Supporting Information

Interfacial Bond Breaking Electron Transfer in Mixed Water-Ethylene Glycol Solutions: Reorganization Energy and Interplay between Different Solvent Modes

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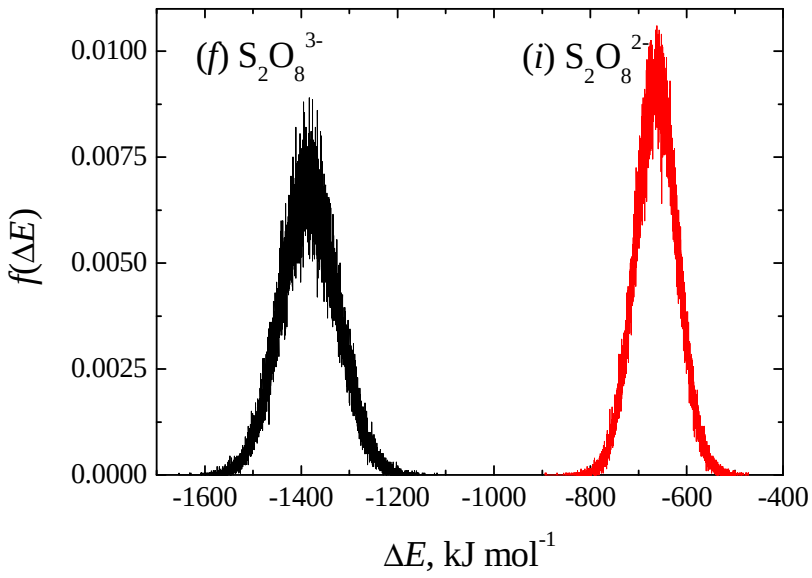
Section A1

Table 1S. Partial charges and van der Waals potential parameters used in the MD simulations.

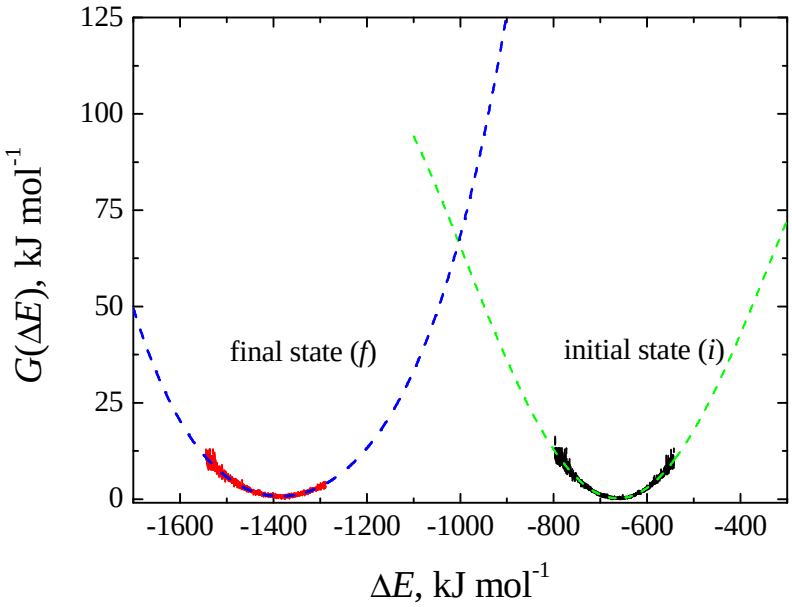
Atom	$S_2O_8^{2-}$	$S_2O_8^{3-}$	σ, Å	ε, kJ mol^{-1}
S	1.4458	1.5439	0.355	1.050
O	-0.7245	-0.8756	0.300	0.714
O*	-0.2722	-0.4169	0.300	0.714

*The oxygen atom of the peroxide group.

Section A2



(a)



(b)

Figure 1S. (**a**) Probability to reach a certain interval of the energy of Coulomb interaction of the reactant (*i*) and product (*f*) with solvent molecules (ΔE) calculated with the help of MD simulations performed for *x*(EG) = 0.5; (**b**) The reaction free energy surface $G_{i(f)}$ as function of ΔE calculated using eq.(15). Dashed lines refer to a parabolic fit.

Section A3

Dealing with the Sumi-Marcus model[8] (i.e. with the Agmond-Hopfield formalism) we have to solve the equation:

$$\frac{\partial P(q,\tau)}{\partial \tau} = \hat{L}\, P(q,\tau)\,, \tag{1a}$$

where τ is time, q is a solvent coordinate and $P(q, \tau)$ is the probability density to find a reactant in initial state.

In eq.1a $\hat{L}$ is the Smoluchowski operator supplemented by a sink term:

$$\hat{L}\, P(q,\tau) = D\left\{\frac{\partial^2}{\partial q^2} + \frac{1}{k_B T}\frac{dU(q)}{dq}\frac{\partial}{\partial q}\right\} P(q,\tau) - k_{in}(q) P(q,\tau)\,, \tag{2a}$$

where D refers to the coefficient of diffusion along q, $D = \dfrac{k_B T}{2\lambda_s \tau_L}$; λ_s is the solvent reorganization energy (a value of 17.8 kcal mol^{-1} was taken for λ_s); τ_L is the solvent relaxation time.

$U(q)$ in eq.2a is a section of the reaction free energy surface (FES):

$$E_i(q,r) = \lambda_s q^2 + U_i^*(r)\,,$$

and (3a)

$$E_f(q,\, r) = \lambda_s (q-1)^2 + U_f^*(r) - e_0 \eta\,,$$

where intramolecular potentials $U_{i(f)}^*(r)$ are the same as in eqs. (6, 7) and η is electrode overvoltage.

The sink term in eq.2a, $k_{in}(q)$, is written as follows:

$$k_{in} = \nu_{in} \exp\left\{-\Delta E_a^*(q)/k_B T\right\}, \tag{4a}$$

where ν_{in} is an effective nuclear frequency factor.

The energy barrier along the intra-molecular degree of freedom, ΔE_a^*, depends on the solvent coordinate q and is defined in the form

$$\Delta E_a^*(q) = U(q,\, q_{saddle}^*(q)) - U(q,\, r = r_0), \tag{5a}$$

where $q_{saddle}^*(q)$ notes the saddle line on the three-dimensional free energy surface $E(q,\, r)$; $q_{saddle}^*(q)$ is defined by a transcendent equation; r_0 refers to the minimum of $U_i^*(r)$.

Two different time scales characterizing different averaged survival times of the product in initial state can be considered (see relevant discussion in ref 7).

$$\tau_a = \int_0^\infty d\tau \int_{q_L}^{q_R} P(q,\tau)\, dq\, d\tau, \tag{6a}$$

and

$$\tau_b = \frac{1}{\tau_a} \int_0^\infty \tau\, d\tau \int_{q_L}^{q_R} P(q,\tau)\, dq\, d\tau, \tag{7a}$$

where q_L and q_R are assumed q values at the left and right boundaries, respectively.

Some details of an original computational scheme developed to solve eq.1a can be found in ref (Nazmutdinov, R.R.; Bronshtein, M.D.; Glukhov, D.V.; Zinkicheva, T.T. Modeling of Solvent Viscosity Effects on the Electroreduction of Pt(II) Aquachlorocomplexes. *J. Solid State Electrochem*. 2008, 12, 445-451). Then the ET rate constant (k) can be defined in two different ways, as $1/\tau_a$ and $1/\tau_b$ (in our case k_a and k_b are nearly equal. The results of calculations are shown in Fig.2S. Note that the relaxation time τ_L is directly proportional to the solvent viscosity.

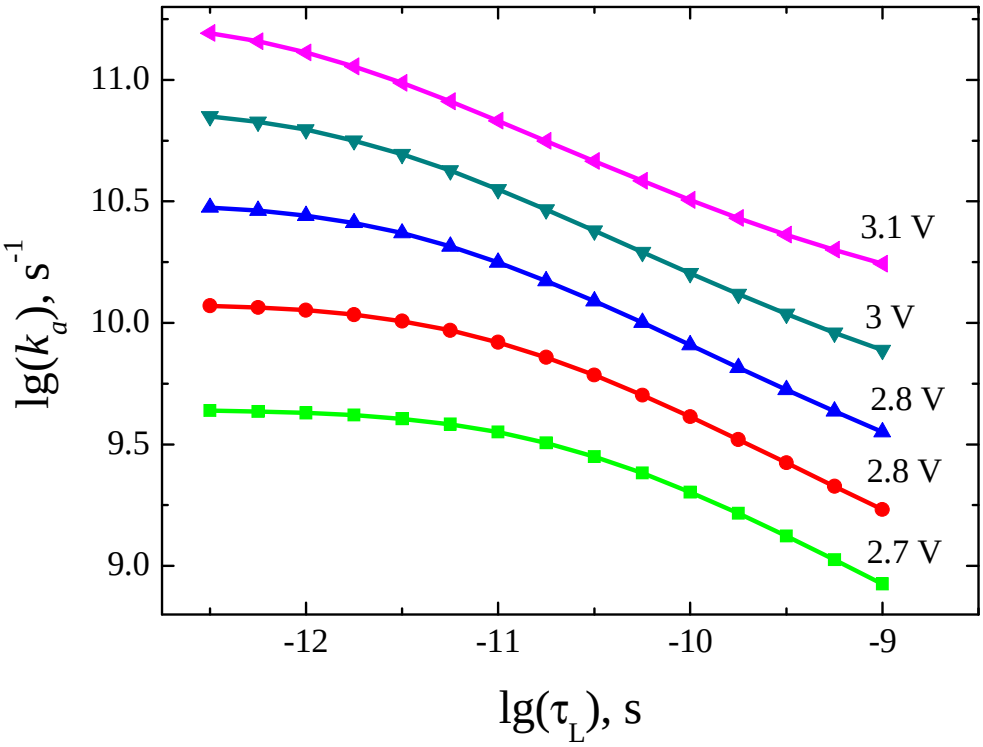


Figure 2S. Rate constant of the first electron transfer at the electroreduction of $S_2O_8^{2-}$ (k) calculated using the Sumi-Marcus model as a function of the solvent relaxation time (τ_L) at different electrode overvoltages.

Section A4

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