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Unusual mechanism for the short-range electron transfer within gold–alkanethiol–ionic-liquid films of subnanometer thickness

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Exploiting nanoscopically tunable composite gold–alkanethiol–ionic-liquid/ferrocene self-assembled systems with tunable electron transfer distance, we discovered in the case of thinner alkanethiol films a thermally activated electron transfer pattern totally controlled by the viscosity-related slow relaxation mode(s) of the ionic liquid acting as the reactant's fluctuating environment. This pattern manifested through the activation enthalpy and volume parameters that are identical to those for viscous flow was explained in terms of the extreme adiabatic mechanism with a vanishing Marcus barrier (via the exponential Franck-Condon-like term approaching unity).

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Electron transfer (ET) by thermally activated hopping over localized centers is a central physical phenomenon occurring within the broad spectrum of matter such as nonconducting crystalline solids, amorphous glasses, fluidic or viscous liquids, and biomolecules [1]. The relevant theoretical framework that tracks back to milestone work by Landau [2] and Zener [3] distinguishes two general patterns of ET including regimes of weak and strong donor-acceptor electronic coupling, also known as nonadiabatic (diabatic) and adiabatic limiting cases (see [1,4–8], e.g., for representative reviews). The perceptive power of basic theoretical notion has been demonstrated in numerous cases of solid, liquid, and biological systems (see, e.g., [1,4,5,9–11]). Development of self-assembling techniques implying application of noble-metal electrodes coated by self-assembled organic (e.g., alkanethiol) monolayer films (SAMs) of essentially variable composition opened virtually unlimited possibilities for the breakthrough in fundamental and innovative nanotechnological developments [12–15]. In particular, the apt possibility of smooth variation in the film thickness allowed for the fine tuning of electronic coupling within an uniquely broad range, hence testing of extreme mechanistic patterns and the changeover between them [14–21]. Thanks to this experimental strategy, for a wide range of SAM implicated heterogeneous systems for the case of long-range electron exchange, the nonadiabatic (diabatic) mechanism has been identified with a high confidence due to the well-recognizable experimental signature of exponential decay of ET rate constant with ET distance [1,4,14–19]. The remarkable feature for nonadiabatic ET is that the rate constant is directly determined by the insulating properties of spacers (SAMs) including their chemical composition and thickness [1,4,13,14].

The situation is quite different for the case of adiabatic ET implying short-range yet outer-sphere electron exchange within the same donor-acceptor motif [15–19]. According to the general theoretical notion, the relevant expression for the rate constant can be presented through) [1,7–9,16–19,22]

$$k_{ET(AD)} \propto \nu_{eff} \exp(-\Delta G_a^*/RT), \tag{1}$$

where ν_{eff} is the effective frequency of a fluctuating medium [7,8,16,17] and ΔG_a^* is the activation free energy due to the Franck-Condon factor (free of the pre-exponential–viscosity related contribution, *vide infra*) [1,4–17]. Hence, depending on the placement of the redox probe (e.g., solid crystal versus viscose solvent), the effective frequency, ν_{eff}, may be related either to the crystal lattice's fixed quasiharmonic ballistic motion (longitudinal optic-mode phonons) [1,8,9] or to the orientational or/and translational relaxation (diffusion) in turn related to the solution (or the immediate) viscosity [1,6–8,16,17,22] expressed by

$$\nu_{eff} \propto \left(\frac{\varepsilon_S}{\varepsilon_\infty}\right)\frac{RT}{\eta}, \tag{2}$$

in which ε_S and ε_∞ are the relative permittivity of the medium at zero and infinite frequencies of the applied field, respectively, and η is the medium's viscosity. This is the case of interest in the present work. Note that the validity of Eqs. (1) and (2) indicates only that both the viscous flow and kinetic ET event are controlled by the same slow relaxational mode(s) of the solvent (solution).

However, notwithstanding the distinct theoretical prediction, unlike the situation with the nonadiabatic ET, currently there is no common opinion on the real possibility for an experimental detection of adiabatic ET or distinguishing it from less basic additional (mimicking) patterns, especially for the case of biomolecular ET (see, e.g., Refs. [17–19]). We do believe that by the thorough exploitation of nanoscopic devices of the present type, with slowly relaxing fluids as fluctuating environments, including viscous molecular liquids and liquid crystals along with relatively novel type of

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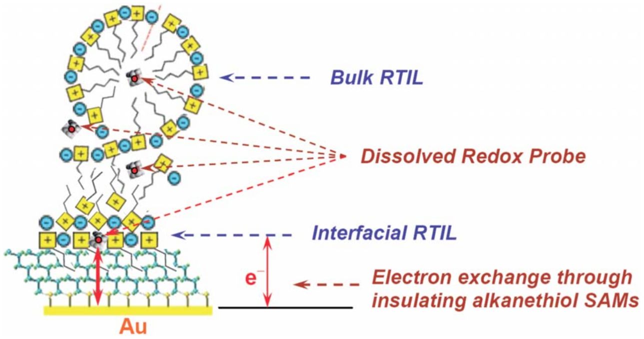

FIG. 1. (Color online) Schematic presentation of the Au/SAM/RTIL/RP multicomponent system (interfacial region) under investigation. Note, the essentially different local order of RTIL in the bulk and surface-adjacent areas, and the interpenetration of aliphatic chains due to SAMs and [bmim] cations, respectively. The RTIL charged components attributable to [bmim] (heads) and $[NTf_2]$ (core) are depicted as squares and circles, and labeled by "+" and "−," respectively.

soft-matter-room-temperature ionic liquids (RTILs), one may attempt to recognize and set general experimental boundaries for the strong coupling (adiabatic) mechanism by resembling the free energy, enthalpy, and volume activation parameters for the "true" short-range ET event and the actual macroscopic viscosity of the medium.

In the previous work [20,21] it has been demonstrated that metal (gold)/SAM/RTIL junctions are either especially stable and defect free or essentially recovered from defects thanks to the specific SAM-RTIL interaction (interpenetration of their alkyl chains, see Fig. 1) to meet the purposes of accurate and reproducible determination of ET rate constants for electron exchange between the electrode and the redox probe solubilized in a typical RTIL, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[bmim][NTf_2]$). RTILs, $[bmim][NTf_2]$ in particular, are known as liquids of exceptional physical properties [23–31] and promises for technological applications [32]. First of all, a broad distribution of relaxational characteristics, involving both the solvent's fast and slow degrees of freedom, emerging with comparable amplitudes, should be outlined. The results of recent studies by dielectric time-resolved light emission and NMR spectroscopy [23–27], along with molecular dynamics (MD) simulations [29–31] indicated essentially inhomogeneous nanostructural organization of RTILs (in both the bulk and surface-adjacent areas), for which relaxation dynamics was found to be biphasic, consisting of a subpicosecond (100 fs to 200 ps) and very pronounced slower components, the latter stretched down to tens and, presumably, hundreds of nanoseconds [27]. The unique physical properties of RTILs, such as an essential microscopic inhomogeneity (the unique mixture of polar and hydrophobic components tending to segregate [29–31], see Fig. 1 below), contrasting them from common molecular liquids but apparently resembling them with some key features of biomolecules, allow for insights in mechanistic details and generalization of the accumulated knowledge on short-range ET phenomenon in soft matter. In addition, it has been demonstrated that in the case of $Au/SAM/[bmim][NTf_2]$ junctions, compared to conventional systems involving common electrolyte solutions, the double-layer pre-equilibrium constituent is negligible and should not notably affect experimental rate constants, hence activation parameters deducible from kinetic studies.

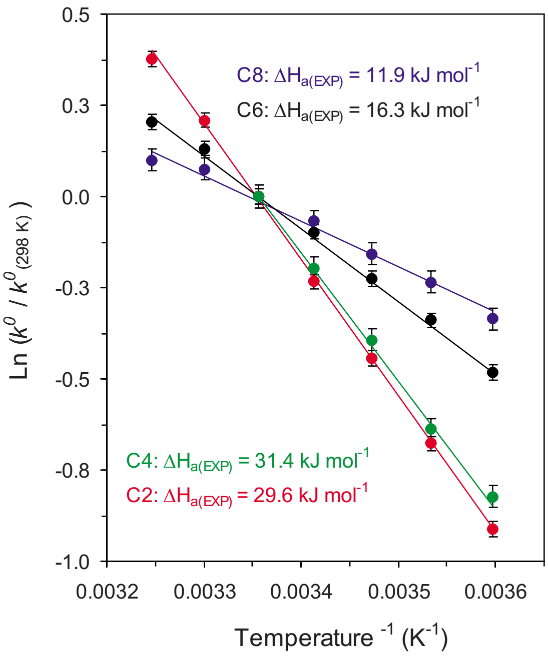

FIG. 2. (Color online) Arrhenius-like plots for the reduced ET rate constants for cases of $Au/SAM/[bmim][NTf_2]/Fe(Cp)_2]^{0/+}$ composite systems involving alkanethiol SAMs with carbon numbers of $c=2$, 4, 6, and 8 (from bottom to top, on the right).

We took the advantage of the advanced methodology of fast-scan cyclic voltammetry [35,36] and related analyses [21,33,34] to extract intrinsic ET rate constants under the conditions of zero overpotential ($\Delta G_o=0$ that is the standard case for the method of fast-scan cyclic voltammetry [35,36]) applied throughout under variable temperature and pressure conditions. The exploited experimental and data processing procedures are described elsewhere [18,21,28]. Our choice of the series of congruent heterogeneous systems invoking alkanethiol SAMs of different chain length, HS-$(CH_2)_n$-CH_3, with $n=1$, 2, 3, 5, and 7, i.e., with a total carbon number of 2, 3, 4, 6, and 8, allowed for inputs to the ET distance from 4.14 to 15.34 Å, i.e., a variation in the electron donor-acceptor coupling (see below) within the range of approximately $5\times10^{-2}-10^{-4}$ eV [21]. Furthermore, as a redox probe for ET, we exploited a ferrocene/ferrocenium couple, $[Fe(Cp)_2]^{0/+}$ (Cp=cyclopentadienyl) that is especially suitable for outer-sphere (electrode) ET studies due to its potentially low impact on interfacial motifs (because of the low charge type) and negligible inner-sphere reorganization accompanying the redox process (validating the simple form of charge-transfer theory) [14,15,33,34]. The heterogeneous assembly with alkanethiol SAM films of variable thickness (i.e., nanoscopically tunable ET distance) under investigation is schematically shown in Fig. 1.

Figure 2 depicts the Arrhenius-like plots for the $Au/SAM/[bmim][NTf_2]/Fe(Cp)_2]^{0/+}$ systems involving alkanethiol SAMs (HS-$(CH_2)_n$-CH_3) with carbon number ($c=n+1$) of 2, 4, 6, and 8, respectively. The values of the

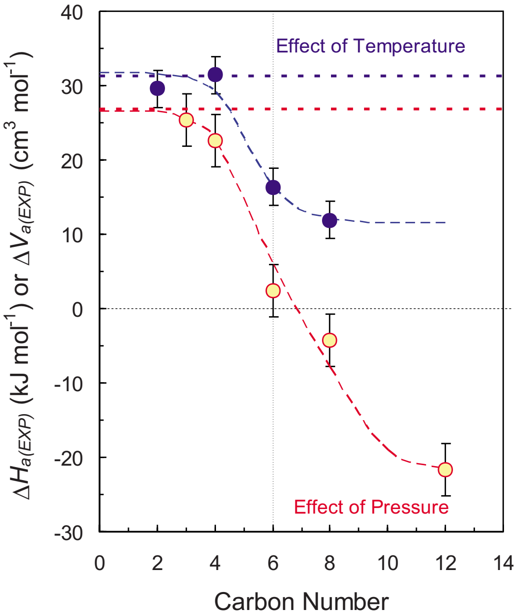

FIG. 3. (Color online) The experimental values of $\Delta H_{a(EXP)}$ (dark symbols) and $\Delta V_{a(EXP)}$ (light symbols) for different Au/SAM/[bmim][NTf$_2$]/Fe(Cp)$_2$]$^{0/+}$ composite systems versus the SAM total carbon number. The curves are depicted as guides for the eye. Horizontal ("asymptotic") dashed lines indicate respective activation values for the RTIL fluidity (standard experimental error for both sets of parameters are the same, see text for details).

activation enthalpies determined by application of

$$\left[\frac{\partial(\ln k_{ET}^{o})}{\partial(1/T)}\right]_P = -\frac{\Delta H_{a(EXP)}}{R} \tag{3}$$

are quoted in Fig. 2 and plotted versus SAM carbon number in Fig. 3. One can notice the peculiar fact that the values of the activation enthalpies for ET determined for essentially short-range ET ($c=2,\ 4$) are indistinguishable from the reported value for the [bmim][NTf$_2$] fluidity (reciprocal viscosity), $\Delta H_{a(\eta)} \approx 31.3$ kJ mol^{-1} (within the same range of standard error, 5%, for both sets of experimental values) [37], found within the comparable temperature range. Definitely, the methodological strategy applied here allows for the rigorous separation of the intrinsic kinetic event from the preceding diffusional component [35,36] (see also discussions within the relevant papers [16,21,28]). Consequently, the reported experimental values of the activation enthalpies along with the activation volumes discussed below are all strictly attributable to the intrinsic ET (thermally activated to-and-fro hopping) between the Au electrode and the redox probe, viz., [Fe(Cp)$_2$]$^{0/+}$. Hence, the coincidence of distinct values for the activation enthalpies of true short-range (adiabatic) ET and the RTIL fluidity is a highly peculiar fact that requires special explanation as far as contemporary ET theory in essence is considered to be applicable.

Formally, from the theoretical standpoint, the values of $\Delta H_{a(EXP)}$ and $\Delta H_{a(\eta)}$ may virtually coincide provided that the contribution of the activation free energy due to an exponential (Franck-Condon-like) term [Eq. (1)] is virtually zero. Indeed, for ΔG_a^* throughout this work it presents [1,4,5,15–19]:

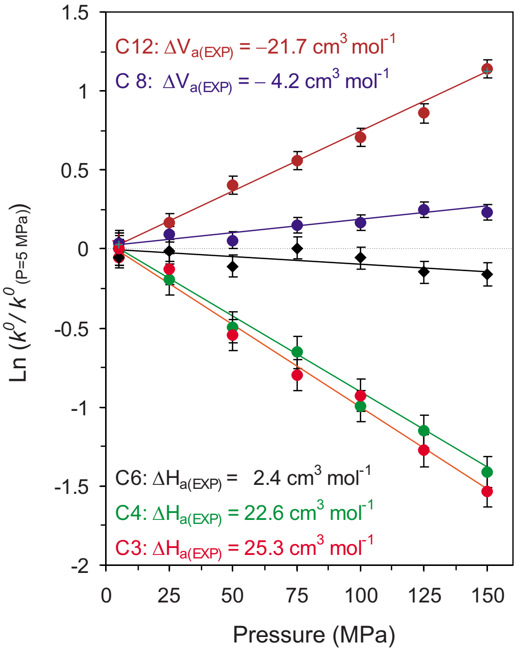

FIG. 4. (Color online) Pressure dependencies of the reduced ET rate constants for cases of Au/SAM/[bmim][NTf$_2$]/Fe(Cp)$_2$]$^{0/+}$ composite systems involving alkanethiol SAMs with carbon numbers of $c=3$, 4, 6, 8, and 12 (from bottom to top, on the right).

$$\Delta G_a^* = \lambda_o/4 - V_{AB}, \tag{4}$$

where V_{AB} is the conventional donor-acceptor electronic coupling parameter [1–9] (with the electrode acting as a reactant) and λ_o is the reorganization free energy that in our case incorporates mostly the outer-sphere component. According to [21], the value of λ_o (that is an essentially free-energy parameter [1,4]) upon decreasing the ET distance drops to approximately 0.12 eV for adiabatic systems with $c \leq 4$, bringing the values of V_{AB} within the range of 0.01–0.05 eV, and the virtual value of $\Delta H_a^* \approx 0$ can be someway deduced assuming that $\Delta G_a^* \approx 0$ and $\Delta S_a^* \approx 0$. Since for the short-range motif (presumably adiabatic case) the value of V_{AB} approaches that of $\lambda_o/4$, it follows that according to Eqs. (1), (2), and (4), indeed $\Delta H_{a(EXP)} \approx \Delta H_{a(\eta)}(!)$; a result that can be anticipated theoretically as an exceptional case. Furthermore, on passing to cases of $c=6$, 8, and 12, the value of λ_o approaches 0.5 eV [21], and the values of V_{AB} vary within the range of 10^{-4}–10^{-3} eV, eventually validating full nonadiabaticity $\Delta H_{a(EXP)} = \lambda_o/4$, in line with Eq. (4) implying negligible values for V_{AB} versus λ_o (provided that $\Delta S_a^* \approx 0$, as already deduced above).

Next we consider high pressure effects on ET patterns within our multicomponent tunable systems. These kinds of experiments allow for the determination of volumes of activation, $\Delta V_{a(EXP)}$, for ET, according to [38,39]:

$$\left[\frac{\partial(\ln k_{ET}^{o})}{\partial(P)}\right]_T = -\frac{\Delta V_{a(EXP)}}{RT}. \tag{5}$$

Figure 4 depicts dependencies for the reduced standard unimolecular ET rate constants on applied hydrostatic pressure for cases of $\mathrm{Au/SAM/[bmim][NTf_2]/Fe(Cp)_2]^{0/+}}$ assemblies involving SAMs with carbon number of 3, 4, 6, 8, and 12, respectively. The values of activation volumes determined through Eq. (5) are quoted in Fig. 4 and plotted versus SAM carbon number in Fig. 3. In striking analogy with the temperature dependence pattern, the plateau value of $\Delta V_{a(EXP)}$ for the adiabatic limit, $c=3$ virtually coincides with the activation volume for the [bmim][NTf$_2$] fluidity at the fixed temperature (298 K), $\Delta V_{a(\eta)} \approx 26.9\ \mathrm{cm^3\ mol^{-1}}$ (within the same range of standard error, 6%, for both sets of experimental values) [28], such that $\Delta V_{a(EXP)} \approx \Delta V_{a(\eta)}(!)$. It follows from Eqs. (1) and (4) [18,39] that

$$\Delta V_{a(EXP)} = \Delta V_a^* + \Delta V_{a(\eta)}, \tag{6}$$

where ΔV_a^* is related to ΔG_a^* and ΔH_a^*. Since for our systems *in the adiabatic limit* probably $\Delta G_a^* \approx 0$, it seems logical to conclude that $\Delta V_a^* \approx 0$ as well, a result that matches the outcome of the temperature (enthalpy) facet. On the contrary, in the well-pronounced nonadiabatic limit at $c=12$, the contribution due to $\Delta V_{a(\eta)}$ becomes strictly zero and the value of $\Delta V_{a(EXP)}$ equals ΔV_a^* [Eq. (6)] that attains the opposite sign compared to $\Delta V_{a(\eta)}$. Hence, as expected on theoretical grounds [18,39], in the extreme nonadiabatic case $\Delta V_{a(EXP)}$ is related solely to ΔV_a^* (but not to $\Delta V_{a(\eta)}$).

In summary, the composite $\mathrm{Au/SAM/[bmim][NTf_2]/Fe(Cp)_2]^{0/+}}$ assemblies were tested for interfacial ET mechanisms operating at various donor-acceptor (electrode-redox probe) separations. For the short-range ET pattern the adiabatic (viscosity-related) mechanism has been firmly demonstrated (versus the nonadiabatic tunneling-controlled one operating at long distances), clearly showing up through the activation enthalpy and volume, the values of which coincided with those for the viscous flow under variable temperature and pressure conditions. Hence, a thermally activated regime of ET has been observed that is entirely controlled by the viscosity-related slow relaxation mode(s) of the ionic liquid positioned within the interfacial zone. This is an important breakthrough in the mechanistic understanding of electron transfer events in nanoscopically tunable heterogeneous systems that may have significant impact on the development of fundamental soft-matter physics and related interdisciplinary fields such as materials and biomolecular sciences, along with their nanotechnological applications. Further systematic experimental work is in progress in this direction toward an in-depth understanding of this odd phenomenon.

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