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The dynamic effects of the solvent in electron transfer reactions

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ABSTRACT. The theories of electron transfer reactions in polar solvents, which describe the dynamic effects of the solvent manifested in these reactions, are examined. The theoretical and the available experimental literature data for these effects are compared.

The bibliography includes 85 references.

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I. Introduction

The mechanism of the elementary step in an electron transfer reaction in the liquid phases is as follows. There are two electronic states corresponding to the location of the electron on the electron donor or acceptor. The energies of these electronic states depend on the polarisation of the solvent and the intramolecular degrees of freedom of the donor and the acceptor. The thermal fluctuations in the polarisation of the medium and in the intramolecular degrees of freedom of the reactants lead to the modulation of the energies of the electronic states and sometimes the energy levels intersect. At this instant the electron tunnels from the donor to the acceptor, after which the polarisation of the medium and the intramolecular degrees of freedom of reactants relax to the new equilibrium position.

The theory of the elementary step in electron transfer reactions originated from the classical study by Marcus,[1] who was able to obtain an expression for the free energy of activation for the reaction. This energy is equal to the free energy which the medium and the intramolecular degrees of freedom of the donor and the acceptor must receive in order to attain the point of intersection of the energy levels of the electron. However, Marcus[1] was unable to calculate the pre-exponential factor in the expression for the reaction rate constant. The first calculation of this factor was achieved[2,3] on the basis of the quantum-mechanical perturbation theory using Fermi's famous "golden rule".[4] Within the framework of this theory, the pre-exponential factor in the expression for the rate constant proved to be proportional to the square of the resonance integral characterising the degree of overlap of the donor and acceptor orbitals. If the resonance integral is sufficiently large or the dynamics of the medium sufficiently slow, the perturbation theory ceases to be applicable and it is necessary to set up a theory going beyond the framework of this approximation.

Such a transition to the region of strong interaction was achieved in studies[5–10] where it was shown that, for a sufficiently large resonance integral, the rate of reaction is controlled by the dynamics of the polarisation of the solvent and, in the case of Debye solvents, is proportional to the frequency of the longitudinal relaxation of the solvent polarisation ν_L. This effect of the proportionality of the reaction rate constant to the frequency ν_L has been called the "dynamic effect of the solvent". It was first confirmed experimentally in studies[11–24] where a linear correlation was demonstrated between ν_L in a series of Debye solvents and the rate constant for electron transfer between the reactants dissolved in these solvents. Arguments have been adduced[25] in support of the fact that the dynamic effect of the solvent is manifested in the electron exchange reaction between benzonitrile and its radical-anion in a series of Debye solvents.[26] A similar conclusion has been reached[27] concerning the electron transfer reaction between anthracene and its radical-anion in a mixture of two Debye solvents with different proportions of the latter.[28] The inverse proportionality of the rate constant for electron transfer to the solvent viscosity, predicted by the theory,[5–10] has been confirmed.[29,30]

The dynamic effects of the solvent are observed not only in Debye solvents, having one Debye relaxation time of the polarisation of the medium, but also in solvents of the type of alcohols, which have two and more polarisation relaxation times.[15,17,20,21,31–35] The theories of electron transfer in such solvents will be examined in the present review together with those of the dynamic effect of the solvent in simpler solvents of the Debye type.

A large group of solvents of the type of glycerol have a continuous distribution of relaxation times of the Cole–Davidson type. The dynamic effects of the solvent in such media have a number of characteristic features distinguishing them from the effects in Debye solvents and also in alcohols. The theories of electron transfer in solvents of the glycerol type will also be examined in the present review.

The dynamic effects of the solvent are not limited to the influence of the reorientation relaxation of the solvent, many effects being associated with the translational motion of the solvent dipoles. These questions will be likewise examined in the present review.

II. Theories of electron transfer reactions based on the structureless dielectric approximation

The electron transfer reactions in a polar medium can be described as transitions between two electronic states at the instant when the energy levels of these states intersect under the influence of thermal fluctuations of the medium. It has been shown[39] that the difference between the energies of these states is

$$-\delta H(t)=H_2(t)-H_1(t)=E_0-E(t), \quad (1)$$

where $H_1(t)$ and $H_2(t)$ are the energies of the first and second electronic states fluctuating in a period t,

$$E(t)=-\int \Delta\mathbf{D}(\mathbf{r})\delta\mathbf{P}(\mathbf{r},t)d\mathbf{r}, \quad (2)$$

where $\Delta\mathbf{D}(\mathbf{r}) = \mathbf{D}_2(\mathbf{r}) - \mathbf{D}_1(\mathbf{r})$ is the difference between the electrostatic inductions of the first and second states, and

$$\delta\mathbf{P}(\mathbf{r},\ t)=\mathbf{P}(\mathbf{r},\ t)-\mathbf{P}_1(\mathbf{r}), \quad (3)$$

where $\mathbf{P}(\mathbf{r},\ t)$ is the polarisation of the solvent and $\mathbf{P}_1(\mathbf{r})$ the equilibrium polarisation of the solvent in the first electronic state;

$$E_0=J_2-J_1+E_r, \quad (4)$$

where J_1 and J_2 are the free energies of the first and second states and E_r is the solvent reorganisation energy:

$$E_r=\frac{c_0}{8\pi}\int \Delta\mathbf{D}(\mathbf{r})^2 d\mathbf{r}. \quad (5)$$

Here c_0 is the familiar Pekarov multiplier:

$$c_0=\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon_S},$$

and ε_∞ and ε_S are the high-frequency and static dielectric constants respectively.

It has also been shown[39] that $E(t)$ fluctuates in conformity with a Gaussian random process. All the properties of Gaussian processes are known to be expressed in terms of a binary correlation function of a random variable. By virtue of the fluctuation-dissipative theorem, in the given case this correlation function is expressed as follows in terms of the complex dielectric constant of the solvents $\varepsilon(\mathbf{q}, \omega)$ at a frequency ω and for a wave vector $\mathbf{q}$:

$$K(\tau)=\langle E(\tau)E(0)\rangle=\frac{kT}{32\pi^5}\int |\Delta\mathbf{D}_q|^2\frac{\varepsilon''(\mathbf{q},\omega)}{\omega|\varepsilon(\mathbf{q},\omega)|^2}$$

$$\exp(-i\omega\tau)d\mathbf{q}\,d\omega, \quad (6)$$

where k is the Boltzmann constant and T the absolute temperature. The angular brackets in Eqn. (6) denote averaging with respect to the random fluctuations in the polarisation of the medium and

$$\Delta\mathbf{D}_q=\int \Delta\mathbf{D}(\mathbf{r})\exp(-\mathbf{qr})d\mathbf{r} \quad (7)$$

is the spatial Fourier transform of the difference between the inductions $\Delta\mathbf{D}(\mathbf{r})$.

Eqns. (1) and (6) are the initial expressions for the construction of the theory of electron transfer in a polar solvent.

1. Theories of electron transfer reactions in solvents with one Debye relaxation time of the polarisation of the medium

We shall consider the simplest case where the solvent in which the reaction takes place is of the Debye type, i.e. its complex dielectric constant assumes the form

$$\varepsilon(\omega)=\varepsilon_\infty+\frac{\varepsilon_S-\varepsilon_\infty}{1-i\omega\tau_D}. \quad (8)$$

On substituting Eqn. (8) in Eqn. (6), we find that the correlation function of the fluctuations of the electronic energy levels assumes the simplest form

$$K(\tau) = 2kTE_r\exp(-\nu_L|\tau|), \quad (9)$$

where $\nu_L = (E_S/E_\infty)(1/\tau_D)$ is the frequency of the longitudinal relaxation of the solvent polarisation, describing the relaxation of the medium under the conditions of a constant charge polarising it.

It has been shown[5,6] that, when the correlation function of the fluctuations of the energy levels of the electron has the form of Eqn. (9), then motion along the coordinate $E(t)$, which in the given instance is the reaction coordinate, has the character of diffusion with two parabolic terms $U_1(E)$ and $U_2(E)$ corresponding to the first and second electronic states:

$$U_1(E) = J_1 + \frac{E^2}{4E_r}, \quad U_2(E) = J_2 + \frac{(E-2E_r)^2}{4E_r}. \quad (10)$$

The transitions between these electronic terms are described by the following system of kinetic equations for the partial populations $\rho_1(E, t)$ and $\rho_2(E, t)$:[5,6]

$$\dot{\rho}_1(E,t)=-\frac{2\pi V^2}{\hbar}\delta(E-E_0)[\rho_1(E,t)-\rho_2(E,t)]+$$
$$+\nu_L\left[1+E\frac{\partial}{\partial E}+\Delta^2\frac{\partial^2}{\partial E^2}\right]\rho_1(E,t), \quad (11)$$
$$\rho_2(E,t)=\frac{2\pi V^2}{\hbar}\delta(E-E_0)[\rho_1(E,t)-\rho_2(E,t)]+$$
$$+\nu_L\left[1+(E-2E_r)\frac{\partial}{\partial(E-2E_r)}+\Delta^2\frac{\partial^2}{\partial(E-2E_r)^2}\right]\rho_2,$$

where $\Delta^2 = 2kTE_r$.

The partial populations $\rho_1(E, t)$ and $\rho_2(E, t)$ have the physical significance of the probabilities of finding an electron in the first or second electronic state respectively when the reaction coordinate assumes a value E. The first term on the right-hand sides of the equations describes the tunnelling of the electron from the donor to the acceptor at the point of intersection of the electronic terms E_0. The rate of such tunnelling is

$$K(E)=\frac{2\pi V^2}{\hbar}\delta(E-E_0), \quad (12)$$

where V is the resonance integral between the electron donor and acceptor, $\delta(E - E_0)$ the Dirac delta-function, and $\hbar$ the Planck constant. The second terms on the right-hand sides of Eqns. (11) describe diffusion in terms of the potentials $U_1(E)$ and $U_2(E)$ for the diffusion coefficient $\Delta^2\nu_L$.

A general solution of Eqns. (11) has been found[5,6] by the method of Green's functions and it has been shown that, in the limit of high activation energies for the reaction, $E_{a1}/kT \gg 1$ and $E_{a2}/kT \gg 1$ and that, for sufficiently long solvation times $t \gg \nu_L^{-1}$, the kinetics of the transitions are exponential as a function of time. It is possible to introduce the rates of the forward (W_{12}) and reverse (W_{21}) transitions respectively, for which the following expressions have been obtained:[5,6]

$$W_{12}=\frac{W_{12}^{NA}}{1+W_{12}^{NA}/W_{12}^{D}}$$
$$(13)$$
$$W_{21}=\frac{W_{21}^{NA}}{1+W_{12}^{NA}/W_{12}^{D}},$$

where W_{12}^{NA} is the rate of the forward non-adiabatic electron transfer reaction, W_{21}^{NA} the rate of the reverse non-adiabatic electron transfer reaction, and W_{12}^{D} the rate of the forward reaction determined by diffusion along the electronic term consisting of two portions of diabatic terms (Fig. 1). W_{12}^{D} is identical with the familiar solution of the Kramers problem[40] concerning the diffusional overcoming of a sharp barrier, for which the following expression has been obtained:[5,6]

$$W_{12}^{D} = \nu_L \frac{|E_0||E_0 - 2E_r|}{|E_0| + |E_0 - 2E_r|} \frac{1}{(2\pi\Delta^2)^{1/2}} \exp\left(-\frac{E_0^2}{4E_r kT}\right). \quad (14)$$

W_{12}^{NA} and W_{21}^{NA} are defined by the usual expressions of the Levich–Dogonadze–Kuznetsov theory:[2,3]

$$W_{12}^{NA} = \frac{\sqrt{2\pi}}{\hbar\Delta} V^2 \exp\left(-\frac{E_0^2}{4E_r kT}\right),$$
$$W_{12}^{NA} = \frac{\sqrt{2\pi}}{\hbar\Delta} V^2 \exp\left[-\frac{E_0 - 2E_r)^2}{4E_r kT}\right]. \quad (15)$$

It is seen from Eqn. (13) that, if the rate of the non-adiabatic reaction is sufficiently low ($W_{12}^{NA} \ll W_{12}^{D}$), then the electron tunnelling stage is rate-limiting and

$$W_{12} = W_{12}^{NA},$$
$$W_{21} = W_{21}^{NA}. \quad (16)$$

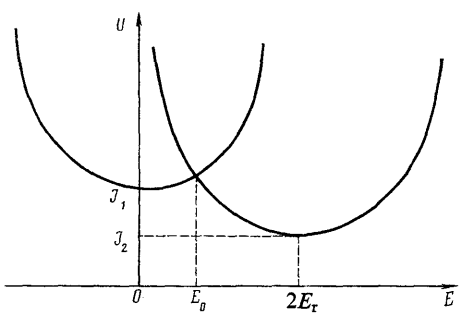


Figure 1. Electronic terms: J_1 = free energy of the first electronic state; J_2 = free energy of the second electronic state; E_0 = point of intersection of the electronic terms; E_r = energy of the reorganisation of the solvent.

On the other hand, if the tunnelling stage is rapid, i.e. $W_{12}^{NA} \gg W_{12}^{D}$, then diffusion along the electronic term is rate-limiting and

$$W_{12} = W_{12}^{D},$$
$$W_{21} = \frac{W_{21}^{NA}}{W_{12}^{NA}} W_{12}^{D} = \exp\left(\frac{J_2 - J_1}{kT}\right) W_{12}^{D}. \quad (17)$$

As can be seen from Eqn. (14), in this case the rate of reaction is proportional to the frequency of the longitudinal relaxation of the solvent polarisation ν_L. This prediction of the theory has been confirmed experimentally in a number of studies.[11–24]

Eqn. (14) has been revised by the present author,[7] who obtained a somewhat different expression for W_{12}^{D}:

$$W_{12}^{D} = \frac{\nu_L}{\pi} \sqrt{\frac{E_r}{\pi kT}} \sin\left(\frac{\pi E_0}{2E_r}\right) \exp\left(-\frac{E_0^2}{4E_r kT}\right). \quad (18)$$

If the reaction proceeds in the inverted regime $\Delta J > E_r$, where $\Delta J = J_2 - J_1$ is the driving force of the reaction, then, as shown by Gennett et al.,[41] not only the rate of the diffusional overcoming of the barrier W_{12}^{D} but also the rates of the non-adiabatic reactions W_{12}^{NA} and W_{21}^{NA} depend on ν_L for not very low values of the latter. In this case Eqns. (15) for W_{12}^{NA} and W_{21}^{NA} cease to be applicable and more complex expressions must be used for them.[41] However, with decrease in ν_L, even in the inverted regime, the validity of Eqns. (15) is restored starting from a certain instant and the rate of reaction depends on the solvent dynamics only in the limit where diffusion along the electronic term is rate-limiting.

Eqns. (13) are applicable for not unduly high values of the resonance integral V. The inequalities

$$V \ll kT, \quad (19)$$

$$\frac{2\pi V^2}{kT\hbar\omega_L}\left(\frac{\pi kT}{E_p}\right)^{1/2} \ll 1, \quad (20)$$

where ω_L is the frequency characterising the rate of movement of the electron-medium system along the reaction coordinate E over the length of the free path, serve as a criterion of their applicability. The following relation has been obtained[42] for ω_L:

$$\omega_L^2 = \left(\frac{2\varepsilon_S + \varepsilon_\infty}{3\varepsilon_\infty g}\right)\omega_f^2, \quad (21)$$

where ω_f is the average thermal rate of free rotation of the solvent dipoles[43] and g is the Kirkwood factor.[43]

On the other hand, if the inequality (20) breaks down and the Landau–Zener adiabaticity parameter

$$k_{el} = \frac{\pi V^2}{kT\hbar\omega_L}\left(\frac{\pi kT}{E_r}\right)^{1/2}$$

becomes sufficiently large, i.e. $k_{el} \gg 1$, then instead of Eqn. (13) it is necessary to employ the following formulae:[42]

$$W_{12} = \frac{W_{12}^{WA}}{1 + W_{12}^{WA}/W_{12}^{D}},$$
$$W_{21} = \frac{W_{21}^{WA}}{1 + W_{12}^{WA}/W_{12}^{D}}, \quad (22)$$

where

$$W_{12}^{WA} = \frac{\omega_L}{2\pi}\exp(-E_0^2/4E_r kT),$$
$$W_{12}^{WA} = \frac{\omega_L}{2\pi}\exp\left[\left(-\frac{(E_0 - 2E_r)^2}{4E_r kT}\right]\right. \quad (23)$$

Eqns. (23) express none other than the rates of reaction within the framework of the transition state theory. Thus Eqns. (22) imply that the reaction proceeds in two stages. Initially the system reaches the top of the barrier by diffusion and then moves dynamically in the immediate vicinity of the top of the barrier at a certain thermal velocity proportional to the frequency ω_L. Throughout this time, the system is on the lower adiabatic electronic term, which is constructed in the usual way from the diabatic terms defined by Eqn. (10).

Using the method of molecular dynamics, the electron transfer reaction has been modelled numerically in a model solvent which is typical of a series of polar aprotic solvents being investigated experimentally at the present time. It was shown that Eqns. (22) agree better than Eqn. (13) with the results of numerical modelling. This apparently means that the inequality (20) breaks down in the model systems. Indeed, substitution of the parameters used in the above study[44] shows that the Landau–Zener parameter k_{el} is large in these systems.

Formulae (13) and (22) were obtained for condition (19). This condition means that the barrier, which the system overcomes by moving along the reaction coordinate, is nearly triangular. If the inequality (19) is reversed, i.e.

$$V \gg kT, \tag{24}$$

then the barrier overcome becomes nearly parabolic and the expression for the rates of reaction assume the following form:[6]

$$W_{12} \frac{\nu_L}{4\pi} \left(\frac{2E_r}{V}\right)^{1/2} \left(\frac{|E_0||E_o - 2E_r|}{E_r^2}\right)^{3/4} \exp\left\{ -\left[\frac{(E_0)^2}{4E_r} - V\left(\frac{|E_0||E_o - 2E_r|}{E_r^2}\right)^{1/2}\right] \frac{1}{kT} \right\},$$
$$W_{21} = W_{12} \exp \frac{\Delta J}{kT}. \tag{25}$$

It also follows from Eqn. (25) that the rates of the forward and reverse reactions must be proportional to ν_L, i.e. in this limit too the theory[6] predicts the dynamic effect of the solvent. We may draw attention to the fact that, subject to condition (24), the free energy of activation for the reaction is not equal to the Marcus value $E_{a1} = E_0^2/4E_r$ but is smaller than the latter by the amount $V(|E_0||E_0 - 2E_r|/E_r^2)^{1/2}$. This quantity is exactly equal to the splitting of the adiabatic electronic terms at the point of intersection of the diabatic terms E_0.

Eqns. (13), (22), and (25) were derived on the assumption of high activation energies. The non-activated ($E_{a1} = 0$, $E_{a2} = 0$) or low-barrier ($E_{a1}/kT \ll 1$, $E_{a2}/kT \ll 1$) electron transfer reactions are also of considerable interest. The solutions of Eqns. (11) for such processes are non-exponential as a function of time. Strictly speaking, it is therefore impossible to introduce time-independent rates of reaction. Nevertheless, numerical analysis of the solution of Eqns. (11) carried out by Rips and Jortner[45] shows that in the range $\nu_L t < 4$, the kinetics of the transitions are nearly exponential and one can introduce the rates of the forward and reverse reactions W_{12} and W_{21} as an approximation.

It has been shown[46] that in both the normal ($\Delta J < E_r$) and the inverted ($\Delta J > E_r$) regimes the rate of reaction can be controlled by the solvent dynamics, whereupon it is proportional to ν_L. This agrees well qualitatively with the results of experiments[31–35] in which a linear correlation was found for non-activated intramolecular electron transfer reactions between the rate of reaction and the lowest solvent relaxation frequency. However, it is noteworthy that the experiments[31–35] were carried out in alcohols, which are not Debye solvents. On the other hand, the prediction[46] that the rate of reaction is proportional to the lowest solvent relaxation frequency was based on an erroneous study[47] in which an attempt was made to extend the present author's results[5,6] to non-Debye solvents. The conclusion[46,48] that the theory and experiment[31–35] agree is therefore controversial. We shall return to the discussion of these experiments below.

The theories examined above were based on the approximation of a linear medium first introduced by Ovchinnikov and Ovchinnikova.[49] The present author[10] was able to extend the treatment outside the framework of this approximation having shown that in the more general situation the rate of reaction may be proportional to ν_L.

All the theories of electron transfer examined hitherto fail to take into account the reorganisation of the intramolecular degrees of freedom of the reactants and reaction products. The first attempt to take into account the reorganisation of the intramolecular degrees of freedom of reactants and products and to estimate its influence on the dynamic effect of the solvent in the rate of reaction was undertaken by Ovchinnikova.[50] As a result of the allowance for the reorganisation of the intramolecular degrees of freedom, electronic transitions are seen to occur not only at the point of intersection of the electronic terms E_0 but also over the entire range of values of the reaction coordinate E. Eqns. (11) were extended by Ovchinnikova[50] as follows:

$$\dot{\rho}_1(E,t) = -K_{12}(E)\rho_1(E,t) + K_{21}(E)\rho_2(E,t) + \nu_L\left[1 + E\frac{\partial}{\partial E} + \Delta^2\frac{\partial^2}{\partial E^2}\right]\rho_1(E,t),$$
$$\dot{\rho}_2(E,t) = -K_{21}(E)\rho_2(E,t) + K_{12}(E)\rho_1(E,t) + \nu_L\left[1 + (E-2E_r)\frac{\partial}{\partial(E-2E_r)} + \Delta^2\frac{\partial^2}{\partial(E-2E_r)^2}\right]\rho_2, \tag{26}$$

where the following expressions were used for $K_{12}(E)$ and $K_{21}(E)$:

$$K_{12}(E) = \frac{\omega_Q}{2\pi}\exp\left[-\frac{(E_0 - E + E_i)^2}{4E_i kT}\right],$$
$$K_{21}(E) = \frac{\omega_Q}{2\pi}\exp\left[-\frac{(E_0 - E - E_i)^2}{4E_i kT}\right]. \tag{27}$$

Here $K_{12}(E)$ is the characteristic frequency of intramolecular vibrations and E_i is the energy of the reorganisation of the intramolecular degrees of freedom. Eqns. (27) were obtained on the assumption that the intramolecular vibrations are classical, i.e. subject to the condition $kT \gg h\omega_Q$. However, Ovchinnikova[50] was not able to solve Eqn. (26). This was done later.[7] Nevertheless, Ovchinnikova[50] reached the generally correct conclusion that intramolecular vibrations hinder the observation of the dynamic effect of the solvent in the rate of electron transfer.

The influence of intramolecular degrees of freedom of the reactants on the rate of electron transfer has also been considered.[51,52] In the theory of Marcus and co-workers,[51,52] the intramolecular vibrations were assumed to be classical ($kT \gg \hbar\omega_Q$) and the theory was based, as in Ovchinnikova's study,[50] on

Eqn. (28), where, however, no account was taken of the reverse reaction. The authors used Eqn. (27) for $K_{12}(E)$ and assumed that the partial rate of the reverse reaction $K_{21}(E)$ was identically equal to zero. They postulated that the reverse reaction may be disregarded for $\Delta J \gg kT$. Generally speaking, this is correct for the reaction as a whole, but the condition $K_{21}(E) \equiv 0$ constitutes a much stronger limitation than $\Delta J \gg kT$. It implies that the reverse reaction is neglected for any value of the coordinate of the medium E.

On the other hand, analysis of the simpler Eqns. (11) shows that $K_{21}(E) \neq 0$ contributes not only to the rate of the reverse reaction W_{21} but also to that of the forward reaction W_{12}. This contribution is fully comparable to the contribution of the forward partial reactions specified by the rate $K_{12}(E)$. This contribution to W_{12} does not vanish in the limit where $\Delta J \gg kT$. Therefore the hypothesis that $K_{21}(E) \equiv 0$ makes the treatment inconsistent with the physics of the process and the formulae presented by Sumi and Marcus[51] for the case where $E_{a1} \gg kT$ hardly describe the reaction adequately or even approximately. As regards the non-activated reaction with $E_{a1} \ll kT$, the conclusion[51,52] that on reorganisation of the intramolecular degrees of freedom and in the limit $\nu_L \to 0$ the reaction kinetics become highly non-exponential while the average reaction time τ_a may be much shorter than ν_L^{-1} and in the limit $\nu_L \to 0$ may cease to depend on ν_L is believeable. Indeed, subject to the condition $E_{a1} \ll kT$, the analysis of Eqns. (11) carried out by Rips and Jortner[46] shows that the hypothesis that $K_{21}(E) \equiv 0$ in the limit where $\Delta J/kT \gg 1$ becomes more acceptable. The prediction[52] that, when account is taken of the intramolecular degrees of freedom of the reactants, the rate of reaction at $\nu_L \to 0$ should be proportional to ν_L^{α}, where α may depend on the ratio E_i/E_r and varies in the range $0 < \alpha < 1$, is also of interest.

The intramolecular electron transfer in dimethylaminobenzonitrile and in diethylaminobenzonitrile has been investigated[53] in a series of solvents. In conformity with the authors' predictions,[51,52] it was observed that the kinetics of the reactions involving these compounds are markedly non-exponential. It has also been shown[53] that the average reaction time τ_α is shorter for these compounds than the longitudinal relaxation time of the solvent ν_L^{-1}. These data confirm the theory developed by Marcus and co-workers.[51,52]

The conclusion that, when account is taken of the intramolecular degrees of freedom of the reactants the rate of reaction as $\nu_L \to 0$ should be proportional to ν_L^{α} was invoked[52] to account for the observed[54] proportionality between the rate of reaction and ν_L^{β}. However, the reactions investigated by McGuire and McLendon[54] were carried in glycerol—a solvent of the non-Debye type. It is therefore not clear at present what lies behind the proportionality of the rate of reaction to ν_L^{β}—the presence of intramolecular degrees of freedom of the reactants or the nature of the solvent (its not being a Debye solvent). Below, we shall return to the discussion of the results of McGuire and McLendon.[54]

The theories considered above describe the reorganisation of the intramolecular degrees of freedom on the assumption that $kT \gg \hbar\omega_Q$. A theory has been developed[55] for electron transfer where account is taken of the reorganisation of the intramolecular degrees of freedom, but, in contrast to Marcus and co-workers,[50–52] it is assumed that the intramolecular vibrations are quantised, i.e. subject to the conditions $kT \ll \hbar\omega_Q$. The author[55] began his treatment with the kinetic equations (26) where, in contrast to Eqn. (27), the following expressions were used for $K_{12}(E)$ and $K_{21}(E)$:

$$K_{12}(E) = \frac{2\pi V^2}{\hbar} \sum_{n=-\infty}^{\infty} \lambda_n \delta(E_0 + n\hbar\omega_Q - E),$$
$$K_{21}(E) = \frac{2\pi V^2}{\hbar} \sum_{n=-\infty}^{\infty} \lambda_n \delta(E_0 - n\hbar\omega_Q - E), \qquad (28)$$

where λ_n is the Franck–Condon factor for the intramolecular oscillator.[56] Eqns. (28) imply that the transitions do not occur solely at the point of intersection of the E_0 terms but also at the points $E_0 + n\hbar\omega_Q$ and $E_0 - n\hbar\omega_Q$ and are accompanied by the emission or absorption of n quanta.

With the aid of a method analogous to that used by the present author,[5,6] Helman[55] found a solution to Eqn. (26) with the coefficients defined by Eqn. (28) and obtained expressions for the reaction rates W_{12} and W_{21}, generalising Eqns. (13). Thus in the limit corresponding to high activation energies, $E_{a1}/kT \gg 1$ and $E_{a2}/kT \gg 1$, Helman[55] obtained expressions for W_{12} and W_{21} identical with Eqns. (13), where

$$W_{12}^{NA} = \frac{\sqrt{2\pi}}{\hbar\Delta} V^2 \lambda_0 \exp\left(-\frac{E_0^2}{4E_r kT}\right),$$
$$W_{21}^{NA} = \frac{\sqrt{2\pi}}{\hbar\Delta} V^2 \lambda_0 \exp\left[-\frac{(E_0 - 2E_r)^2}{4E_r kT}\right]. \qquad (29)$$

It is seen from Eqns. (13) and (29) that, for the observation of the dynamic effect of the solvent, the following criterion must be satisfied:

$$\frac{2\pi V^2}{\hbar}\lambda_0 \gg \lambda_L \frac{|E_0|\,|E_0 - 2E_r|}{|E_0| + |E_0 - 2E_r|}. \qquad (30)$$

Since $\lambda_0 < 1$, the observation of the dynamic effect of the solvent in the presence of intramolecular degrees of freedom of the reactants requires larger values of the resonance integral V than in the case where the degree of reorganisation of these degrees of freedom is small or is altogether absent. The result of Helman's study[55] was reproduced by Onuchic et al.[57] Results similar to Helman's[55] were also obtained subsequently in later studies.[58,59] The solution found by Helman[55] was refined by the present author.[7]

All the theories examined hitherto describe reactions occurring under homogeneous conditions. The theories of reactions occurring on the electrode are constructed similarly. The present author[60] began with Eqn. (26), where, in contrast to Eqn. (27), the partial rates $K_{12}(E)$ and $K_{21}(E)$ are defined by the following expressions:

$$K_{12}(E) \int \frac{\rho(\varepsilon)}{n_e} f(\varepsilon) K_{12}(\varepsilon, E)\, d\varepsilon,$$
$$K_{21}(E) = \int \frac{\rho(\varepsilon)}{n_e} [1 - f(\varepsilon)] K_{21}(\varepsilon, E)\, d\varepsilon. \qquad (31)$$

Here $f(\varepsilon)$ is the Fermi distribution of electrons in the electrode, $K_{12}(\varepsilon, E)$ and $K_{21}(\varepsilon, E)$ are the partial rate of the forward and reverse electron transfer from the energy level ε in the electrode to the energy level in the reactant, and $\rho(\varepsilon)$ is the density of electronic

states in the electrode. The general expressions quoted by the present author[7,61] are valid for the rates $K_{12}(\varepsilon, E)$ and $K_{21}(\varepsilon, E)$. In view of the very cumbersome nature of these formulae, we do not quote them here.

The kinetic equations (26), with the partial rates $K_{12}(E)$ and $K_{21}(E)$ expressed in the form of Eqns. (31), were solved[60] with the aid of the method used previously;[7] the following formulae were obtained for the rates of reaction W_{12} and W_{21}:

$$W_{12} = \frac{\overline{K}_{12}}{1 + \overline{K}_{12}/W_{12}^{eD}}, \qquad W_{21} = \frac{\overline{K}_{21}}{1 + \overline{K}_{12}/W_{12}^{eD}}, \tag{32}$$

where

$$\overline{K}_{12} = \frac{1}{\sqrt{2\pi}\Delta}\int K_{12}(E)\exp\left(-\frac{E^2}{2\Delta^2}\right)dE, \tag{33}$$

$$\overline{K}_{12} = \frac{1}{\sqrt{2\pi}\Delta}\int K_{21}(E)\exp\left(-\frac{E^2}{2\Delta^2}\right)dE,$$

$$W_{12}^{eD} = \frac{\nu_L}{\pi}\left(\frac{E_r}{\pi kT}\right)^{1/2}\sin\left(\frac{\pi E_0'}{2E_r}\right)\exp\left[-\frac{(E_0')^2}{4E_r kT}\right], \tag{34}$$

$$E_0' = e\xi - kT\ln(c_{z-1}/c_z) + E_r. \tag{35}$$

Here e is the electronic charge, Z and $Z-1$ are the charges on the reactant and the reaction product respectively, c_Z and c_{Z-1} are their concentrations, and ξ is the electrode overpotential. Eqns. (32) are analogous to Eqns. (13) describing homogeneous reactions.

Knowing Eqns. (32) for the reaction rates, it is possible to find the transient current of the reaction:[60]

$$i = i_0\left[1 - \exp\left(\frac{e\xi}{kT}\right)\right], \tag{36}$$

where

$$i_o = -\frac{ec_z}{2\kappa}\frac{\nu_L}{\pi}\left(\frac{E_r}{\pi kT}\right)^{1/2}\sin\left(\frac{\pi E_0'}{2E_r}\right)\exp\left[-\frac{(E_0')^2}{4E_r kT}\right]\times$$

$$\times\ln\left\{1 + \pi\left(\frac{\pi kT}{E_r}\right)^{1/2}\frac{\overline{K}_{12}^0}{\nu_L}\frac{\exp[(E_0')/4E_r kT]}{\sin(\pi E_0'/2E_r)}\right\}. \tag{37}$$

In deriving Eqn. (37), it was assumed that

$$\overline{K}_{12} = \exp(-2\kappa r)\,\overline{K}_{12}^0, \tag{38}$$

where the parameter κ^{-1} characterises the scale of the decay of the electronic resonance integral between the reactant and the electrode with distance from the electrode. Eqn. (38) is usually a satisfactory approximation.

It is evident from Eqns. (36) and (37) that, when the resonance integral is fairly small and the inequality

$$\overline{K}_{12}^0 \ll \frac{\nu_L}{\pi}\left(\frac{E_r}{\pi kT}\right)^{1/2}\sin\left(\frac{\pi E_0'}{2E_r}\right)\exp\left[-\frac{(E_0')^2}{4E_r kT}\right], \tag{39}$$

holds, then the second term in the logarithmic expression is small. Expanding the logarithm in series in terms of this small parameter, one can obtain

$$i_0 = -\frac{ec_z}{2\kappa}\overline{K}_{12}^0. \tag{40}$$

This agrees exactly with the results of the non-adiabatic Dogonadze–Kuznetsov theory.[62] On the other hand, if the resonance integral is fairly large or the solvent exhibits a fairly slow polarisation relaxation, i.e. the inequality

$$\overline{K}_{12}^0 \gg \frac{\nu_L}{\pi}\left(\frac{E_r}{\pi kT}\right)^{1/2}\sin\left(\frac{\pi E_0'}{2E_r}\right)\exp\left[-\frac{(E_0'2}{4E_r kT}\right], \tag{41}$$

which is the opposite of the inequality (39), holds, then the following result can be readily obtained from Eqn. (37):

$$i_o = -\frac{ec_z}{2\kappa}\frac{\nu_L}{\pi}\left(\frac{E_r}{\pi kT}\right)^{1/2}\sin\left(\frac{\pi E_0'}{2E_r}\right)\exp\left[-\frac{(E_0')^2}{4E_r kT}\right]\times$$

$$\times\ln\left\{\pi\left(\frac{\pi kT}{E_r}\right)^{1/2}\frac{\overline{K}_{12}^0}{\nu_L}\frac{\exp[(E_0')/4E_r kT]}{\sin(\pi E_0'/2E_r)}\right\}. \tag{42}$$

It follows from Eqn. (42) that, similarly to the processes occurring under homogeneous conditions, the reaction at the electrode subject to condition (41) is controlled by the solvent dynamics and its rate as well as the current are proportional to ν_L in this limit. This theoretical prediction has been confirmed experimentally.[13–15,18–23]

Eqns. (32)–(42) describe the kinetics of the reaction occurring in the region of the normal overpotentials ξ, i.e. subject to the condition $|e\xi| \ll E_r$. For the non-activated region, where $e\xi > -E_r$, and also in the region of anomalous overpotentials, where $e\xi \simeq -E_r$, an approach different from that used previously[7] is required.

Such an approach to the problem of electron transfer from the reactants to the electrode has been developed.[63] The authors began with Eqns. (26), where $K_{12}(E)$ was specified by Eqn. (31) and $K_{21}(E)$ was assumed to be identically equal to zero. They used the variational principle, with the aid of which they found expressions for the rate of reaction on the electrode in both normal and non-activated regions and also in the anomalous range of overpotentials. However, as already mentioned in discussing the studies of Marcus and co-workers,[51,52] the approximation $K_{21}(E) \equiv 0$ is incorrect in the normal region and the formulae of Morgan and Wolynes[63] therefore describe the reaction incorrectly in this case. For normal overpotentials, Eqns. (32)–(42) should be used. As mentioned in the discussion of homogeneous reactions, in the non-activated and anomalous regions, the approximation $K_{21}(E) \equiv 0$ becomes reasonable and the formulae obtained by the above workers[63] for these situations are more believable. The theory of Morgan and Wolynes[63] predicts that, in solvents with a fairly slow relaxation of the polarisation of the medium in the anomalous and non-activated ranges of overpotentials and also in the normal region, the reaction is controlled by the solvent dynamics and its rate is proportional to ν_L. The formulae of the above workers[63] supplement the present author's theory,[60] because they describe the reaction in other ranges of overpotentials.

Thus in both homogeneous and heterogeneous electron transfer reactions in Debye solvents with a fairly slow relaxation of the medium, the reaction begins to be controlled by the solvent

dynamics and the rate of reaction is proportional in this limit to ν_L. This conclusion is qualitatively consistent with the available experimental data.

2. Theories of electron transfer reactions in solvents with two (or more) relaxation times of the polarisation of the medium

The dielectric properties of many solvents of the type of alcohols, where the molecules are linked by a network of hydrogen bonds, are not described by the simple equation (8). The following relation is applicable to such solvents:[64]

$$\varepsilon(\omega)=\varepsilon_\infty+(\varepsilon_S-\varepsilon_\infty)\sum_{i=1}^{N} f_i(1-i\omega\tau_i)^{-1}, \tag{43}$$

where τ_i are quantities differing greatly in magnitude.

If Eqn. (43) is now substituted in Eqn. (6), the correlation function for the fluctuations of the electronic energy levels becomes

$$K(\tau)=2kTE_r\left[\sum_{i=1}^{N}\delta_i\exp(-\nu_i|\tau|)\right], \tag{44}$$

where the correlation times ν_i^{-1} and the coefficients δ_i are expressed in some way in terms of f_i and τ_i. The coefficients δ_i satisfy the relation

$$\sum_{i=1}^{N}\delta_i=1. \tag{45}$$

A general theory of homogeneous electron transfer reaction, applicable to solvents with an arbitrary dielectric losses spectrum and therefore valid for any correlation function $K(\tau)$, has been constructed.[65] This theory is based on the summation of series in powers of V^2 by Padé's method of approximants. It has been shown that the kinetics of transitions with high reaction activation energies are exponential. The following general expressions have been obtained[65] for the rates W_{12} and W_{21}:

$$W_{12}=\frac{W_{12}^{NA}}{1+W_{12}^{NA}/W_{12}^{S}}, \qquad W_{21}=\frac{W_{21}^{NA}}{1+W_{12}^{NA}/W_{12}^{S}}, \tag{46}$$

where W_{12}^{NA} and W_{21}^{NA} are again defined by Eqns. (15) and it has been found that the rate W_{12}^{S} is given by

$$(W_{12}^{S})^{-1}=\int_0^\infty d\tau\left\{\frac{1}{[1-M^2(\tau)]^{1/2}}\exp\left[\frac{E_0^2}{\Delta^2}\frac{M(\tau)}{1+M(\tau)}\right]-1\right\}+$$
$$+\exp\left(\frac{\Delta J}{kT}\right)\int_0^\infty d\tau\left\{\left(\exp\left[\frac{(E_0-2E_r)}{\Delta^2}\frac{M(\tau)}{1+M(\tau)}\right]\right)\Big/ \Big/(1-M^2(\tau))^{1/2}-1\right\}, \tag{47}$$

where

$$M(\tau)=\frac{K(\tau)}{K(0)}. \tag{48}$$

Eqns. (46) extend Eqns. (13) to reactions occurring in media with an arbitrary dielectric constant $\varepsilon(q, \omega)$ and they are therefore applicable to electron transfer reactions in solvents where the correlation function $K(\tau)$ has an arbitrary form.

Eqns. (46) have also been obtained independently by Hynes[42] with the aid of the theory of stable states and Padá's method of approximants, used, however, in a somehwat different way than in the present author's study,[65] and by Sparpaglione and Mukamel,[66,67] while Fonseca[68] showed that Eqns. (46) are not restricted by the approximation involved in Padá's method of approximants but represent an exact solution for reactions in which correlation functions of type (44) play a significant role.

Eqns. (46) as well as Eqns. (13) are applicable only subject to conditions (19) and (20). On the other hand, if the Landau–Zener adiabaticity parameter k_{el} becomes fairly large, i.e. $k_{el} \gg 1$, then, as shown by Hynes,[42] it is essential to use the following expressions instead of Eqns. (46):

$$W_{12}=\frac{W_{12}^{WA}}{1+W_{12}^{WA}/W_{12}^{S}}, \qquad W_{21}=\frac{W_{21}^{WA}}{1+W_{12}^{WA}/W_{12}^{S}}, \tag{49}$$

where W_{12}^{WA} and W_{21}^{WA} are defined by Eqns. (23).

Eqns. (49) constitute an extension of Eqns. (22) to cases where the reactions take place in media with an arbitrary dielectric constant $\varepsilon(q, \omega)$. If all the correlation times ν_i^{-1} are of the same order of magnitude, only short times $|\tau| \ll \nu_i^{-1}$ contribute to the integral (47). Therefore, having expanded the correlation function in series in terms of the parameter $|\tau|$ and having substituted $K(\tau) = K(0) + K'(0)|\tau|$ in Eqn. (47) and then having evaluated this integral, we obtain finally[42,66]

$$(W_{12}^{S})^{-1}=-\frac{K(0)}{K'(0)}\left[\frac{1}{|E_0|}+\frac{1}{|E_0-2E_r|}\right]\sqrt{2\pi}\Delta\exp\left(\frac{E_0^2}{4E_rkT}\right). \tag{50}$$

The result represented by Eqn. (50) differs from Eqn. (14) only in the replacement of ν_L by $-K'(0)/K(0)$, i.e. for the case where all the correlation times have the same order of magnitude we can describe the reaction with the aid of an effective frequency of polarisation fluctuations:

$$\nu_{ef}=-\frac{K'(0)}{K(0)}. \tag{51}$$

Having substituted Eqn. (44) in Eqn. (51), we obtain a simple relation:

$$\nu_{ef}=\sum_{i=1}^{N}\nu_i\delta_i. \tag{52}$$

By virtue of the relation between ν_i, δ_i and f_i, τ_i, formula (52) can be rewritten in another form:

$$\nu_{ef}=\frac{\varepsilon_S}{\varepsilon_\infty}\sum_{i=1}^{N}f_i\tau_i^{-1}. \tag{53}$$

Eqn. (53) was first obtained by Hynes[42] for two relaxation times of the medium and was then extended to the case of N relaxation times.[69] Admittedly, in the latter study[69] it was claimed erroneously

that Eqns. (52) and (53) differ, although it can be shown that they are equivalent. Furthermore, one should note that Helman[69] obtained an expression for W_{12}^{S} somewhat different from Eqn. (50), which in our view is associated with two causes. Firstly, Helman[69] adopted initial postulates different from those used by Sparpaglione and Mukamel[66] and Hynes[42] and, secondly, he developed[69] an incorrect approximation for the evaluation of one of the final integrals.

Eqn. (52) for the case of two relaxation times has also been found by another method.[70] The results represented by Eqns. (46) and (49) have been obtained subject to condition (19). If the inequality (19) is reversed, then the rate of reaction assumes a form analogous to that defined by Eqn. (25) with the sole difference that ν_L has now been replaced by ν_{ef}.

As already mentioned, Eqns. (50)–(53) were derived on the assumption that all the correlation times ν_i^{-1} have the same order of magnitude. On the other hand, if one of the times $\nu_1^{-1} \gg \nu_2^{-1}, \ldots, \nu_N^{-1}$, then the situation is less clear. There exists only the theory of electron transfer in solvents with two markedly different relaxation times.[72] Furthermore, electron transfer in the case with several markedly different relaxation times for the solvent has been investigated by the numerical evaluation of integrals (47) in two studies.[73,74] Fonseca[68] also investigated electron transfer by numerical methods.

The theoretical and experimental data for electron exchange between metallocenes in a number of alcohols have been compared[73] on the basis of Eqns. (49) and (47). It was shown that these formulae account for a large part of the rate of electron transfer between metallocenes in alcohols.

As already mentioned, the present author[72] developed a theory of electron transfer in solvents with two markedly different relaxation times of the medium. The linear correlation observed[31–35] between the rate of reaction and the lowest relaxation frequency of the solvent was explained by this theory. This explanation of the experimental data[31–35] differs from that quoted for the same data in another study,[46] which was based on Helman's erroneous investigation.[47]

Eqns. (46) were derived on the assumption that the reaction proceeds under homogeneous conditions. Reactions occurring at an electrode in solvents of the type of alcohols have been studied in only one investigation,[75] where the relaxation of the solvent was modelled by two relaxation times. These results[75] are analogous to those of the present author.[72] The theory developed in the latter investigation[72] explained qualitatively the experimental data.[15,20,21]

3. Theories of electron transfer reactions in solvents with a continuous distribution of relaxation times of the polarisation of the medium

In many solvents of the type of glycerol, the dielectric properties cannot be described by either the simple Debye model [Eqn. (8)] or by the more complex Eqn. (43). In such solvents, there is a continuous distribution of the relaxation times of the polarisation and the Cole–Davidson equation is applicable to them:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{(\varepsilon_S - \varepsilon_\infty)}{(1 - i\omega\tau_0)^\beta}, \tag{54}$$

where τ_0 is the characteristic relaxation time and β is the Cole–Davidson parameter, which satisfies the inequality $0 < \beta \leqslant 1$.

The microscopic mechanism underlaying Eqn. (54) is at present obscure. There are two hypotheses concerning the nature of this relation. According to the first, the solvent is microscopically homogeneous and Eqn. (54) holds at each point in it. According to the second hypothesis, the solvent is microscopically inhomogeneous and Debye's model [Eqn. (8)] holds at each point in it but with a Debye time τ which varies randomly from point to point. Under these conditions, Eqn. (54) is applicable only on the macroscopic scale and is obtained by averaging Eqn. (8) over the distribution of the Debye times $g(\tau)$, which has the following form according to Bötcher and Bordewijk:[76]

$$g(\tau) = \begin{cases} \dfrac{\sin(\pi,\beta)}{\pi\tau}\left(\dfrac{\tau}{\tau_0 - \tau}\right)^\beta & (\tau < \tau_0), \\ 0 & (\tau > \tau_0). \end{cases} \tag{55}$$

The theory of electron transfer in glycerol type solvents has been constructed in accordance with two hypotheses concerning the nature of the relaxation of the polarisation of the medium. If the first hypothesis concerning the nature of Eqn. (54) is adopted as a basis, then electron transfer can be described within the framework of the formalism of Sparpaglione and Mukamel[66] and the reaction rates are defined by Eqns. (46), where $M(\tau)$ is found with the aid of Eqns. (48), (6), and (54). The integrals (47) have been evaluated with the aid of Eqn. (54) in a study[74] where the expression

$$W_{12}^{S} = \frac{\sqrt{2}\beta[8kTE_r]^{1/2-1/\beta}}{\Gamma(1/\beta - 1/2)\,[4\Gamma(\beta+1)\,\varepsilon_\infty/\varepsilon_S]^{1/\beta}} \times$$
$$\times [|E_0|^{1-2/\beta} + |E_0 - 2E_r|^{1-2/\beta}]^{-1}\tau_0^{-1}\exp\left(-\frac{E_0^2}{4E_r kT}\right), \tag{56}$$

where $\Gamma(x)$ is a gamma-function,[77] was obtained in the limit corresponding to high activation energies for the reaction.

The theory employing the second hypothesis concerning the nature of Eqn. (54) as a basis has been developed by Rips and Jortner.[78,79] They showed that the reaction kinetics are described by the following formula:

$$n_1(t) = \int_0^\infty \exp[-W_{12}(\tau)]\,g(\tau)\,d\tau, \tag{57}$$

where $n_1(t)$ is the population of the first electronic state and $W_{12}(\tau)$ is defined by Eqn. (13). In the derivation of Eqn. (57), it was assumed that the reverse reaction may be neglected.

On the basis of Eqn. (57), Rips and Jortner[78,79] predicted that, in the reaction regime controlled by the solvent dynamics, the rate of reaction is given by

$$W^{DC} = W_{12}^{NA}\left(\frac{\varepsilon_S}{\varepsilon_\infty}\frac{\hbar E_r}{4\pi V^2\tau_0}\right)^\beta. \tag{58}$$

Two conclusions follow from Eqn. (58). Firstly, the rate of reaction depends on the characteristic relaxation time of the medium τ_0 less than in the case of Debye solvents. Secondly, the rate of reaction in this limit is proportional to $V^{2(1-\beta)}$ when account is taken of Eqn. (15).

The available experimental data on intramolecular electron transfer[80] support the theory of Rips and Jortner[78,79] rather than that of Sparpaglione and Mukamel.[74] Indeed, the observed[80] dependence of the rate of reaction on τ_0 is described satisfactorily by

Eqn. (58) when τ_0 is varied within the limits of two orders of magnitude. The dependence of the rate of reaction on V, described by Eqn. (58), also agrees well with experiment.

As already mentioned, McGuire and McLendon[54] likewise observed the proportionality of the rate of reaction to $\tau_0^{-\beta}$. The reaction which they investigated[54] occurred in glycerol—a solvent of the Cole–Davidson type. Rips and Jortner[78,79] therefore explained this proportionality by Eqn. (58). However, since the proportionality of the rate of reaction to $\tau_0^{-\beta}$ was deduced[54] on the basis of indirect considerations, the reliability of the interpretation of these results[54] within the framework of the theory of Rips and Jortner[78,79] is at present unclear.

4. The dynamic effect of the diffusion polarisation of the solvent in the rate of electron transfer

The theories of electron transfer reactions examined above took into account only the reorientation relaxation of the polarisation of the solvent. On the other hand, in certain solvents the rate of relaxation of the polarisation via the self-diffusion of the dipoles of the medium may be comparable to the rate of relaxation of the polarisation associated with the reorientation of the solvent molecules. The theory of electron transfer taking into account both pathways to the relaxation of the solvent polarisation has been developed.[81] It was shown that the rate of reaction is expressed by the formula

$$W_{12} = \frac{W_{12}^{NA}}{1+W_{12}^{NA}/W_{12}^{DII}}, \tag{59}$$

where

$$W^{DII} = \tilde{\nu}_{ef}\frac{|E_0||E_0-2E_r|}{|E_0|+|E_0-2E_r|}\frac{1}{(2\pi\Delta^2)^{1/2}}\exp\left(-\frac{E_0^2}{4E_rkT}\right), \tag{60}$$

and

$$\tilde{\nu}_{ef} = \nu_L + \frac{\epsilon_S}{\epsilon_\infty}D\frac{c_0}{64\pi^4E_r}\int|\Delta D_q|^2q^2dq. \tag{61}$$

In Eqn. (61), D is the self-diffusion coefficient of the solvent molecules and ΔD_q is defined by Eqn. (7).

Eqn. (59) is applicable only for $V \ll kT$. Subject to the condition $V \gg kT$, a formula has been obtained[81] for the rate of reaction differing from Eqn. (25) only in the replacement of ν_L by $\tilde{\nu}_{ef}$. A formula for $\tilde{\nu}_{ef}$, convenient for making estimates, was also obtained in the above study:[81]

$$\tilde{\nu}_{ef} = \nu_L + \frac{\varepsilon_S}{\varepsilon_\infty}D\frac{2.048(R_2^3+R_1^3)R}{R(R_2+R_1)R_1^2R_2^2-2R_1^3R_2^3}. \tag{62}$$

It is valid for $R \geqslant R_1 + R_2$, where R_1 and R_2 are the radii of the reactants and R is the distance between them.

The estimates made in the above study[81] by Eqn. (62) show that in solvents such as methanol and nitrobenzene, where the diffusion coefficients of the solvent molecules are fairly large and the values of ν_L are fairly small, the contribution of the diffusion-dependent solvent polarisation to $\tilde{\nu}_{ef}$ may become dominant.

III. Conclusion

The dynamic effects of the solvent examined in this review have been described within the framework of the continuous model of a structureless dielectric. At the same time, if the dimensions of the reactants are comparable to those of the solvent molecules, the structureless dielectric approximation becomes poor and it is necessary to construct a theory of electron transfer on a basis which takes into account the molecular structure of the solvent models.

There exist at the present time two approaches to allowance for the molecular structure of the solvent in devising a theory of electron transfer. The first of these (phenomenological) is based on the fact that the relaxation time of the centre of gravity of the fluorescence spectrum of a polar molecule dissolved in the given solvent coincides with ν_S^{-1}, where ν_S^{-1} is the effective frequency of the fluctuations in the polarisation of the medium, which enters into the preexponential factor for the reaction rate constant. This approach has been developed in a number of studies.[36–38]

The second approach to allowing for the molecular structure of the solvent in the electron transfer theory is based on different approximations of the theory of the liquid state. In particular, it is represented by a study,[82] where it was shown that, in a continuous description of the solvent, it is possible to overestimate the activation energy for the reaction. However, in the same investigation an important conclusion was reached: if the energy of the reorganisation of the solvent is regarded not as a theoretically calculated parameter but as an adjustable parameter derived from experimental data, then the expressions for the reaction rate constants obtained within the framework of the continuous approximation can provide an excellent description of the reaction kinetics.

Finally, we may note that the dynamic effect of the solvent may be manifested not only in electron transfer reactions but also in the more general charge transfer reactions,[83–85] but a detailed discussion is outside the scope of the present review.

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