies, however, appear when calculating the differential quantities (the entropy, enthalpy and volume of activation).

Appendix

In this Appendix the values of the coefficients $S_1(\tilde{R}_i, \tilde{R})$, $S_2(\tilde{R}_i, \tilde{R})$ are given. From eq. (63) we have

$$S_1(\tilde{R}_i, \tilde{R}) = -\left(\frac{1}{\tilde{R}_i} - \frac{1}{\tilde{R}}\right) - 12\eta \sum_{l=0}^2 \frac{L_l}{S_{1l}} (s_l \tilde{R}_i - 1) G^{(1)}(s_l),$$

where

$$G^{(n)}(s_l) = \exp[s_l(\tilde{R}_i - n)] \int_{s_l \tilde{R}_i}^{s_l \tilde{R}} \frac{e^x}{x^3} dx,$$

$$L_l = L(s_l), S_{1l} = S'(s_l).$$

For $S_2(\tilde{R}_i, \tilde{R})$ we analogously have

$$S_1(\tilde{R}_i, \tilde{R}) = -\left(\frac{1}{\tilde{R}_i} - \frac{1}{\tilde{R}}\right) + (12\eta)^2 \sum_{l=0}^2 \left\{ \left[\left(\frac{L_l(2+\eta)}{S_{1l}^2} - \frac{2L_l^2 S_{2l}}{S_{1l}^3} \right) (s_l \tilde{R}_i - 1) + \frac{L_l^2}{S_{1l}^2} (s_l \tilde{R}_i^2 - 2s_l \tilde{R}_i + 2) \right] G^{(2)}(s_l) \right. \\ \left. + \frac{L_l^2}{S_{1l}^2} \frac{s_l \tilde{R}_i - 1}{s_l^3} \left(\frac{1}{\tilde{R}^2} \exp[s_l(\tilde{R}_i + \tilde{R} - 2)] - \frac{1}{\tilde{R}_i^2} \exp[2s_l(\tilde{R}_i - 1)] \right) \right\},$$

where $S_{2l} = S''(s_l)$.

References

- [1] R.A. Marcus, J. Chem. Phys. 24 (1956) 966.
- [2] R.A. Marcus, Ann. Rev. Phys. Chem. 15 (1964) 155.
- [3] R.A. Marcus and N. Sutin, Biochim. Biophys. Acta 811 (1985) 265.
- [4] D.V. Matyushov, Chem. Phys. 164 (1992) 31.
- [5] D.V. Matyushov, Chem. Phys. Letters 203 (1993) 131.
- [6] R.A. Marcus, Discussions Faraday Soc. 29 (1960) 21.
- [7] B.S. Brunshwig, J. Logan, M.D. Newton and N. Sutin, J. Am. Chem. Soc. 102 (1980) 5798.
- [8] N.R. Kestner, Y. Logan and J. Jortner, J. Phys. Chem. 78 (1974) 2148.
- [9] T. Holstein, Phil. Mag. B 37 (1978) 499.
- [10] P. Siders and R.A. Marcus, J. Am. Chem. Soc. 103 (1981) 748.
- [11] L.D. Zusman, Chem. Phys. 49 (1980) 295.
- [12] D.F. Calef and P.G. Wolynes, J. Phys. Chem. 87 (1983) 3387.

- [13] I. Rips and J. Jortner, *J. Chem. Phys.* 87 (1987) 2090.
- [14] M. Sparpaglione and S. Mukamel, *J. Chem. Phys.* 88 (1988) 1465.
- [15] I. Rips and J. Jortner, *Chem. Phys. Letters* 133 (1987) 411.
- [16] L.D. Zusman, *Chem. Phys.* 119 (1988) 51.
- [17] G.E. McManis and M.J. Weaver, *J. Chem. Phys.* 90 (1989) 912.
- [18] M.Ya. Ovchinnikova, *Teor. Eksp. Khim.* 17 (1981) 651.
- [19] H. Sumi and R.A. Marcus, *J. Chem. Phys.* 84 (1986) 4094.
- [20] W. Nadler and R.A. Marcus, *J. Chem. Phys.* 86 (1987) 3906.
- [21] Yu.I. Kharkats, *Elektrokhimiya* 12 (1976) 1284.
- [22] R.D. Cannon, *Chem. Phys. Letters* 49 (1977) 299.
- [23] E.D. German and A.M. Kuznetsov, *Electrochim. Acta* 26 (1981) 1595.
- [24] B.S. Brunschwig, S. Ehrenson and N. Sutin, *J. Phys. Chem.* 90 (1986) 3657.
- [25] I. Rips, J. Klafter and J. Jortner, *J. Chem. Phys.* 89 (1988) 4288.
- [26] W.R. Fawcett and L. Blum, *Chem. Phys. Letters* 187 (1991) 173.
- [27] W.R. Fawcett and M. Opallo, *J. Electroanal. Chem.* 331 (1992) 815.
- [28] Y. Zhou, H.L. Friedman and G. Stell, *J. Chem. Phys.* 91 (1989) 4885; *Chem. Phys.* 152 (1991) 185.
- [29] A.A. Kornyshev and J. Ulstrup, *Chem. Phys. Letters* 126 (1986) 74.
- [30] J. Ulstrup, *J. Phys. Chem.* 91 (1987) 5153.
- [31] D.V. Matyushov, *Ukr. Chem. J.* (1993), in press.
- [32] D.V. Matyushov, *Mol. Phys.* (1993), in press.
- [33] A.I. Karasevskii, D.V. Matyushov and A.V. Gorodiskii, *Dokl. Akad. Nauk SSSR* 297 (1987) 1156.
- [34] A.I. Karasevskii, D.V. Matyushov and A.V. Gorodiskii, *Chem. Phys.* 142 (1990) 1.
- [35] B. Bagchi and A. Chandra, *Phys. Rev. Letters* 64 (1990) 455.
- [36] M. Maroncelli, J. MacInnis and G.R. Fleming, *Science* 243 (1989) 1674.
- [37] B.V. Felderhof, *J. Chem. Phys.* 67 (1977) 493.
- [38] S. Lee and J.T. Hynes, *J. Chem. Phys.* 88 (1989) 6853.
- [39] B.V. Felderhof, *Physica* 76 (1974) 486.
- [40] J.S. Hoyer and G. Stell, *J. Chem. Phys.* 61 (1974) 562.
- [41] G. Nienhuis and J.M. Deutch, *J. Chem. Phys.* 55 (1971) 4213.
- [42] J.S. Hoyer and G. Stell, *J. Chem. Phys.* 64 (1975) 1952.
- [43] S.I. Pekar, *Sov. Phys. JETP* 16 (1946) 341.
- [44] H.J. Kim and J.T. Hynes, *J. Phys. Chem.* 94 (1990) 2736.
- [45] J.N. Gehlen, D. Chandler, H.J. Kim and J.T. Hynes, *J. Phys. Chem.* 96 (1992) 1748.
- [46] R.A. Marcus, *J. Chem. Phys.* 96 (1992) 1753.
- [47] J.S. Hoyer and G. Stell, *J. Chem. Phys.* 73 (1980) 461.
- [48] P.G. Wolynes, *J. Chem. Phys.* 86 (1987) 5133.
- [49] I. Rips, J. Klafter and J. Jortner, *J. Chem. Phys.* 88 (1988) 3246.
- [50] J.S. Hoyer and G. Stell, *J. Chem. Phys.* 77 (1982) 5173.
- [51] W.F. Brown, *Dielectrics* (Springer, Berlin, 1956).
- [52] M.S. Wertheim, *Mol. Phys.* 25 (1973) 221.
- [53] M.S. Wertheim, *J. Chem. Phys.* 55 (1971) 4291.
- [54] R.J. Baxter, *J. Chem. Phys.* 52 (1970) 4557.
- [55] G.E. McManis, A. Gochev, R.M. Nielson and M.J. Weaver, *J. Phys. Chem.* 93 (1989) 7733.
- [56] H. Heitele, F. Pöllinger, S. Weeren and M.E. Michel-Beyerle, *Chem. Phys.* 143 (1990) 325.
- [57] L.I. Kristalik, N.M. Alpatova and E.V. Ovsyannikova, *Electrochim. Acta* 36 (1991) 435.
- [58] A.A. Kornyshev and A.G. Volkov, *J. Electroanal. Chem.* 180 (1984) 363.
- [59] D.Y.C. Chan, D.J. Mitchell and B.W. Ninham, *J. Chem. Phys.* 70 (1979) 2946.
- [60] M.S. Wertheim, *Phys. Rev. Letters* 10 (1963) 321.
- [61] W.R. Smith and D. Henderson, *Mol. Phys.* 19 (1970) 411.
- [62] I.Z. Fisher, *Statistical theory of liquids (GIFML, Moscow, 1961)* (in Russian).
- [63] T. Gennett, D.F. Milner and M.J. Weaver, *J. Phys. Chem.* 89 (1985) 2787.
- [64] A. Kapturkiewicz and W. Jaenicke, *J. Chem. Soc. Faraday Trans. I* 83 (1987) 2727.
- [65] A.S. Baranskii, K. Winkler and W.R. Fawcett, *J. Electroanal. Chem.* 313 (1991) 367.
- [66] Z.B. Alfassi, R.E. Huie, M. Kumar and P. Neta, *J. Phys. Chem.* 96 (1992) 767.
- [67] R. van Eldik, T. Asano and W.J. Le Noble, *Chem. Rev.* 89 (1989) 549.
- [68] T.W. Swaddle, in: *Inorganic high pressure chemistry: kinetics and mechanisms*, ed. R. van Eldik (Elsevier, Amsterdam, 1986) p. 273.

- [69] T.W. Swaddle, *Inorg. Chem.* 29 (1990) 5017.
- [70] Y. Marcus, *Ion solvation* (Wiley, New York, 1985).
- [71] M. Kanesato, M. Ebihara, Y. Sasaki and K. Saito, *J. Am. Chem. Soc.* 105 (1983) 5711.
- [72] M.A. Murgia and S. Wherland, *Inorg. Chem.* 30 (1991) 139.
- [73] I.R. Gould, R.H. Young, R.E. Moody and S. Farid, *J. Phys. Chem.* 95 (1991) 2068.