

# Analysis of Electron Transfer Processes across Liquid/Liquid Interfaces: Estimation of the Equilibrium Free Energy of Activation

S. Harinipriya and M. V. Sangaranarayanan\*

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

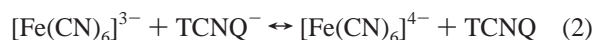
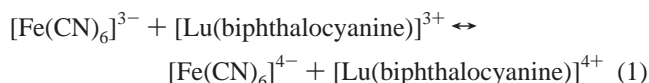
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The equilibrium free energy of activation for electron-transfer processes across liquid/liquid interfaces is estimated using the desolvation energies, interfacial solvation numbers, and inner potential difference between the bulk and the interface for the ionic species and dielectric permittivities. The analysis employing a sharp boundary model is shown to yield a quantitative expression pertaining to the free energy of activation, solvent reorganization energy, and the rate constant. The methodology is applied to the electron transfer of  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  with (i)  $[\text{Lu}(\text{bipthalocyanine})]^{4+}/[\text{Lu}(\text{bipthalocyanine})]^{3+}$  and (ii)  $\text{TCNQ}/\text{TCNQ}^-$  redox couples in water/1,2 dichloroethane interface.

## 1. Introduction

The analysis of charge-transfer phenomena across liquid/liquid interfaces is a frontier area of research on account of its fundamental importance in ion transport across membranes,<sup>1</sup> fabrication of ion-selective electrodes,<sup>2</sup> photoinduced processes,<sup>3</sup> phase transfer catalysis<sup>4</sup> etc. Despite this extensive role, a rigorous formulation and quantitative interpretation is rendered difficult in view of the necessity to incorporate satisfactorily, the interfacial potential distribution, ionic solvation energies and dielectric permittivities in conjunction with the nature of the boundary existing between the immiscible electrolyte solutions. Although the experimental studies in this context employ diverse techniques such as cyclic voltammetry,<sup>5a</sup> scanning electrochemical microscopy (SECM),<sup>6</sup> second harmonic generation (SHG),<sup>7</sup> etc., the rationalization of the data in terms of the system parameters with the help of the constituents of the interface has remained elusive.

In this Article, a phenomenological thermodynamic approach for evaluating the equilibrium free energy of activation pertaining to electron transfer processes across liquid/liquid interfaces is suggested, using a sharp boundary model. A sharp boundary model becomes valid when the two solvents are highly immiscible. A notable feature of the formalism consists of the explicit incorporation of various extent of interfacial desolvation of the reactants, inner potential differences of the species involved, dielectric permittivity of the nonaqueous solvent, and bulk solvation numbers of ions in aqueous and organic phases. The qualitative validity of the procedure is demonstrated for the redox reactions



occurring at the water/1,2-dichloroethane (1,2 DCE) interface; TCNQ denotes 7,7,8,8-tetracyanoquinodimethane.

## 2. Composition of the Equilibrium Free Energy of Activation Using a Sharp Boundary Model

For a general redox reaction  $\text{Ox}_1 + \text{Red}_2 \leftrightarrow \text{Ox}_2 + \text{Red}_1$ , where  $\text{Ox}_1$  and  $\text{Ox}_2$  refer to the oxidant in the aqueous and organic phase respectively,  $\text{Red}_1$  and  $\text{Red}_2$  being the reduced species, the equilibrium free energy of activation ( $\Delta G_{\text{eq,sharp}}^\ddagger$ ) may be represented (cf. Scheme 1) as<sup>8</sup>

$$\Delta G_{\text{eq,sharp}}^\ddagger = (w_{r_1} + w_{p_1})/2 + \Delta G_{\text{et}_1} \quad (3)$$

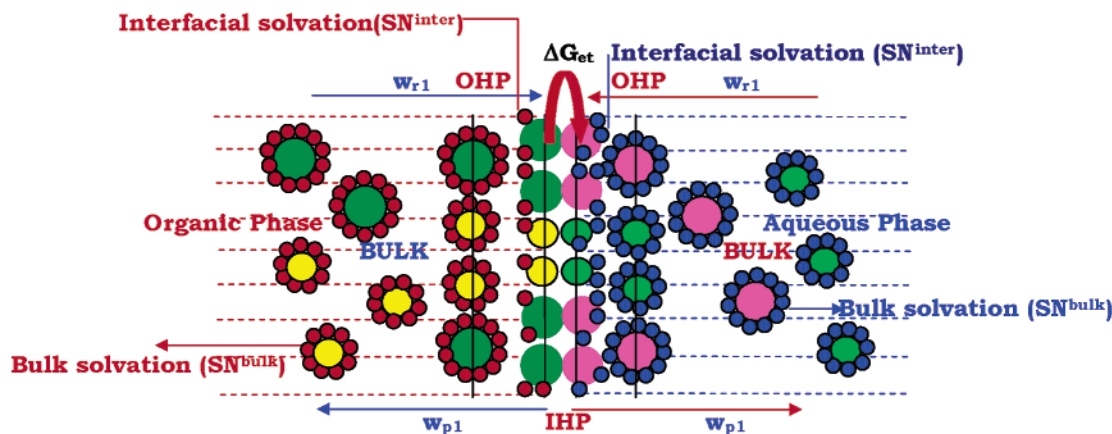
In eq 3,  $w_{r_1}$  denotes the work done in bringing the reactants ( $\text{Ox}_1$  and  $\text{Red}_2$  in the aqueous and organic phases) from bulk to the interface,  $w_{p_1}$  being the work involved in the transfer of products.<sup>8</sup>  $\Delta G_{\text{et}_1}$  denotes the free energy change involved in the electron transfer between the reactants. The above equation is reminiscent of the Marcus theory<sup>9</sup> of electron-transfer processes wherein the overall free energy of activation is partitioned into different contributions involving the reactants and products mediated by dipolar polarization.

**2.1. Work Terms and Interfacial Solvation Behavior of Ions.** The work term pertaining to the reactants,  $w_{r_1}$  may be written as

$$w_{r_1} = \Delta G_{\text{Ox}_1-s_1}^{\text{inter}} + \Delta G_{\text{Red}_2-s_2}^{\text{inter}} \quad (4)$$

where  $\Delta G_{\text{Ox}_1-s_1}^{\text{inter}}$  and  $\Delta G_{\text{Red}_2-s_2}^{\text{inter}}$  refer to the interfacial Gibbs free energy of solvation of  $\text{Ox}_1$  and  $\text{Red}_2$  in the solvents denoted as  $s_1$  and  $s_2$ , respectively. An exact estimate of these parameters is rendered difficult in view of the electrostatic potential profiles and diverse nature of interfacial interactions.<sup>10</sup> However, one may anticipate that  $\Delta G^{\text{inter}}$  should be considerably diminished at the interface from the bulk value because desolvation of ions is a prerequisite for electron-transfer processes in general. However, the precise extent of desolvation of ions is not known at metal/electrolyte as well as at liquid/liquid interfaces. Consequently, we introduce a parameter  $\text{SN}_{\text{Ox}_1}^{\text{inter}}/\text{SN}_{\text{Ox}_1}^{\text{bulk}}$  that reflects the extent of desolvation of  $\text{Ox}_1$  during its transport from bulk to the interfacial region. Analogous considerations apply for other species  $\text{Ox}_2$ ,  $\text{Red}_1$ , and  $\text{Red}_2$ . Assuming such a strategy to be valid,  $\Delta G_{\text{Ox}_1-s_1}^{\text{inter}}$  and  $\Delta G_{\text{Red}_2-s_2}^{\text{inter}}$  may be

\* Corresponding author. E-mail: mvs@chem.iitm.ac.in.

**SCHEME 1: Representation of the Transport Processes Involved in the Electron Transfer Reaction  $\text{Ox}_1 + \text{Red}_2 \leftrightarrow \text{Ox}_2 + \text{Red}_1$ <sup>a</sup>**

<sup>a</sup> Key: green circles,  $\text{Ox}_2$ ; yellow circles,  $\text{Red}_2$ ; light green circles,  $\text{Red}_1$ ; pink circles,  $\text{Ox}_1$ ; IHP and OHP denote the inner and outer Helmholtz planes, respectively.

written as

$$\Delta G_{\text{Ox}_1-s_1}^{\text{inter}} = \frac{\text{SN}_{\text{Ox}_1}^{\text{inter}}}{\text{SN}_{\text{Ox}_1}^{\text{bulk}}} \Delta G_{\text{Ox}_1-s_1}^{\text{bulk}} + z_{\text{Ox}_1} e \Delta \phi_{\text{Ox}_1} \quad (5)$$

and

$$\Delta G_{\text{Red}_2-s_1}^{\text{inter}} = \frac{\text{SN}_{\text{Red}_2}^{\text{inter}}}{\text{SN}_{\text{Red}_2}^{\text{bulk}}} \Delta G_{\text{Red}_2-s_1}^{\text{bulk}} + z_{\text{Red}_2} e \Delta \phi_{\text{Red}_2} \quad (6)$$

where  $\Delta \phi_{\text{Ox}_1}$  and  $\Delta \phi_{\text{Red}_2}$  refer to the inner potential difference of  $\text{Ox}_1$  and  $\text{Red}_2$  respectively from bulk to interface,  $\Delta G_{\text{Ox}_1-s_1}^{\text{bulk}}$  and  $\Delta G_{\text{Red}_2-s_1}^{\text{bulk}}$  being the tabulated bulk desolvation energies.  $z_i$  represents the charge of the species “i” ( $i = \text{Ox}_1, \text{Red}_1, \text{Ox}_2, \text{Red}_2$ ). Thus  $w_{r1}$  becomes

$$w_{r1} = \frac{\text{SN}_{\text{Ox}_1}^{\text{inter}}}{\text{SN}_{\text{Ox}_1}^{\text{bulk}}} \Delta G_{\text{Ox}_1-s_1}^{\text{bulk}} + \frac{\text{SN}_{\text{Red}_2}^{\text{inter}}}{\text{SN}_{\text{Red}_2}^{\text{bulk}}} \Delta G_{\text{Red}_2-s_2}^{\text{bulk}} + z_{\text{Ox}_1} \Delta \phi_{\text{Ox}_1} + z_{\text{Red}_2} e \Delta \phi_{\text{Red}_2} \quad (7)$$

In an analogous manner,  $w_{p1}$  of the product is given by

$$w_{p1} = -\frac{\text{SN}_{\text{Ox}_2}^{\text{inter}}}{\text{SN}_{\text{Ox}_2}^{\text{bulk}}} \Delta G_{\text{Ox}_2-s_2}^{\text{bulk}} - \frac{\text{SN}_{\text{Red}_1}^{\text{inter}}}{\text{SN}_{\text{Red}_1}^{\text{bulk}}} \Delta G_{\text{Red}_1-s_1}^{\text{bulk}} - z_{\text{Ox}_2} \Delta \phi_{\text{Ox}_2} - z_{\text{Red}_1} e \Delta \phi_{\text{Red}_1} \quad (8)$$

$\Delta \phi_{\text{Ox}_2}$  and  $\Delta \phi_{\text{Red}_1}$  being the inner potential difference of  $\text{Ox}_2$  and  $\text{Red}_1$ . The negative signs indicate the movement of  $\text{Ox}_2$  and  $\text{Red}_1$  in a direction opposite to that of the reactants.<sup>8</sup>

The intrinsic Gibbs free energy change  $\Delta G_{\text{et}1}$  associated with the electron transfer between  $\text{Ox}_1$  and  $\text{Red}_2$  is given by

$$\Delta G_{\text{et}1} = -e(n_1 E_{\text{Ox}_1/\text{Red}_1}^{0,s_1} + n_2 E_{\text{Ox}_2/\text{Red}_2}^{0,s_2}) \quad (9)$$

where  $e$  represents the electronic charge and  $n_1$  and  $n_2$  denote the number of electrons in  $\text{Ox}_1/\text{Red}_1$  and  $\text{Ox}_2/\text{Red}_2$  couples ( $n_1 = n_2 = 1$  in the reactions considered here). At equilibrium,<sup>11</sup> because the activities of oxidized and reduced species are equal,

the equilibrium potentials of  $\text{Ox}_1/\text{Red}_1$  and  $\text{Ox}_2/\text{Red}_2$  become identical with the respective standard electrode potentials. Combining eqs 3–9, we obtain

$$\Delta G_{\text{eq,sharp}}^{\ddagger} = \left\{ \frac{\text{SN}_{\text{Ox}_1}^{\text{inter}}}{\text{SN}_{\text{Ox}_1}^{\text{bulk}}} \Delta G_{\text{Ox}_1-s_1}^{\text{bulk}} + \frac{\text{SN}_{\text{Red}_2}^{\text{inter}}}{\text{SN}_{\text{Red}_2}^{\text{bulk}}} \Delta G_{\text{Red}_2-s_2}^{\text{bulk}} - \frac{\text{SN}_{\text{Ox}_2}^{\text{inter}}}{\text{SN}_{\text{Ox}_2}^{\text{bulk}}} \Delta G_{\text{Ox}_2-s_2}^{\text{bulk}} - \frac{\text{SN}_{\text{Red}_1}^{\text{inter}}}{\text{SN}_{\text{Red}_1}^{\text{bulk}}} \Delta G_{\text{Red}_1-s_1}^{\text{bulk}} \right\} / 2 - \{ z_{\text{Ox}_2} e \Delta \phi_{\text{Ox}_2} + z_{\text{Red}_1} e \Delta \phi_{\text{Red}_1} - z_{\text{Ox}_1} e \Delta \phi_{\text{Ox}_1} - z_{\text{Red}_2} e \Delta \phi_{\text{Red}_2} \} / 2 - e(n_1 E_{\text{Ox}_1/\text{Red}_1}^{0,s_1} + n_2 E_{\text{Ox}_2/\text{Red}_2}^{0,s_2}) \quad (10)$$

It is imperative to point out that the reactant and solvent characteristics are reflected in the solvation numbers, Gibbs free energies, and inner potential differences whereas the intrinsic reactivity of the redox couple arises via the standard electrode potentials.

**2.2. Inner Potential Difference of Ions and Solvation Numbers in Aqueous and Organic Phases.** The electrostatic part of the work term in the free energy of activation is written via the difference in the inner potentials ( $\Delta \phi_i^s$ ) of the species  $i$  in a chosen solvent  $s$ , when transferred from the bulk to the interface. There are several methods by which the inner potential difference can be evaluated. Among them, mention may be made of<sup>12</sup> employing (i) the Nernst equation, taking into account the activity dependence of the chemical potential of the ions, (ii) standard ion-transfer potentials, which quantify the relative affinity of an ion in the two phases, and (iii) the Gouy–Chapman theory and its refinements. Here, we employ the Boltzmann distribution to evaluate  $\Delta \phi_i^s$ , whereby  $\Delta \phi_i^s$  may be represented as<sup>13</sup>

$$C_i^{\text{sur},s} = C_i^{\text{bulk},s} \exp\{-z_i F \Delta \phi_i^s / RT\} \quad (11)$$

where  $C_i^{\text{sur},s}$  and  $C_i^{\text{bulk},s}$  denote the surface and the bulk concentration of the species  $i$  ( $\text{Ox}_1, \text{Red}_1, \text{Ox}_2, \text{Red}_2$ ) in solvent  $s$  (org, aq).

The bulk desolvation energies of the reactants and products are still required for evaluating the free energy of activation from eq 10. Though these quantities in the aqueous phase have been tabulated from experimental techniques such as compress-

**TABLE 1: Inner Potentials of  $i$ -th Species ( $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Lu}^{3+}$ ,  $\text{Lu}^{4+}$ ,  $\text{TCNQ}^-$ ) in the Organic and Aqueous Phase at 298 K Estimated from Eq 11**

$C_i^{\text{sur},s}/C_i^{\text{bulk},s}$	$e\Delta\phi_i^s$ (eV) for $z_i = 2$	$e\Delta\phi_i^s$ (eV) for $z_i = 3$	$e\Delta\phi_i^s$ (eV) for $z_i = 4$	$e\Delta\phi_i^s$ (eV) for $z_i = -1$
0.05	0.038	0.026	0.019	-0.070
0.10	0.030	0.020	0.015	-0.059
0.15	0.024	0.016	0.012	-0.049
0.20	0.021	0.014	0.010	-0.041
0.25	0.018	0.012	0.009	-0.036
0.30	0.016	0.010	0.008	-0.031
0.35	0.014	0.009	0.007	-0.027
0.40	0.012	0.008	0.006	-0.024
0.45	0.010	0.007	0.005	-0.021
0.50	0.009	0.006	0.004	-0.018

<sup>a</sup> In this approximation, the ionic charges alone are assumed to influence the inner potential difference.

ibility measurements, ultrasonic methods, viscosity data, etc.,<sup>14</sup> the solvation details in the organic phase are not easy to obtain. Because our primary interest lies in an approximate order of magnitude calculation, we employ the Born charging process<sup>14</sup> for obtaining the solvation energies of ions in the organic phase viz.

$$\Delta G_{i-s}^{\text{bulk}} = -\frac{e^2}{2r_i} \left(1 - \frac{1}{\epsilon_s}\right) \quad (12)$$

where  $\Delta G_{i-s}^{\text{bulk}}$  denotes the bulk solvation energy of the species  $i$  in a chosen solvent  $s$ ,  $\epsilon_s$  is the dielectric permittivity of the solvent,  $r_i$  being the radius of the  $i$ -th ion.

Whereas the solvation numbers of ions in the aqueous phase are tabulated quantities in general, those in the organic phase are seldom available. In view of this, a simple prescription based on intuitive and geometric considerations is proposed whereby

$$\text{SN}_{i-s}^{\text{bulk}} = \frac{r_i^3}{r_s^3} \quad (13)$$

$\text{SN}_{i-s}^{\text{bulk}}$  denotes the bulk solvation number of  $i$  in the solvent  $s$ ,  $r_i$  and  $r_s$  being the radius of the ion and that of the solvent, respectively. The above equation follows from the definition of the solvation number (SN) as the ratio between the volume of the bare ion and effective volume of the solvent molecules.<sup>14</sup>

**2.3. Evaluation of the Equilibrium Free Energy of Activation.** The expression for  $\Delta G_{\text{eq,sharp}}^{\ddagger}$  contains various quantities pertaining to the ionic species and solvent molecules. To demonstrate its applicability, we focus our attention on two redox couples viz (i)  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Lu}(\text{bipthalocyanine})]^{4+}/[\text{Lu}(\text{bipthalocyanine})]^{3+}$  and (ii)  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  and  $\text{TCNQ}/\text{TCNQ}^-$  at the water/(1,2-DCE) interface.

To obtain  $\Delta\phi_i^s$ , the bulk and the interfacial concentrations are required. If the ratio  $C_i^{\text{sur},s}/C_i^{\text{bulk},s}$  is varied from 0.05 to 0.5 (very dilute solution to more concentrated) appropriate values of  $\Delta\phi_i^s$  can be evaluated. The value of  $C_i^{\text{sur},s}/C_i^{\text{bulk},s} > 0.5$  is not employed, because  $\Delta\phi_i^s$  is neglected at higher concentrations, in general. Table 1 provides the dependence of the inner potential difference of  $i$ -th species in the solvent  $s$ , upon the concentration ratio  $C_i^{\text{sur},s}/C_i^{\text{bulk},s}$ .

**2.3.1. Equilibrium Free Energy of Activation for the Reaction between  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  and  $[\text{Lu}(\text{bipthalocyanine})]^{4+/3+}$ .** For the

above reaction,<sup>5a</sup>  $\Delta G_{\text{eq,sharp}}^{\ddagger}$  may be written as

$$\Delta G_{\text{eq,sharp}}^{\ddagger} = \left\{ \frac{\text{SN}_{\text{Fe}^{3+}}^{\text{inter}}}{\text{SN}_{\text{Fe}^{3+}}^{\text{bulk}}} \Delta G_{\text{Fe}^{3+}-\text{water}}^{\text{bulk}} + \frac{\text{SN}_{\text{Lu}^{3+}}^{\text{inter}}}{\text{SN}_{\text{Lu}^{3+}}^{\text{bulk}}} \Delta G_{\text{Lu}^{3+},1,2-\text{DCE}}^{\text{bulk}} - \frac{\text{SN}_{\text{Lu}^{4+}}^{\text{inter}}}{\text{SN}_{\text{Lu}^{4+}}^{\text{bulk}}} \Delta G_{\text{Lu}^{4+},1,2-\text{DCE}}^{\text{bulk}} - \frac{\text{SN}_{\text{Fe}^{2+}}^{\text{inter}}}{\text{SN}_{\text{Fe}^{2+}}^{\text{bulk}}} \Delta G_{\text{Fe}^{2+}-\text{water}}^{\text{bulk}} \right\} / 2 - \{ z_{\text{Fe}^{3+}} e \Delta \phi_{\text{Fe}^{3+}} + z_{\text{Lu}^{3+}} e \Delta \phi_{\text{Lu}^{3+}} - z_{\text{Lu}^{4+}} e \Delta \phi_{\text{Lu}^{4+}} - z_{\text{Fe}^{2+}} e \Delta \phi_{\text{Fe}^{2+}} \} / 2 - e(n_1 E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{0,\text{water}} + n_2 E_{\text{Lu}^{4+}/\text{Lu}^{3+}}^{0,1,2-\text{DCE}}) \quad (14)$$

using eq 10. For brevity, we denote the redox couple  $[\text{Lu}(\text{bipthalocyanine})]^{4+}/[\text{Lu}(\text{bipthalocyanine})]^{3+}$  as  $\text{Lu}^{4+}/\text{Lu}^{3+}$ . The solvation numbers  $\text{SN}_{\text{M}^{n+}-s}$  of  $\text{Lu}^{3+}$  and  $\text{Lu}^{4+}$  ions in the organic phase may be computed using

$$\text{SN}_{\text{Lu}^{3+},1,2-\text{DCE}}^{\text{bulk}} = \frac{r_{\text{Lu}^{3+}}^3}{r_{1,2-\text{DCE}}^3} \quad \text{and} \quad \text{SN}_{\text{Lu}^{4+},1,2-\text{DCE}}^{\text{bulk}} = \frac{r_{\text{Lu}^{4+}}^3}{r_{1,2-\text{DCE}}^3} \quad (15)$$

and the radius of  $\text{Lu}^{3+}$  and  $\text{Lu}^{4+}$  has been estimated as<sup>5a</sup> 0.88 and 0.95 Å, respectively. These equations yield the bulk solvation numbers of  $\text{Lu}^{3+}$  and  $\text{Lu}^{4+}$  in 1,2-DCE as 24.3 and 19.3, whereas those of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  are tabulated as 11 and 12, respectively.<sup>14</sup> The interfacial solvation numbers of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  in water and  $\text{Lu}^{3+}$  and  $\text{Lu}^{4+}$  ions in 1,2-DCE are reported in Table 2 assuming different values for the ratio of  $\text{SN}_{\text{M}^{n+}-s}^{\text{inter}}/\text{SN}_{\text{M}^{n+}-s}^{\text{bulk}}$ , which reflect various extents of desolvation of the ionic species. The hydration energies<sup>14</sup> of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions are 51.45 and 20.42 eV; however, for computing the solvation free energies of  $\text{Lu}^{3+}$  and  $\text{Lu}^{4+}$  ions in 1,2-DCE, the Born charging process given by eq 12 is employed. Because the dielectric permittivity of 1,2-dichloroethane is<sup>15</sup> 10.42, we obtain the bulk desolvation energies of  $\text{Lu}^{3+}$  and  $\text{Lu}^{4+}$  as 72.40 and 67.07 eV, respectively. The standard reduction potential for  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  in water<sup>11</sup> is 0.77 V whereas that of  $[\text{Lu}(\text{bipthalocyanine})]^{4+}/[\text{Lu}(\text{bipthalocyanine})]^{3+}$  in 1,2-DCE has been measured<sup>5</sup> as -0.538 V. Consequently,  $\Delta G_{\text{et}_1}$  follows as -0.232 eV from eq 9. Using the above parameters, the equilibrium free energy of activation ( $\Delta G_{\text{eq,sharp}}^{\ddagger}$ ) is evaluated (Table 2) for reaction 1, when  $C_i^{\text{sur},s}/C_i^{\text{bulk},s} = 0.05$ , because this value represents the maximum contribution of the inner potential difference, as shown in Table 1.

In terms of the numerical factors,

$$\Delta G_{\text{eq,sharp}}^{\ddagger} = -0.234 + 2.34 \text{SN}_{\text{Fe}^{3+}}^{\text{inter}} + 1.49 \text{SN}_{\text{Lu}^{3+}}^{\text{inter}} - 1.74 \text{SN}_{\text{Lu}^{4+}}^{\text{inter}} - 0.85 \text{SN}_{\text{Fe}^{2+}}^{\text{inter}} \quad (16)$$

where  $\Delta G_{\text{eq,sharp}}^{\ddagger}$  is in eV.

**2.3.2. Equilibrium Free Energy of Activation for the Reaction between  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  and  $\text{TCNQ}^{0/-}$ .** Reaction 2 at the water/1,2-DCE interface has been investigated using scanning electrochemical microscopy<sup>6</sup> (SECM), and it is imperative to verify the validity of eq 10 in this case. However, the molecular radii of TCNQ and  $\text{TCNQ}^-$ , essential for computing the solvation numbers and energies are not directly available. Hence these are estimated indirectly with the help of the diffusion controlled

**TABLE 2: Dependence of the Free Energy of Activation ( $\Delta G_{\text{Eq,Sharp}}^\ddagger$ ) and Rate Constant  $k_r$  upon the Extent of Desolvation of Ionic Species at the Interface Using Eqs 16 and 18 for Reactions 1 and 2, Respectively**

ions	solvent	extent of desolvation	SN <sup>inter</sup>	$\Delta G_{\text{eq,sharp}}^\ddagger$ (eV)		$k_r$ (M <sup>-1</sup> cm s <sup>-1</sup> )		$\lambda$ (eV)	
				rxn 1	rxn 2	rxn 1	rxn 2	rxn 1	rxn 2
Fe <sup>3+</sup>	water	0.25	8.25	13.39	20.40	≈0	≈0	53.55	81.60
Fe <sup>2+</sup>	water	0.25	9.00						
Lu <sup>3+</sup>	1,2-DCE	0.25	18.23						
Lu <sup>4+</sup>	1,2-DCE	0.25	14.48						
TCNQ	1,2-DCE	0.25	12.44						
TCNQ <sup>-</sup>	1,2-DCE	0.25	8.17						
Fe <sup>3+</sup>	water	0.50	5.50	8.85	13.41	≈0	≈0	35.39	53.64
Fe <sup>2+</sup>	water	0.50	6.00						
Lu <sup>3+</sup>	1,2-DCE	0.50	12.15						
Lu <sup>4+</sup>	1,2-DCE	0.50	9.65						
TCNQ	1,2-DCE	0.50	8.29						
TCNQ <sup>-</sup>	1,2-DCE	0.50	5.45						
Fe <sup>3+</sup>	water	0.75	2.75	4.31	6.28	≈0	≈0	17.22	25.12
Fe <sup>2+</sup>	water	0.75	3.00						
Lu <sup>3+</sup>	1,2-DCE	0.75	6.08						
Lu <sup>4+</sup>	1,2-DCE	0.75	4.83						
TCNQ	1,2-DCE	0.75	4.15						
TCNQ <sup>-</sup>	1,2-DCE	0.75	2.72						
Fe <sup>3+</sup>	water	0.90	1.10	1.58	2.11	$7.1 \times 10^{-16}$	$8.38 \times 10^{-25}$	6.33	8.44
Fe <sup>2+</sup>	water	0.90	1.20						
Lu <sup>3+</sup>	1,2-DCE	0.90	2.43						
Lu <sup>4+</sup>	1,2-DCE	0.90	1.93						
TCNQ	1,2-DCE	0.90	1.66						
TCNQ <sup>-</sup>	1,2-DCE	0.90	1.09						
Fe <sup>3+</sup>	water	0.93	0.77	1.04	1.25	$9.68 \times 10^{-7}$	$2.98 \times 10^{-10}$	4.16	5.00
Fe <sup>2+</sup>	water	0.93	0.84						
Lu <sup>3+</sup>	1,2-DCE	0.93	1.70						
Lu <sup>4+</sup>	1,2-DCE	0.93	1.35						
TCNQ	1,2-DCE	0.93	1.16						
TCNQ <sup>-</sup>	1,2-DCE	0.93	0.76						
Fe <sup>3+</sup>	water	0.935	0.72	0.95	1.14	$3.22 \times 10^{-5}$	$1.74 \times 10^{-8}$	3.80	4.56
Fe <sup>2+</sup>	water	0.935	0.78						
Lu <sup>3+</sup>	1,2-DCE	0.935	1.58						
Lu <sup>4+</sup>	1,2-DCE	0.935	1.26						
TCNQ	1,2-DCE	0.935	1.08						
TCNQ <sup>-</sup>	1,2-DCE	0.935	0.71						
Fe <sup>3+</sup>	water	0.94	0.66	0.86	0.95	$1.07 \times 10^{-3}$	$2.92 \times 10^{-5}$	3.42	3.80
Fe <sup>2+</sup>	water	0.94	0.72						
Lu <sup>3+</sup>	1,2-DCE	0.94	1.46						
Lu <sup>4+</sup>	1,2-DCE	0.94	1.16						
TCNQ	1,2-DCE	0.94	0.995						
TCNQ <sup>-</sup>	1,2-DCE	0.94	0.65						
Fe <sup>3+</sup>	water	0.945	0.61	0.79	0.86	0.016	$9.04 \times 10^{-4}$	3.14	3.44
Fe <sup>2+</sup>	water	0.945	0.66						
Lu <sup>3+</sup>	1,2-DCE	0.945	1.34						
Lu <sup>4+</sup>	1,2-DCE	0.945	1.06						
TCNQ	1,2-DCE	0.945	0.91						
TCNQ <sup>-</sup>	1,2-DCE	0.945	0.599						
Fe <sup>3+</sup>	water	0.95	0.55	0.67	0.75	1.56	0.09	2.69	3.00
Fe <sup>2+</sup>	water	0.95	0.60						
Lu <sup>3+</sup>	1,2-DCE	0.95	1.22						
Lu <sup>4+</sup>	1,2-DCE	0.95	0.97						
TCNQ	1,2-DCE	0.95	0.83						
TCNQ <sup>-</sup>	1,2-DCE	0.95	0.55						
Fe <sup>3+</sup>	water	0.955	0.50	0.59	0.55	43.98	167.30	2.35	2.20
Fe <sup>2+</sup>	water	0.955	0.54						
Lu <sup>3+</sup>	1,2-DCE	0.955	1.09						
Lu <sup>4+</sup>	1,2-DCE	0.955	0.87						
TCNQ	1,2-DCE	0.955	0.75						
TCNQ <sup>-</sup>	1,2-DCE	0.955	0.49						
Fe <sup>3+</sup>	water	0.96	0.44	0.49	0.48	$1.73 \times 10^3$	$3.44 \times 10^3$	1.97	1.92
Fe <sup>2+</sup>	water	0.96	0.48						
Lu <sup>3+</sup>	1,2-DCE	0.96	0.97						
Lu <sup>4+</sup>	1,2-DCE	0.96	0.77						
TCNQ	1,2-DCE	0.96	0.66						
TCNQ <sup>-</sup>	1,2-DCE	0.96	0.44						
Fe <sup>3+</sup>	water	0.965	0.39	0.41	0.28	$5.35 \times 10^4$	$6.18 \times 10^6$	1.62	1.12
Fe <sup>2+</sup>	water	0.965	0.42						
Lu <sup>3+</sup>	1,2-DCE	0.965	0.85						
Lu <sup>4+</sup>	1,2-DCE	0.965	0.68						



TABLE 2 (Continued)

ions	solvent	extent of desolvation	SN <sup>inter</sup>	$\Delta G_{\text{eq,sharp}}^{\ddagger}$ (eV)		$k_r$ (M <sup>-1</sup> cm s <sup>-1</sup> )		$\lambda$ (eV)	
				rxn 1	rxn 2	rxn 1	rxn 2	rxn 1	rxn 2
TCNQ	1,2-DCE	0.965	0.58						
TCNQ <sup>-</sup>	1,2-DCE	0.965	0.38						
Fe <sup>3+</sup>	water	0.97	0.33	0.31	0.16	$2.10 \times 10^6$	$8.96 \times 10^8$	1.24	0.64
Fe <sup>2+</sup>	water	0.97	0.36						
Lu <sup>3+</sup>	1,2-DCE	0.97	0.73						
Lu <sup>4+</sup>	1,2-DCE	0.97	0.58						
TCNQ	1,2-DCE	0.97	0.50						
TCNQ <sup>-</sup>	1,2-DCE	0.97	0.33						
Fe <sup>3+</sup>	water	0.975	0.28	0.24	-0.04	$3.31 \times 10^7$	$1.61 \times 10^{12}$	0.96	-0.16
Fe <sup>2+</sup>	water	0.975	0.30						
Lu <sup>3+</sup>	1,2-DCE	0.975	0.61						
Lu <sup>4+</sup>	1,2-DCE	0.975	0.48						
TCNQ	1,2-DCE	0.975	0.42						
TCNQ <sup>-</sup>	1,2-DCE	0.975	0.27						
Fe <sup>3+</sup>	water	0.98	0.22	0.13	-0.12	$2.56 \times 10^9$	$3.310 \times 10^{13}$	0.51	-0.48
Fe <sup>2+</sup>	water	0.98	0.24						
Lu <sup>3+</sup>	1,2-DCE	0.98	0.49						
Lu <sup>4+</sup>	1,2-DCE	0.98	0.39						
TCNQ	1,2-DCE	0.98	0.33						
TCNQ <sup>-</sup>	1,2-DCE	0.98	0.22						

rate constants, as shown below. The equilibrium free energy of activation for the reaction 2 follows from eq 10 as

$$\Delta G_{\text{eq,sharp}}^{\ddagger} = \left\{ \frac{\text{SN}_{\text{Fe}^{3+}}^{\text{inter}}}{\text{SN}_{\text{Fe}^{3+}}^{\text{bulk}}} \Delta G_{\text{Fe}^{3+}-\text{water}}^{\text{bulk}} + \frac{\text{SN}_{\text{TCNQ}^{-}}^{\text{inter}}}{\text{SN}_{\text{TCNQ}^{-}}^{\text{bulk}}} \Delta G_{\text{TCNQ}^{-}-1,2-\text{DCE}}^{\text{bulk}} - \frac{\text{SN}_{\text{TCNQ}}^{\text{inter}}}{\text{SN}_{\text{TCNQ}}^{\text{bulk}}} \Delta G_{\text{TCNQ}-1,2-\text{DCE}}^{\text{bulk}} - \frac{\text{SN}_{\text{Fe}^{2+}}^{\text{inter}}}{\text{SN}_{\text{Fe}^{2+}}^{\text{bulk}}} \Delta G_{\text{Fe}^{2+}-\text{water}}^{\text{bulk}} \right\} / 2 - \{ z_{\text{Fe}^{3+}} e \Delta \phi_{\text{Fe}^{3+}} + z_{\text{TCNQ}^{-}} e \Delta \phi_{\text{TCNQ}^{-}} - z_{\text{TCNQ}} e \Delta \phi_{\text{TCNQ}} - z_{\text{Fe}^{2+}} e \Delta \phi_{\text{Fe}^{2+}} \} / 2 - e (n_1 E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{0,\text{water}} + n_2 E_{\text{TCNQ}/\text{TCNQ}^{-}}^{0,1,2-\text{DCE}}) \quad (17)$$

The solvation numbers  $\text{SN}_{\text{M}^{n+}-s}$  of TCNQ and TCNQ<sup>-</sup> in the organic phase is evaluated employing

$$\text{SN}_{\text{TCNQ}-1,2-\text{DCE}}^{\text{bulk}} = \frac{r_{\text{TCNQ}}^3}{r_{1,2-\text{DCE}}^3} \quad \text{and} \quad \text{SN}_{\text{TCNQ}^{-}-1,2-\text{DCE}}^{\text{bulk}} = \frac{r_{\text{TCNQ}^{-}}^3}{r_{1,2-\text{DCE}}^3} \quad (18)$$

The radius of TCNQ and TCNQ<sup>-</sup> has been estimated as<sup>5b</sup> 0.765 and 0.665 Å, respectively, and hence their bulk solvation numbers follow as 16.58 and 10.89. The interfacial solvation numbers of TCNQ and TCNQ<sup>-</sup> are calculated as in the earlier case and reported in Table 2. Employing eq 12, the bulk desolvation energies of TCNQ and TCNQ<sup>-</sup> are estimated as 83.29 and 95.80 eV using the above radius values. The standard reduction potential of TCNQ/TCNQ<sup>-</sup> couple in 1,2-DCE has been reported<sup>5c</sup> as -0.105 V and hence  $\Delta G_{\text{et1}}$  is deduced as -0.665 eV from eq 9. Thus, in terms of numerical factors,  $\Delta G_{\text{eq,sharp}}^{\ddagger}$  becomes

$$\Delta G_{\text{eq,sharp}}^{\ddagger} = -0.705 + 2.34 \text{SN}_{\text{Fe}^{3+}}^{\text{inter}} + 8.80 \text{SN}_{\text{TCNQ}^{-}}^{\text{inter}} - 5.02 \text{SN}_{\text{TCNQ}}^{\text{inter}} - 0.85 \text{SN}_{\text{Fe}^{2+}}^{\text{inter}} \quad (19)$$

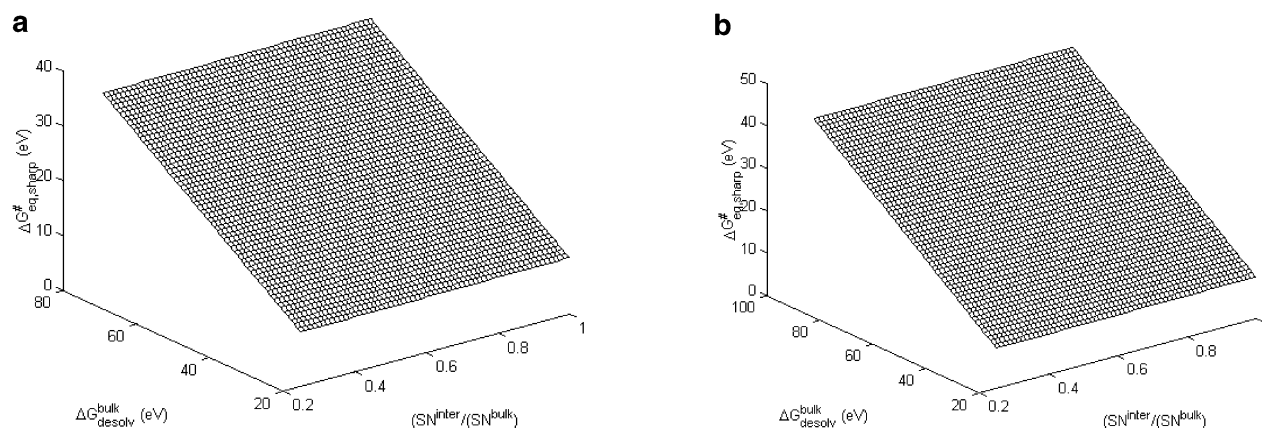
at  $C_i^{\text{sur},s}/C_i^{\text{bulk},s} = 0.05$ . When the values of  $C_i^{\text{sur},s}/C_i^{\text{bulk},s}$  are increased to 0.5, the first terms of eqs 16 and 19 become -0.232 and -0.709, thus indicating that low values of  $C_i^{\text{sur},s}/C_i^{\text{bulk},s}$

influence  $\Delta G_{\text{eq,sharp}}^{\ddagger}$  to a greater extent for both the reactions. Hence, the equilibrium free energy of activation depends largely upon the magnitude of the interfacial (de)solvation numbers of the species involved.

**2.4. Interfacial Solvation Characteristics and Intrinsic Reactivity of the Redox Reactions.** The equilibrium free energy of activation,  $\Delta G_{\text{eq,sharp}}^{\ddagger}$  varies with the extent of ionic desolvation and is a measure of the shielding effect of solvent molecules. Parts a and b of Figure 1 depict the interplay between the bulk solvation number of ions and the solvent shielding factor (denoted as  $\text{SN}_i^{\text{inter}}/\text{SN}_i^{\text{bulk}}$ ). As anticipated, an enhancement in the ratio  $\text{SN}_i^{\text{inter}}/\text{SN}_i^{\text{bulk}}$  yields larger values of  $\Delta G_{\text{eq,sharp}}^{\ddagger}$ . Further, the interfacial solvation numbers control the reaction rate by either increasing or decreasing the activation energy barrier.

The value of  $\Delta G_{\text{et1}}$  in comparison with the work terms needs to be analyzed to determine their relative importance in influencing  $\Delta G_{\text{eq,sharp}}^{\ddagger}$ . As shown earlier,  $\Delta G_{\text{et1}}$  is evaluated as -0.232 and -0.665 eV from eq 9 for the reactions represented by eqs 1 and 2, whereas the work term  $(w_{r1} + w_{p1})/2$  varies from ca. (i) 0.45 to 13.25 eV for reaction 1 and (ii) -0.32 to +20.20 eV for reaction 2, depending upon the extent of (de)solvation of the ions at the interface (0.25–0.98). This large variation in the values of the work terms between the two reactions may be attributed to the higher hydrophobicity of [Lu(bipthalocyanine)]<sup>4+/3+</sup> than the TCNQ<sup>-/0</sup> couple. Thus the work terms turn out to be a major factor in determining the rate of the reaction which is ascribed to the predominant role played by the solvation characteristics of ions as manifested by the parameters such as  $(\text{SN}_{\text{Ox}_1}^{\text{inter}}/\text{SN}_{\text{Ox}_1}^{\text{bulk}}) \Delta G_{\text{Ox}_1-s}^{\text{desolv}}$ ,  $(\text{SN}_{\text{Ox}_2}^{\text{inter}}/\text{SN}_{\text{Ox}_2}^{\text{bulk}}) \Delta G_{\text{Ox}_2-s}^{\text{desolv}}$ , etc. Consequently, the electronic coupling between the reactants appears to be less effective in decreasing the activation energy barrier.

**2.5. Solvent Reorganization Energy and Rate Constants.** The solvent reorganization energy ( $\lambda$ ) reflects the extent of change in the solvent atmosphere, when the reactants are converted to the products.<sup>16</sup> If the overpotential is zero,<sup>17</sup>  $\lambda \approx 4\Delta G_{\text{eq}}^{\ddagger}$  in the case of electron transfer at metal/electrolyte interfaces. For liquid/liquid interfaces, when the concentration of aqueous phase is much higher than that of the organic phase, the analogy with metal/electrolyte interfaces holds good and hence the above expression for  $\lambda$  is grossly adequate.<sup>5</sup> In view



**Figure 1.** Dependence of the equilibrium free energy of activation upon the bulk solvation number and solvent shielding effect, as obtained from eqs 16 and 19. The range of values chosen are (a) 0.25:0.0125:1.00 for  $SN_i^{\text{inter}}/SN_i^{\text{bulk}}$  and 20:0.9167:75 for the bulk desolvation energy of ions for the redox reaction 1 and (b) 0.25:0.0125:1.00 for  $SN_i^{\text{inter}}/SN_i^{\text{bulk}}$  and 20:1.1667:90 for the bulk desolvation energy of ions for the redox reaction 2.

of this, the solvent reorganization energy  $\lambda$  has also been estimated for different extent of desolvation as shown in Table 2.  $\lambda$  spans a wide range, viz. 0.51 to 53.55 eV, for the reaction 1 and from  $-0.48$  to  $+81.60$  eV for the other reaction, being essentially dictated by the interfacial solvation numbers. For extremely effective desolvation of species, negative  $\Delta G_{\text{eq}}^{\ddagger}$  vis a vis  $\lambda$  arises, leading to the enhancement in the reaction rate. Interestingly,  $\lambda$  for reaction 1 has been reported as 3.21 eV by Marcus using a continuum dielectric model<sup>18–20</sup> and by Benjamin<sup>21</sup> employing simulation studies. If  $SN_i^{\text{inter}}/SN_i^{\text{bulk}}$  is assumed to be 0.945, a value of 3.14 eV for  $\lambda$  is obtained from the present phenomenological approach consistent with the above value of 3.21 eV reported.<sup>18–21</sup> We may note that a large extent of desolvation of the reactants is indeed anticipated because maximum desolvation leads to an inverse proportionality between the solvent shielding factor and  $\lambda$ .

The rate constant  $k_r$  pertaining to the electron transfer across liquid/liquid interfaces may be expressed as<sup>19</sup>

$$k_r = \kappa \nu V_r \exp \left\{ - \frac{\Delta G_{\text{eq,sharp}}^{\ddagger}}{RT} \right\} \quad (20)$$

where  $\kappa$  is the Landau–Zener factor, normally assumed as unity,<sup>10</sup>  $\nu$  being the frequency<sup>16</sup> of the molecular motion  $\sim 10^{18} \text{ s}^{-1}$ .  $V_r$ , the “mean molar reaction volume”, incorporates various configurations of the reactant pairs and may be evaluated assuming the ions as hard spheres<sup>19</sup> viz.

$$V_r = 2\pi(r_{\text{Ox}_1} + r_{\text{Red}_2})(\delta R)^3 \quad (21)$$

where  $r_{\text{Ox}_1}$  and  $r_{\text{Red}_2}$  refer to the radius of  $\text{Ox}_1$  and  $\text{Red}_2$  and  $\delta R$  is the length scale arising from the weighting of the reactant configurations. In general, for reaction of the type (1) and (2), the values of  $(r_{\text{Ox}_1} + r_{\text{Red}_2})$  and  $\delta R$  are customarily assumed to be 10 and 1 Å, respectively.<sup>19</sup> Table 2 depicts the rate constants for the electron-transfer reaction of  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  in water with (i)  $[\text{Lu}(\text{bipthalocyanine})]^{4+}/[\text{Lu}(\text{bipthalocyanine})]^{3+}$  and (ii)  $\text{TCNQ}^-/\text{TCNQ}$  in 1,2-DCE, for different  $\Delta G_{\text{eq,sharp}}^{\ddagger}$  values. From Table 2, it is noticed that as the extent of desolvation increases, the rate of electron transfer is enhanced. For values of  $SN_i^{\text{inter}}/SN_i^{\text{bulk}}$  ranging from 0.25 to 0.75, the rate of the reaction tends to zero, because large positive values of  $\Delta G_{\text{eq,sharp}}^{\ddagger}$  are obtained. However, it is interesting to note that the rate constant increases for reaction 1, ca. from  $10^{-5}$  to  $10^9 \text{ M}^{-1} \text{ cm s}^{-1}$  and from  $10^{-8}$  to  $10^{12} \text{ M}^{-1} \text{ cm s}^{-1}$  for reaction 2, as the solvent shielding factor decreases. Further, one may

anticipate an efficient method of accelerating a reaction if greater interfacial desolvation of the reactants can be achieved. It is essential to emphasize here that these values for rate constants have been obtained using  $\kappa \nu$  as  $10^{18} \text{ s}^{-1}$ . Moreover, the rate constant for the heterogeneous electron-transfer reaction between the redox couple  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  and  $\text{TCNQ}^{-/0}$  as represented by eq 2 has been reported as  $0.06 \text{ M}^{-1} \text{ cm s}^{-1}$ , whereas the present analysis, when  $\Delta G_{\text{eq,sharp}}^{\ddagger}$  equals 0.75 eV, yields a value of  $0.09 \text{ M}^{-1} \text{ cm s}^{-1}$ , consistent with the experimental data<sup>6</sup> deduced with the help of SECM techniques. Analogously, for reaction 1,  $k_r$  is deduced as  $0.016 \text{ M}^{-1} \text{ cm s}^{-1}$  for  $\Delta G_{\text{eq,sharp}}^{\ddagger} = 0.79 \text{ eV}$  in gross agreement with the value of  $0.03 \text{ M}^{-1} \text{ cm s}^{-1}$  evaluated by Marcus from dielectric continuum model.

### 3. Perspectives and Summary

The foregoing analysis has provided a macroscopic framework whereby the free energy of activation for a chosen redox reaction can be evaluated from various parameters of the reactants and solvents. Although the computed rate constant is in satisfactory agreement with the “experimental data” pertaining to the reactions of  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  with  $\text{TCNQ}^-/\text{TCNQ}$  and  $[\text{Lu}(\text{bipthalocyanine})]^{4+}/[\text{Lu}(\text{bipthalocyanine})]^{3+}$  at the water/1,2 dichloroethane interface for a specific choice of parameters, several refinements need to be carried out. Among them, mention may be made of the need for accurate values for the solvation characteristics of ions. As is well-known, strongly solvated ions are less reactive and the present formalism is consistent with this postulate because the rate constant is effectively nonzero only when the extent of (de)solvation of the ions is  $\geq 0.93$ . The origin of the desolvation behavior and its influence due to the driving force needs further analysis. By invoking the approximate relation between  $\lambda$  and  $\Delta G_{\text{eq,sharp}}^{\ddagger}$  viz  $\lambda \approx 4\Delta G_{\text{eq,sharp}}^{\ddagger}$ , the solvent reorganization energy obtained here is in agreement with that deduced by Marcus using a sharp boundary model with the help of dielectric continuum theories. However, the composition of  $\lambda$  in terms of microscopic solvent polarization parameters requires a detailed investigation.<sup>22</sup> The interfacial potential distribution has not been explicitly incorporated here, although for investigating the effect of the electrical double layer on charge-transfer kinetics, the potential distribution too needs to be accounted for more rigorously. This limitation, coupled with the more reliable estimates of the bulk solvation numbers of the ions in the organic phase needs to be overcome for a quantitative description of electron-transfer processes across liquid/liquid interfaces.

In summary, the following conclusions emerge from the present analysis: (i) the work terms involving the solvation characteristics of reactants and products dictate the magnitude of the equilibrium free energy of activation, (ii) the electrostatic part ( $\Delta\phi_i$ ) constituting the work term is negligible in comparison with the chemical part viz. solvation characteristics of the species, and (iii) the magnitude of the solvent shielding factor dictates the feasibility of electron-transfer reactions at liquid/liquid interfaces.

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