Reorganization energy of electron transfer. Supplementary material

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I. REORGANIZATION ENERGIES IN MOLECULAR SOLVENTS

The details of calculations of reorganization energies in 15 molecular solvents are presented here. The adopted geometry of the donor-acceptor complex is two spheres with the radii $R_D = R_A = R_0$ separated by the distance R between their geometrical centers. The van der Waals radii of the solutes are modified in microscopic theories by the corresponding solute-solvent hard sphere radii R_1. In the simplest additive scheme, they can be approximated as sums of the solute and solvent hard-sphere radii $R_1 = R_0 + \sigma_s/2$, where σ_s is the solvent hard-sphere diameter. Alternatively, R_1 can be calculated from protocols established in the liquid-state theories.[1,2] Given this definition, the distance between the solute centers R is assumed to exceed $2R_1$ for outer-sphere electron transfer. The electric field of the donor-acceptor complex in reciprocal space becomes[3]

$$\Delta \tilde{\mathbf{E}}_0^L(\mathbf{k}) = \frac{4\pi i e \mathbf{k}}{k^2} j_0(kR_1) \left[1 - e^{i\mathbf{k}\cdot\mathbf{R}}\right], \qquad (S1)$$

where the subscript "L" indicates the longitudinal (proportional to the reciprocal space wave vector $\mathbf{k}$) projection of the field; $j_0(x)$ is the spherical Bessel function of zeroth order.[4] The solvent reorganization energy is obtained[3,5] by integrating the field squared with the longitudinal susceptibility function $\chi^L(k)$

$$\lambda = \frac{1}{2} \int \frac{d\mathbf{k}}{(2\pi)^3} \chi^L(k) |\Delta \tilde{\mathbf{E}}_0^L|^2. \qquad (S2)$$

By substituting eqn (S1), one obtains

$$\lambda = 8e^2 \int_0^\infty j_0(kR_1)^2 \left[1 - j_0(kR)\right] \chi^L(k) dk. \qquad (S3)$$

This equation is used to calculate the solvent reorganization energies for 15 molecular solvents with their properties listed in Table S1.

A. Solvent properties

The physical properties of molecular polar liquids required to perform calculations are listed in Table S1. They include the static dielectric constant ϵ_s, the squared

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refractive index $\epsilon_\infty = n_D^2$, the hard-sphere diameter σ_s,[6] and the molecular dipole moment m. The effective condensed-matter dipole moment m' is calculated according to the Wertheim's theory.[7] The dipole moment is modified due to the fact that the permanent dipole $\mathbf{m}$ and the induced dipole $\mathbf{p}$ at a given molecule add up to produce a higher averaged value specified by m'. The liquid polarity is specified by the effective polarity parameter[8] y_{eff} (Gaussian units)

$$y_{\text{eff}} = (4\pi/9)\beta\rho\langle(\mathbf{m} + \mathbf{p})^2\rangle, \qquad (S4)$$

where ρ is the number density of the liquid and $\beta = (k_B T)^{-1}$. The molecular polarizability α required to determine m' in the mean-field Wertheim theory is taken from ϵ_∞ according to the Clausius-Mossotti equation. The values of y_{eff} and the polarity parameter

$$y' = (4\pi/9)\beta\rho(m')^2 \qquad (S5)$$

based on m' are also listed in Table S1. This latter parameter becomes

$$y = (4\pi/9)\beta\rho m^2 \qquad (S6)$$

for nonpolarizable liquids. Also listed in the Table are the Pekar parameter c_0 and the $k = 0$ values of the longitudinal susceptibility

$$4\pi\chi^L(0) = q^2 \left(1 - \epsilon_s^{-1}\right), \qquad (S7)$$

where

$$q = \frac{\epsilon_\infty + 2}{3\epsilon_\infty}. \qquad (S8)$$

B. Nonlocal susceptibility functions

The longitudinal susceptibility function is parametrized with the structure factor $S_B(k, 2\xi^L)$ from the mean-spherical approximation (MSA) for dipolar fluids.[9] Given that the dipolar structure factor tends to unity at $k \to \infty$, the longitudinal susceptibility function is the product of the $k \to \infty$ limit $\chi(\infty)$ and the MSA structure factor[5]

$$\chi^L(k) = \chi(\infty)S_B(k, 2\xi^L). \qquad (S9)$$

The MSA solution gives the orientational structure factors in terms of the Baxter function $Q(k\sigma_s, \xi)$ obtained as the solution of Percus-Yevick integral equations for hard sphere fluids[2,10]

$$S_B(k\sigma_s, \xi) = |Q(k\sigma_s, \xi)|^{-2}, \qquad (S10)$$

Table S1. Physical parameters of polar solvents used in the calculations

Solvent	ϵ_∞	ϵ_s	c_0	$4\pi\chi^L(0)$	σ_s, Å	m, D	y'	y_{eff}
formamide	2.091	109.5	0.469	0.421	3.99	3.37	11.52	11.78
methanol	1.760	35.87	0.540	0.493	3.77	2.87	7.049	7.251
ethanol	1.848	24.55	0.500	0.462	4.41	1.66	1.333	1.553
n-propanol	1.915	20.33	0.473	0.442	4.89	3.09	4.40	4.63
t-butanol	1.919	12.47	0.441	0.426	5.3	1.66	0.752	0.987
water	1.776	78.46	0.550	0.496	2.87	1.834	6.53	6.74
PC[a]	2.014	64.92	0.481	0.435	5.3	4.94	10.78	11.03
ETG[b]	2.047	40.7	0.464	0.424	4.621	2.31	3.278	3.536
nitromethane	1.902	32.7	0.495	0.453	4.36	3.56	7.188	7.419
acetone	1.839	20.7	0.496	0.461	4.78	2.69	3.179	3.397
acetonitrile	1.798	35.94	0.528	0.482	4.14	3.92	10.51	10.72
benzonitrile	2.326	25.2	0.390	0.369	5.72	4.18	7.19	7.49
pyridine	2.271	12.91	0.363	0.363	5.15	2.37	2.509	2.806
1,1-dichloroethane	1.997	10.0	0.401	0.401	5.09	1.82	1.109	1.358
chlorophorm	2.079	4.9	0.277	0.340	5.05	1.15	0.394	0.659

[a] PC=propylene carbonate
[b] ETG=ethylene glycol

where

$$Q(k\sigma_s, \xi) = 1 - 12\xi \int_0^1 e^{ik\sigma_s t} \\ \left[a(\xi)(t^2 - 1)/2 - b(\xi)(t - 1) \right] dt \quad \text{(S11)}$$

and $a(\xi) = (1 + 2\xi)/(1 - \xi)^2$, $b(\xi) = -3\xi/(2(1 - \xi)^2)$. The longitudinal structure factor of the MSA solution is obtained by setting $\xi = 2\xi^L$ (eqn (S9)).

The polarity parameter ξ^L in the MSA structure factor is defined to satisfy the $k = 0$ limit in eqn (S7)

$$\frac{(1 - 2\xi^L)^4}{(1 + 4\xi^L)^2} = \frac{\chi^L(0)}{\chi(\infty)}. \quad \text{(S12)}$$

The $k \to \infty$ asymptote for the susceptibility function is[5]

$$\chi_m(\infty) = \frac{3y}{16\pi} \left(1 + \frac{y'}{y} \right)^2, \quad \text{(S13)}$$

where y' and y are given by eqn (S5) and (S6), respectively. The calculation of the susceptibility function requires four input parameters: ϵ_∞, ϵ_s, y', and y. The solvent hard-sphere diameter σ_s is additionally needed to calculate λ in eqn (S3).

II. DERIVATION OF EQN (55)

The free energy invested in transferring electron is equal to the free energy of solvating an effective solute retaining all the repulsive and nonpolar interactions of the actual donor-acceptor complex, but interacting with the medium by the electrostatic potential[11]

$$\Delta V = \sum_j \Delta\nu(j), \quad \Delta v(j) = -\mathbf{m}_j \cdot \Delta\mathbf{E}_0. \quad \text{(S14)}$$

The free energy of solvation can be found by thermodynamic integration[2]

$$\Delta F = \int_0^1 d\lambda \langle \Delta V \rangle_\lambda. \quad \text{(S15)}$$

The statistical average $\langle \Delta V \rangle_\lambda$ is taken with the interaction potential $\lambda\Delta V$ and can be expanded in the perturbation series

$$\langle \Delta V \rangle_\lambda = \langle \Delta V \rangle_1 + \beta(1 - \lambda)\langle(\delta\Delta V)^2\rangle_1, \quad \text{(S16)}$$

where $\delta\Delta V = \Delta V - \langle \Delta V \rangle_1$. Substituting eqn (S16) to eqn (S15), one obtains

$$\Delta F = \langle \Delta V \rangle_1 + \frac{1}{2}\beta\langle(\delta\Delta V)^2\rangle_1 \quad \text{(S17)}$$

The average energy gaps in two electron-transfer states are connected to ΔV by the following equations

$$X_1 = \Delta E_0 + \langle \Delta V \rangle_0, \quad X_2 = \Delta E_0 + \langle \Delta V \rangle_1, \quad \text{(S18)}$$

where ΔE_0 is the vacuum energy gap. The Stokes-shift reorganization energy is given by

$$\lambda^{\text{St}} = \frac{1}{2}(X_1 - X_2) \quad \text{(S19)}$$

Assuming that the electrostatic interaction averages out to zero in the state $\lambda = 0$ when only repulsions and nonpolar interactions are present, $\langle \Delta V \rangle_0 = 0$, one obtains

$$\Delta F = -2\lambda^{\text{St}} + \lambda. \quad \text{(S20)}$$

The absolute value of this equation is eqn (55) in the main text.

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