What is the solvent longitudinal time scale controlling electron transfer rates?

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Solvent motions play a significant role in controlling the rates and the adiabaticity of electron transfer (ET) processes with small activation barriers.1-6 As these motions become slow, a nonadiabatic reaction will turn adiabatic. Kosower and Huppert5 have found a correlation between photochemical intramolecular ET rates and $\tau_1^*$, the solvent longitudinal time in alcohols. $\tau_1^*$ is precisely defined for the Debye model7 in which the solvent has a single dielectric relaxation time, $\tau_1$, i.e., $\tau_1^* = \left( \epsilon_\infty / \epsilon_0 \right) \tau_1$. Here $\epsilon_\infty$ and $\epsilon_0$ denote the optical and the zero frequency values of the solvent dielectric function $\epsilon(\omega)$, respectively. The precise definition of the solvent time scale relevant for ET rates for an arbitrary (non-Debye) solvent is an open question, which is of considerable current interest. Kosower6 and Eisenthal5 have emphasized the significance of solvent polarity which affects the activation barriers, and whose role should be distinguished from that of solvent dynamics (viscosity).

We have developed a theory for ET rates in polar solvents8 by utilizing the formal analogy of this problem with the calculation of nonlinear optical line shapes.9,10 The approach is based on reduced equations of motion for the density matrix in Liouville space. An approximate resummon of the perturbative series for the rate to infinite order in the electronic coupling was performed, based on the assumption of separation of time scales between the off-diagonal density matrix elements (the coherences) and the diagonal elements (populations). The resulting expression interpolates continuously between the nonadiabatic and the adiabatic limits of the rate, satisfies the detailed balance condition, reproduces the entire Kramers turnover curve as a function of the solvent longitudinal time scale, provides a microscopic definition for the reaction free energy, and generalizes Marcus free energy relation to the adiabatic regime. In this note we focus on the adiabatic limit whereby the ET rate from state $|a \rangle$ (donor) to $|b \rangle$ (acceptor) is

$$K = (1/\tau_1) \exp(-q_n^2/2),$$

(1a)

where $\tau_1 = \tau(q_a) + \tau(q_b)$ is the relevant solvent time scale and where $\tau(q_n)$ is the solvent time scale function controlling the ET rate,

$$\tau(q_n) = \exp(-q_n^2/2) \int_0^\infty dt \frac{1}{\sqrt{1-M^2(t)}}$$

$$\times \exp \left[ \frac{q_n^2 M(t)}{1 + M(t)} - 1 \right],$$

(1b)

with

$$q_n = \frac{E - \delta_n}{\sqrt{k_B T |\delta_a - \delta_b|}}, \quad n = a, b,$$

(1c)

$$Q(t) = \int_0^\infty \frac{d\omega}{\omega} \exp(-i\omega t) \frac{1}{\epsilon_0} \frac{1}{\epsilon(\omega)},$$

(2)

and $M(t) = Q(t)/Q(0)$. Here $E$ is the reaction exothermicity and $\delta_a$ ($\delta_b$) is the average value of the solvation coordinate when the ET system is in the state $|a \rangle$ ($|b \rangle$). $q_n^2/2 = \Delta G_{ab}^*/(k_B T)$ and $q_n^2/2 = \Delta G_{ba}^*/(k_B T)$, where $\Delta G_{ab}^*$ ($\Delta G_{ba}^*$) is the activation free energy for the forward (reverse) reaction. As the solvent is varied, $\delta_n$ and consequently $q_n$, and the activation barriers will vary primarily with the solvent polarity. Approximate relations between $\delta_n$ and polarity measures such as ET(30) may be derived11 in agreement with the relationships proposed by Eisenthal.5 The dynamical effects of the solvent affect the rate via $M(t)$, which is the normalized correlation function for the longitudinal polarization of the solvent.8,12 In order to explore the

In Fig. 1, we display the solvent time scale function $\tau(q)/\tau(0)$ for a Debye solvent ($N = 1$). Making use of the experimental dielectric function $\varepsilon(\omega)$, we have calculated $\tau(q)$ for linear alcohols (propanol to decanol) and found it to be virtually identical, apart from an overall scaling factor. $\tau(q)$ for propanol and decanol is displayed in Fig. 1 as well. For a Debye solvent $\tau(q)$ is proportional to the longitudinal time scale $\tau_\parallel = \tau_\perp (\varepsilon_\infty / \varepsilon_0)$, and for barrierless reactions $\tau(0) = (2\ln 2) \tau_\perp$, in agreement with the mean first passage time calculated by Sumi and Marcus for the Debye model in the adiabatic limit. The present expression for $\tau(q)$ generalizes this relation and defines precisely the relevant solvent time scale ($\tau(0)$) for any non-Debye solvent with an arbitrary $\varepsilon(\omega)$. The correlation $K = 1/\tau_\parallel$, found by Kosower and Huppert may be rationalized since $\tau_\parallel$ is the dominant relaxation time ($\varepsilon_\infty > \varepsilon_\perp c_\perp$) and the linear alcohols are approximately Debye solvents. The present theory separates clearly the solvent polarity effects which affect $q_a$ and $q_b$ and the solvation dynamics which enter via the frequency-dependent dielectric function $\varepsilon(\omega)$ and $M(t)$.

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\[ F(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \exp(-i\omega t) \frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \sum_{j=1}^{N} c_j \exp(-t/\tau_j) \]  

Using Eqs. (2), we then get

\[ M(t) = \sum_{j=1}^{N} c_j' \exp(-t/\tau_j') \]  

Note that $\Sigma c_j = \Sigma c_j' = 1$. Equations (1)–(4) show that the relevant solvent time scales for ET are $\tau_j$ [Eq. (4)] (which are related to the solvent longitudinal correlation function) and not $\tau_j$ [Eq. (3)]. For the Debye model ($N = 1$), we have $\tau_j' = (\varepsilon_\infty / \varepsilon_0) \tau_j$. Note, however, that in general we cannot obtain $\tau_j'$ from $\tau_j$ by simply multiplying with $(\varepsilon_\infty / \varepsilon_0)$. The correct procedure is to use $\varepsilon(\omega)$ to get $M(t)$ [Eq. (2)] whose Laplace transform will subsequently yield $\tau_j'$. To illustrate the difference between $\tau_j$ and $\tau_j'$, we consider propanol at 23°C which has three relaxation times $\tau_1$, i.e., 408, 21, and 2 ps. The corresponding relaxation times $\tau_j'$, evaluated using Eqs. (2) and (4), are 80, 15, and 1.4 ps.

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