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Observation of Marcus Inverted Region for Bimolecular Photoinduced Electron Transfer Reactions in Viscous Media

Manoj Kumbhakar,^{1,} Arpan Manna,² Mhejabeen Sayed,¹ Anil Kumar,² and Haridas Pal^{1,*}*

¹Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400 085,
India

²Physical and Material Chemistry Division, National Chemical Laboratory, H. J. Bhabha Road, Pune-
411 008, India.

AUTHOR INFORMATION

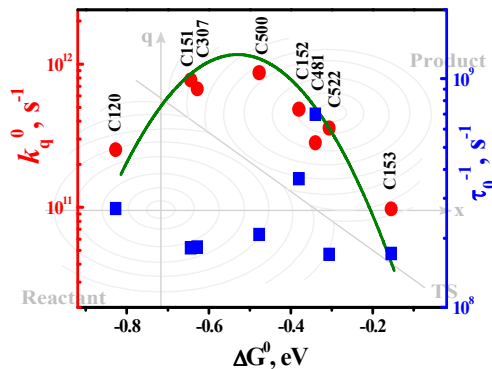
Corresponding Author

*manojk@barc.gov.in (MK), hpal@barc.gov.in (HP), Phone:+91-22-25590296/5396.

ABSTRACT: The general observation of Marcus inverted region (MIR) for bimolecular electron transfer (ET) reactions in different viscous media, e.g. micelles, reverse micelles, vesicles, ionic liquids, DNA scaffold, etc. has been doubted in some recent publications arguing limitations in Stern-Volmer (SV) analysis to account for the static and transient stages of quenching in these slow diffusing media. Thus, following a theoretical treatment based on a spherically symmetric diffusion equation coupled with conventional Marcus ET description, it has been suggested that the MIR observed in viscous media arises due to the inadequate consideration of different quenching regimes and also due to the differential excited-state lifetimes of the fluorophores used than a genuine one (JACS 2012, 134, 11396). However, the overall treatment in this study is severely compromised by setting the minimum solvent reorganization energy (λ_s) to ~ 0.96 eV while fitting the experimental data, which unambiguously suggests that the inversion in ET rate will never appear in the exergonicity ($-\Delta G^0$) range of 0.16 to 0.71 eV, as is the case for the studied ET systems. Besides, the applicability of the conventional Marcus ET model (instead of Sumi-Marcus two-dimensional ET model) in such extremely viscous media with exceptionally slow solvent response is highly debatable and perhaps is the main cause of the failure in fitting the experimental data quite satisfactorily. In the present study involving ultrafast ET quenching for coumarin derivatives by dimethylaniline donor in viscous ionic liquid media, we demonstrate clear MIR for the intrinsic ET rates, directly obtained from the ultrafast decay components of 1-10 ps, a time scale in which diffusion of reactants is negligible and the ET rates are either faster than or at the most competitive with the solvent reorganization. The appearance of MIR at $\Delta G^0 \sim -0.5$ eV, significantly lower than expected from the λ_s value, further substantiate the non-applicability of conventional ET description but certainly advocate for the applicability of the Sumi-Marcus two dimensional ET model in such media. Moreover, no obvious correlation has experimentally been observed between the excited state lifetimes of the coumarin derivatives and the ET rates for a large number of dyes used in the present study. Based on the present results and drawing inferences from reported literatures in viscous media, we conclude that the appearance of MIR is not only very much genuine but also the mechanistic model necessary to account the observed facts for the bimolecular ET reactions in a viscous medium is

the two dimensional ET description, which deals with an extremely slow relaxing solvent coordinate and a fast relaxing intramolecular coordinate to describe the ET reactions.

TOC GRAPHICS



KEYWORDS: Bimolecular electron transfer, Viscous ionic liquid media, Marcus inversion region, Ultrafast electron transfer rate, Reactant diffusion, Solvent relaxation dynamics, Coumarin dyes.

INTRODUCTION

Electron-transfer (ET) reactions in solution have been extensively investigated over the last few decades, particularly after the experimental validation of the quadratic relationship between ET rates and the free energy of reactions, as theoretically predicted by Prof. R. A. Marcus¹⁻³ in mid- fifties. However, the observation of Marcus behavior, particularly the Marcus inverted region (MIR), is mostly limited to intramolecular ET and charge recombination reactions where diffusion of donors (D) and acceptors (A) are essentially absent. But in the case of bimolecular ET reactions, where prior reactant diffusion is a pre-requisite to bring the D and A in the close proximity to form the encounter complex, the diffusional rate (k_d) imposes the upper limit for the observed ET rate. Thus, with an increase in the exergonicity ($-\Delta G^0$), the experimentally observed rate constant (k_{obs}) changes from being activation controlled ET (k_{et}) to diffusion limited reaction rate (k_d). These three rate constants are generally related as,⁴⁻⁷

$$k_{obs}^{-1} = k_{et}^{-1} + k_d^{-1} \quad (1)$$

and when $k_{et} > k_d$, the expected MIR for bimolecular ET reactions is mostly become obscured by the diffusion limited condition of the reaction, i.e. $k_{obs} \cong k_d$; leading to the observation of Rehm-Weller behavior.⁸

Based on conventional ET theory, the rate constant k_{et} for outer sphere ET reaction is expressed as,^{1-4,6,9-11}

$$k_{et} = \frac{1}{1 + 4\pi V_{el}^2 \tau_s / \hbar \lambda_s} \left\{ \frac{2\pi}{\hbar} \frac{V_{el}^2}{\sqrt{4\pi \lambda_s k_B T}} \exp \left(-\frac{(\Delta G^0 + \lambda_s)^2}{k_B T} \right) \right\} \quad (2)$$

where ΔG^0 is the free energy change of the reaction, λ_s is the solvent reorganization energy, V_{el} is the electronic coupling between the reactant and product states and τ_s is the solvent relaxation time.¹²

Therefore to observe MIR, the $|\Delta G^0|$ should be more than λ_s and to observe this behavior for

bimolecular ET reactions the value of λ_s should be reasonably low such that MIR occurs at reasonably lower ΔG^0 values that can be experimentally accessed easily. In reality, however, the scarcity of suitable series of reactants to achieve exceedingly high reaction exergonicity (>2 eV) is often a formidable task to suppress the diffusion limited region of reaction exergonicity and hence to observe MIR for most bimolecular ET reactions involving high λ_s values.

On the contrary, manipulation of λ_s seems plausible under certain experimental conditions and over the past decade there have been extensive efforts to unravel the intricacies of bimolecular ET reactions in different constrained conditions with the aim to control the dynamics of the reaction,¹³ in an effort to mimic nature's design of photosynthetic reaction center.⁴ In this context, a promising approach, with large-sized electron donor (i.e. fullerenes) and small-sized electron acceptor to elevate the value of k_d with a concurrent decrease in the reorganization energy (λ), as reported by Guldi and Asmus,¹⁴ clearly demonstrate MIR for bimolecular ET reaction. However, the strict size restriction imposes limitation of this methodology for many practical applications. The demonstration of MIR for long-range slow ET from various electron donors in solution to encapsulated electron acceptor, $\text{Fe}(\text{bpy})_3^{2+}$ (in zeolite supercage) by Fukuzumi & coworkers¹⁵ also seems quite limited for wider applications, as one of the reactant requires special ship-in-bottle synthesis to secure it to fit suitably inside the cage.

A conscious attempt to circumvent the limiting situation arising from reactant diffusion as well as the non-availability of highly exergonic reactant pairs towards the observation of MIR for bimolecular ET reactions has been made by judicious selection of micro-heterogeneous media, e.g. micelles.¹⁶ Due to the entanglement of the reactants with the surfactant chains in these systems (i.e. simulating a kind of intramolecular ET situation) and the slower solvent reorganization inside micelles (which leads to partial contribution of solvent reorganization energy, λ_s , towards total reorganization energy, $\lambda = \lambda_s + \lambda_i$; where, λ_i is the intramolecular reorganization energy), the MIR has been found to appear at much lower exergonicity (~ 0.7 eV) compared to that expected in homogeneous fast relaxing solvents of similar polarity. Similar inversion in ET rates at much lower exergonicity (~ 0.5 eV) for intercalated dyes with

nucleobases in DNA scaffolds has also been reported by Fukuzumi & coworkers.¹⁷ Moreover, tuning the appearance of MIR on the exergonicity scale by ~ 0.3 eV has been demonstrated by suitable selection/alteration of micellar microenvironment alone.^{18,19} Similar tuning of ~ 0.1 eV for the appearance of MIR by varying the composition of copolymer/IL media has also been reported by Bhattacharyya & coworkers. All these results in microheterogeneous media have been rationalized by invoking the two-dimensional ET (2DET) model, proposed by Sumi & Marcus.²⁰⁻²² Of late, observation of MIR has also been reported by many groups in different high viscosity media, e.g. room temperature ionic liquids (ILs), reverse micelles, vesicles, etc., where solvent reorganization is in general very slow, showcasing the 2DET model of ET reaction.²³⁻⁴¹

Surprisingly, all these experimental observations of MIR in various viscous media have been contradicted recently by Rosspeintner et. al.⁴² Before addressing the results and interpretations of these authors, a brief account of the relevant experimental methodologies, assumptions and theoretical background of bimolecular ET in the context of MIR is presented for an easy perception of the various arguments put forward with the present experimental results.

Evaluation of ET rates: In most of the studies involving bimolecular ET reactions, the Stern-Volmer (SV) fluorescence quenching kinetics is generally applied following steady-state (SS) and time resolved (TR) measurements (time-correlated single photon counting, TCSPC and fluorescence up-conversion, FU) to estimate the reaction rates.⁴³ In the SS data, the positive deviation from SV linearity is often observed at the higher quencher concentrations, even in the absence of any ground state complex formation and is ascribed to the quenching involving close vicinity D-A pairs at the moment of photo-excitation (i.e. static quenching). Contrary to SS results, however, linear SV plots are mostly observed for the same set of reaction pairs,⁴⁴ where average lifetime values obtained from TCSPC results are correlated with the quencher concentration, reflecting mainly the dynamic part of the quenching, with negligible contribution from static or transient quenching, even if not absent completely.^{23-29,32-34} In view of this, simple Smoluchowski approach for predicting effective k_q values

1 derived from linear SV plots of lifetime data have been considered for Marcus correlation and
2 subsequent analysis. In all these studies, MIR is clearly observed and the exergonicity for the onset of
3 MIR found to be dependent on the relative propensity of the solvation and the ET rates.^{16,18,19,23-26,30-41}
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8 With advanced theoretical approach to account for the quenching dynamics, encompassing the static
9 quenching at early time scales to the diffusion limited conditions at longer time, a quantitative analysis
10 for different quenching components is in principle possible, as an alternative to SV analysis, and may be
11 important in viscous media like the systems discussed above, where the effect of retarded reactant
12 diffusion on the observed reaction rate would be very pronounced. In this context, recent attempts to
13 analyse fluorescence quenching kinetics in viscous media by fitting fluorescence decays considering
14 spherically symmetric diffusion reaction equation coupled with conventional Marcus description of
15 distant dependent ET, as independently applied by Maroncelli & coworkers⁴⁵ and Vauthey &
16 coworkers,^{42,46} is in essence very similar to the treatments applied earlier by Szabo, Grampp, Tachiya
17 and Fayer.⁴⁷⁻⁵³ It has been meticulously shown by Maroncelli and coworkers⁴⁵ that a careful
18 incorporation of the transient component can justifiably explain the origin of higher quenching rates as
19 apparently observed in ILs (as estimated from SV analysis), than expected from normal diffusion
20 controlled rate. With this improvised description of quenching process, the authors argued that a single
21 set of ET parameters can give quite satisfactory comparison of the ET results in ILs and in conventional
22 viscous solvents. However, the authors also highlighted an important observation from their analysis
23 that the adopted model falls short in representing the experimental data very convincingly even in the
24 cases of their best fits, possibly due to several inaccuracies in the inputs of ET parameters in these
25 analysis. We feel that one of the limitations on their treatment is the consideration of conventional ET
26 model that is not truly applicable in a viscous and slow relaxing solvent media.
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54 Simultaneous fitting of SS and TR data based on differential encounter theory⁴⁷ (DET, developed by
55 Tunitskii & Bagdasar'yan⁵⁴ and recently reviewed by Burshtein⁵⁵) and conventional Marcus ET
56 expression (*cf.* eq. 2) for single channel non-adiabatic ET has been reported by the groups of Angulo,⁵³
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Gramp,⁵⁶ Rosspeintner⁵⁷ and Vauthey.^{42,46} In their treatment for the fitting of the nanosecond time-resolved data, the dynamic solvent effect has been excluded because of the small electronic coupling element ($V_{el} \sim 8 \text{ cm}^{-1}$) required for these fits.⁵⁷ For the fitting of the sub-picosecond TR data, although the general Marcus expression is used along with the incorporation of the solvent dielectric relaxation time and the transition to vibronically excited successor states in the refined DET model (with V_{el} as high as $\sim 400 \text{ cm}^{-1}$),⁵³ the treatment however was limited to the variations in ΔG^0 , V_{el} and λ_s as a function of D-A separation (r), only. Such an approximation is legitimate for ET reactions in normal solvents where solvent dielectric response is very fast and ET reaction can be viewed as occurring along an unified single reaction coordinate (X').⁵⁸ On the contrary, in slow relaxing solvents the value of effective λ_s is not only a function of r , but also a function of temporal evolution of solvent reorganization. Therefore, time evolution of reactant population along solvent coordinate X due to sluggish solvent relaxation in viscous media should be explicitly taken into consideration to define the reaction coordinate.^{27,28} It is quite easy to visualize that the ET reaction in the later cases essentially involves two dicoordinates for the effective potential energy surface, one is the solvent corordinate, X , that accounts for the polarization response of the medium to the evolving charge distribution of the reactant and the other is the intramolecular coordinate, q , that accounts for the relaxation along the internal and low-frequency nuclear degrees of freedom that seems to be always very fast (i.e. the 2-dimensional ET model²⁰⁻²²).

Conventional Marcus vs. Sumi-Marcus ET Model: The conventional Marcus theory^{1-3,6,10} describes ET in two limiting regimes; the non-adiabatic regime (weak coupling, $V_{el} \ll k_B T$, $4\pi V_{el}^2 \tau_s / \hbar \lambda_s \ll 1$), where reactant move through the transition state region many times before it converts to the product state and the adiabatic regime (strong coupling, $V_{el} \gg k_B T$, $4\pi V_{el}^2 \tau_s / \hbar \lambda_s \gg 1$), where reactant state passes through the transition state once only along the unified X' coordinate to convert to the product state and V_{el} only determines the activation barrier height. This model do not address the effect of temporal evolution of solvent reorganization in either of the two limiting cases of

the ET reactions, as first discussed by Zusman^{59,60} and later reported with detailed theoretical treatment by Sumi and Marcus,²⁰ emphasizing the solvent frictional coupling on the reaction rate. A concise account of the Sumi-Marcus ET model, i.e. interplay between solvent controlled regime in which solvation dynamics is the rate-limiting step and a slow- solvent relaxation regime in which the rate is controlled by thermal ET along the vibrational coordinate, has been discussed in the context of ultrafast ET and proton transfer experiments by Barbara & coworkers⁶¹ and rationally been implemented in the works of ET in non-diffusive electron donating solvents by Yoshihara & coworkers.⁶²⁻⁶⁶ The influence of dynamic solvent effects in ET studies for U-shaped donor bridge-acceptor molecules in normal solvents has been decisively addressed by Paddon-Row & coworkers.^{67,68} The merits of molecular model for solvation on ET reaction, developed by Matyushov, alongside the dielectric continuum model have also been addressed by Zimmt and Waldeck.⁶⁹⁻⁷¹

Observation of MIR in Viscous Media and the dispute thereof: Combining the conventional Marcus formulation coupled with DET, to account for all the stages of bimolecular ET quenching in IL and dimethylsulfoxide (DMSO)/glycerol (GLY) mixed solvents, it has been recently concluded by Vauthey & coworkers^{42,46} that the MIR observed in these systems are not genuine but apparently arises from (1) the neglect of different quenching regimes (i.e. static, transient or non-stationary and stationary regimes) in the simple SV analysis and (2) different excited state lifetimes of the fluorephores considered in the donor-acceptor series. These arguments have also been extended to doubt the ET results in various organized assemblies and termed these observations of MIR in these viscous media as spurious.

With due credit to the approach considered by these authors by incorporating diffusion kinetics in the treatment of bimolecular ET in viscous media, the limited results reported⁴² based on the above analysis and the conclusions drawn from that are largely not substantiated and rather raises several confusions than perhaps addressing the real problem, as are discussed below,

(i) Though the first argument of transient effects is theoretically well established for long and certainly can lead to some estimation of the quenching rates following a simple SV analysis in a viscous medium and consequently can influence the Marcus correlation curve to some extent when there is a broad distribution of fluorophore lifetimes,⁷² but, these aspects would necessarily not affect the intrinsic ET rate (k_0 , in the static quenching regime, where influence of diffusion is negligible), directly measured using ultrafast technique like FU and thus will mainly be determined by the energetics of the D-A pairs.

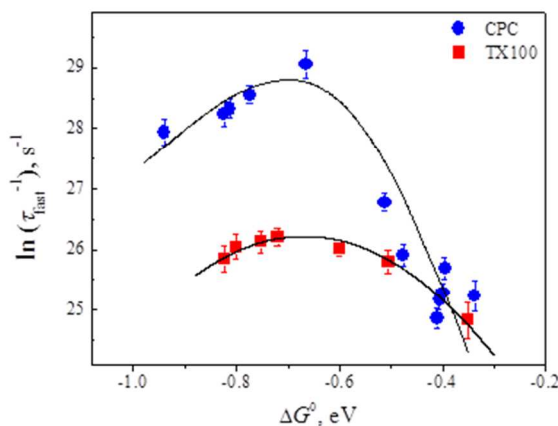


Figure 1. Marcus correlation plot for coumarin-DMAN systems in CPC (at contact) and TX-100 micelles (close vicinity). Revised plot from ref.^{27,28}

With ultrafast quenching experiments, the MIR has already been reported for k_0 in various micelles where D and A are either at contact where surfactant is used directly as a reactant or at close proximity at higher quencher concentrations as would be the case in other micelles (Figure 1).^{27,28} Observation of MIR for similar ultrafast ET is also reported in [pmim][BF₄] IL by Bhattacharyya & coworkers.³⁷ Surprisingly, however, such MIR is reported to be absent in IL and DMSO/GLY solvents, even for the k_0 values reported by Rosspeintner et al. from their model based analysis of the experimental data.⁴² Such a discrepancy suggests that either the adopted theoretical model to deal the bimolecular ET is not truly applicable in all viscous media or there could be some inadequacies in the ET and or solvation parameters used in their theoretical analysis. In their case, we presume, both the factors are equally responsible. Considering the slow solvent relaxation in viscous media compared to usual fast relaxing

solvents, e.g. acetonitrile, etc. the Sumi-Marcus description of ET is better suited than the conventional Marcus ET model in correlating the experimental data. Thus, as a sequel to this inappropriate selection of ET model, there is a compromise in selecting the ET parameters, used as inputs in the analysis, leading to unsupported conclusions for the observed facts.

(ii) The obvious flaw in their experimental data treatment using conventional Marcus expression is the selection of the reorganization energy range. While fitting the individual data sets, the values of solvent reorganization at infinite separation, $\lambda_s(R_\infty)$ and at contact distance, $\lambda_s(R_0)$ in DMSO/GLY are fixed as about 1.92 and 0.96 eV, respectively, ignoring the contribution of inner-sphere reorganization energy (*cf.* supporting information in ref. 24). In the absence of any time-dependent solvent reorganization energy term in the numerator of the reactivity equation, eq. 2 (for frictional solvent effect, as discussed earlier), which is grossly incorrect for a slow solvent relaxation case, the appearance of Marcus inversion is only and only be expected when the $-\Delta G^0$ exceeds at least 0.96 eV, whatever may be the values for the other ET parameters used. Therefore, it is not surprising, that the k_0 values calculated following this procedure would not show MIR within the studied exergonicity region of ~ 0.16 - 0.71 eV, as reported by these authors. Moreover, according to the literature reports and also as transpires from conventional Marcus ET theory, the reaction distance, R ($R = R_0 + L$, where L represents the decay length of V_{el}) should increase with $-\Delta G^0$.⁷³ The estimated R values, however, do not show the expected trend, suggesting the inherent discrepancy in their analysis.

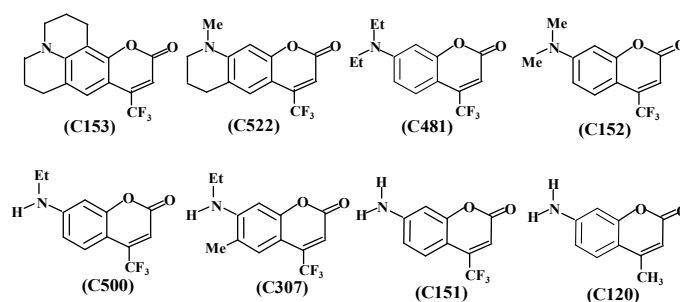
As an obvious outcome of the limitations discussed above regarding the attempted fits of the fluorescence transients based on conventional Marcus model employed by Vauthey & coworkers,⁴² the fitted curves visually suffer from nonconformity of the experimental data in most cases, which in turn severely affects the extracted ET kinetics and the consequent Marcus correlation curves. Similar limitations even for the best fits, due to several inaccuracies in the inputs of ET parameters has also been documented by Maroncelli and coworkers for their analysis.⁴⁵

(iii) The other argument that invokes differential lifetimes of the fluorophores as the origin of MIR for the quenching rates in viscous media seems to be a mere coincidence with limited number of data points they considered. In fact, with additional data points in the present experimental study the argument of differential lifetime of coumarin dyes as the origin of MIR for the current series of coumarin dyes is completely invalidated.

Based on the above discussions, ET in these slow relaxing solvents certainly deserves a serious rethinking on the adopted ET model and conclusion drawn thereof. Further it is essential to demonstrate MIR from the directly estimated ET rates in viscous media, instead of employing standard SV analysis. Therefore, an in-depth reconsolidation of this ubiquitous elementary reaction of bimolecular ET in different viscous media (IL's as well as in organized assemblies) is felt to be the need of the hour, and the present study has been undertaken with the intension to explore the role of activation barrier crossing and lifetime (τ_0) distribution of the probe dyes on the observed ET rates (from the correlation between k_0 and τ_0^{-1} with ΔG^0 , respectively).

To address the issue of MIR for bimolecular ET reactions in viscous media, thus, we have investigated fluorescence quenching studies of a series of coumarin dyes (Chart 1) in two ionic liquid solvents, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim][NTf₂], $\eta \sim 37$ cP, abbreviated as **IL1**) and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Hmim][NTf₂], $\eta \sim 81$ cP, abbreviated as **IL2**) by N,N-dimethylaniline (DMAN) as the quencher. The details of these chemicals are provided in the supporting information.

Chart 1. Chemical structures of the coumarin dyes used in the present study.



Experimental Methods & Analysis Procedures: Time resolved fluorescence experiments were performed with FU measurements for the early stages of the quenching kinetics and with TCSPC measurements for the longer time quenching kinetics. To ensure that the fluorescence decays reflect the excited-state population, measurements were recorded at emission maxima of the dyes where influence of dynamic Stokes shift is negligible.

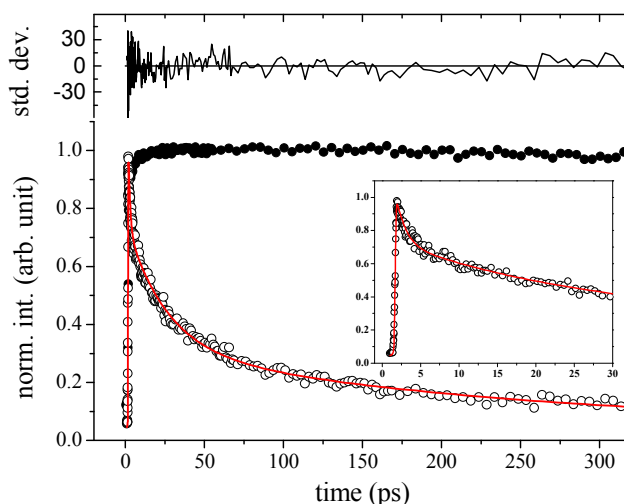


Figure 2. Fluorescence decay trace for C500-DMAN system (open circle) in IL1 measured in the FU setup. Insets show the residual for the fit and the early part of the fluorescence transient. The solid circles represent the fluorescence transient in the absence of any quencher.

In both the IL media, coumarin dyes show strong non-exponential decay profiles from FU measurements in the presence of DMAN (Figure 2) though the transients show no obvious decay in the absence of quencher.^{27,28,32,33,37} The fluorescence transients were rigorously fitted by convolution method using a Gaussian shape for the instrument response function (IRF, ~ 200 fs) and a multi-exponential decay function, expressed in general as,

$$I(t) = \sum A_i \exp(-t / \tau_i) \quad (3)$$

where τ_i is the fluorescence lifetime and A_i is the pre-exponential factor for the i -th component of the decay.⁷⁴ The fit parameters thus obtained are listed in Table 1. The estimated shortest fluorescence

lifetime components, which range between 1 - 10 ps (τ_1 , henceforth called as τ_{fast}) for different coumarin dyes, in the presence of quencher are several orders of magnitude shorter than the normal fluorescence lifetime (τ_0) of the dyes in the absence of quencher.⁷⁵ Though all the estimated time components are not possible to be directly attributed to distinct physical processes related to the diffusion influenced quenching dynamics, but the observed fastest decay time (τ_{fast}) in the presence of DMAN can safely be assigned to the ultrafast ET process, as the diffusion of the reactants would be negligible in the concerned time scale. Accordingly, the inverse of this shortest lifetime component is considered as the direct measure of the intrinsic ET rate ($\tau_{\text{fast}} = k_0^{-1}$)⁷⁶ for the concerned donor-acceptor system. Examples of similar methodology to estimate the ultrafast ET rate are quite abundant in the literature. To be emphasized that, in the present analysis, both τ_i and A_i , can be determined with sufficient accuracy following multi-exponential fitting, as the fastest lifetime component is nearly an order of magnitude higher than the timescale of the IRF (nearly six times for the fastest C500-DMAN pair) and thus the estimation of k_0 is very accurate.

The time scale for this ultrafast quenching is similar to the earlier reports, where ET is effectively dominated by static quenching for the initial about few ps time-spans following photoexcitation.^{42,45,46} The root mean square distance that a quencher can diffuse ($\sqrt{2D\tau}$,⁴³ where D is the relative diffusion coefficient) within 10 ps is only ~ 0.26 Å in IL1 and ~ 0.18 Å in IL2 (*cf. supporting information*). These distances are much smaller than the average molecular diameter of the coumarin dyes used (~ 7.4 Å, following Edward's volume addition method⁷⁷). Hence, the effect of reactant diffusion in this ultra-short time scale can simply be neglected.

In the present context, it could be possible that, the reorientational motion of the reactants can marginally influence the estimated intrinsic ET dynamics.^{78,79} However, if we consider the average rotational correlation time as estimated in the present work for the coumarin dyes in the studied ILs (*cf. Figure 3*), the shortest values are found to be in the range of 100-200 ps (along with another few ns component),⁸⁰⁻⁸³ which is orders of magnitude longer than the fastest ET components for the studied

systems. These considerations largely suggest that in a high viscous medium an excited fluorophore undergoes ultrafast ET reaction with one of the closely situated quencher molecules that can give a sizable donor–acceptor electronic coupling and this fast interaction effectively occurs under the non-diffusive (both translational and rotational) conditions.²⁷

Table 1. Fluorescence decay and ET parameters of Coumarin-DMAN systems in ILs at 295±1 K.

IL	Dyes	τ_0 , ns ^a	Decay time constants (τ_i), ps (%) ^b	$E(A/A^-)^c$	E_{00} , eV	ΔG^0 , eV ^d	$k_q \times 10^8$, M ⁻¹ s ⁻¹ ^e
IL1	C153	5.81	10.26 (0.91), 55.42 (9.99), 298.18 (89.10)	-1.69	2.55	-0.155	4.10
	C522	5.86	2.8 (0.41), 29.23 (9.36), 294.01 (90.23)	-1.63	2.64	-0.306	7.98
	C481	1.43	3.54 (0.76), 25.63 (11.03), 185.10 (88.21)	-1.66	2.70	-0.340	4.90
	C152	2.74	2.07 (0.62), 25.56 (12.57), 218.33 (86.81)	-1.63	2.71	-0.380	9.01
	C500	4.81	1.15 (0.52), 24.91 (13.34), 239.96 (86.14)	-1.61	2.79	-0.477	9.11
	C307	5.45	1.49 (0.99), 34.63 (18.28), 220.3 (80.73)	-1.68	3.01	-0.628	3.71
	C151	5.50	1.29 (0.86), 22.52 (12.83), 249.1 (86.31)	-1.57	2.92	-0.644	6.87
	C120	3.70	3.97 (1.91), 38.69 (90.44), 302.1 (67.65)	-1.61	3.14	-0.827	1.32
IL2	C153	5.74	10.01 (0.03), 55.28 (0.17), 189.07 (99.80)		2.57	-0.175	2.86
	C522	5.65	3.50 (0.15), 32.02 (12.92), 180.55 (86.93)		2.64	-0.304	4.61
	C481	1.81	3.80 (0.98), 31.67 (10.93), 134.57 (88.09)		2.69	-0.324	8.29
	C152	2.95	2.18 (0.31), 24.88 (13.03), 159.61 (86.66)		2.70	-0.362	6.59
	C500	5.13	1.14 (0.64), 23.07 (13.58), 125.22 (85.78)		2.80	-0.487	7.23
	C307	5.83	1.58 (0.95), 30.59 (21.97), 180.01 (77.08)		2.98	-0.598	7.89
	C151	4.98	2.24 (2.46), 36.02 (26.86), 130.2 (70.68)		2.93	-0.658	6.90
	C120	3.69	6.90 (6.44), 52.28 (56.33), 198.7 (37.33)		3.12	-0.807	1.51

^a: measured with TCSPC setup in absence DMAN. The decays were single exponential in nature; ^b: measured from FU setup in presence of 1.0 M DMAN; ^c: the redox potentials (in volts) were measured in ACN. The redox potential of DMAN in ACN is 0.76 V; ^d: the Born correction has not been included in the free energy calculation⁸⁴; ^e: obtained following simple SV analysis of the average lifetime data recorded with TCSPC setup.

To examine if there is any connection between the differential lifetimes of the coumarin dyes with the observed MIR in the studied viscous media, SV analysis has also been performed using the average lifetime ($\langle\tau\rangle$) values obtained from TCSPC measurements following eq. 4, as reported in most of the studies showing MIR in various viscous media. Under the condition of non-diffusive quenching, the value of k_q is equivalent to the k_{et} for the studied systems.

$$\frac{\tau_0}{\langle\tau\rangle} = 1 + k_q \tau_0 [\text{DMAN}] \quad (4)$$

The reaction free energy in ILs has been estimated using the following Rehm-Weller expression,⁴

$$\Delta G^0 = E(D/D^+) - E(A/A^-) - E_{00} - \frac{e^2}{4\pi\epsilon_0\epsilon_{IL}R_0} \quad (5)$$

where E_{00} is the excitation energy of the coumarins in the S_1 state, e is the charge of an electron, ϵ_{IL} is the static dielectric constants of the reaction medium.^{81,84-86} The R_0 ($=R_A + R_D$) is the center to center distance between the interacting coumarin (R_A) and DMAN (R_D). The calculated free energy values are listed in Table 1.

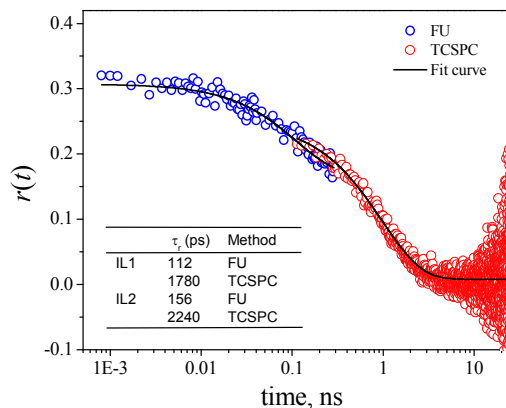


Figure 3. Fluorescence anisotropy decay of C153 in IL1.

RESULTS AND DISCUSSION

Inversion in intrinsic ET rates: The variation of k_0 with ΔG^0 values for coumarin-DMAN systems in ILs is shown in Figure 4. It is clearly evident that the ET rate increases initially with an increase in exergonicity, reaches a maximum value at around -0.5 eV and then decreases gradually with exergonicity at even higher exergonicity region. Thus MIR and the full bell-shaped Marcus correlation curve for bimolecular ET are clearly evident for the studied electron donor-acceptor systems in the IL solvents, similar to that reported earlier for micellar media too. Interestingly, the MIR and bell-shaped correlation is also clearly seen for the second fastest decay constants, which occur in the range of 20-60 ps and as a result appears in between the static and transient regime of the diffusion process.

In addition to the MIR observed in the present cases, the other interesting observation is that the inversion appears at a much lower exergonicity than one would expect considering the conventional Marcus ET model, where solvent relaxation is considered to be very fast. Solvent reorganization time in ILs is known to span from sub-ps to few ns and the contribution of the

ultrafast solvation component with < 10 ps relaxation time is only around 10-20% of the total solvent relaxation.^{82,83,87-95} As a consequence, in ILs the slow diffusive solvent reorganization has to compete with ultrafast ET dynamics; and since this solvent relaxation is very slow, its role towards the free energy of activation for the ET reaction is less effective (2-DET model) than expected from the consideration of the conventional ET theory, where due to very fast solvent relaxation the reactant state is always in thermal equilibrium along the solvent coordinate. It implies that in the slow solvent relaxation cases the ET has to occur along the q coordinate, from a large distribution of temporally evolving non-equilibrated reactant states in the X coordinate (*cf.* Chart 2).^{6,63} Therefore, not only the time-dependent D-A separation due to diffusional motion of the reactants, but also the temporal evolution of the solvent configuration is also of colossal significance in dealing with the bi-molecular ET dynamics in a viscous media, where diffusion of reactant as well as solvent reorganization are largely retarded. As a consequence the oversimplified DET model based on conventional ET seems to be inappropriate for reactions in viscous media,⁴² even though the model could be applicable for reactions in conventional fast relaxing solvents.⁵⁸

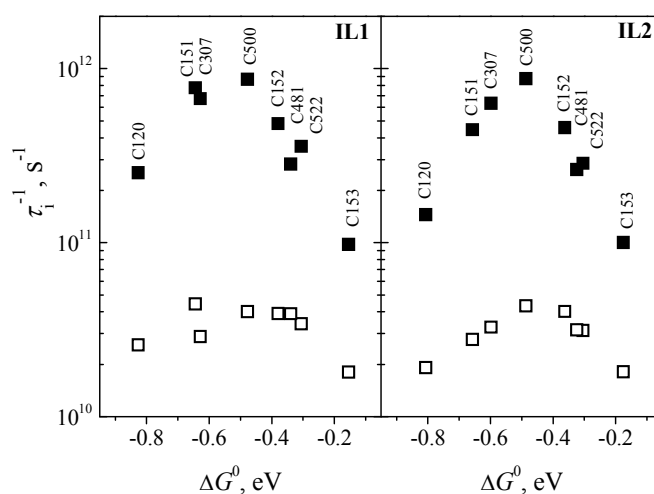
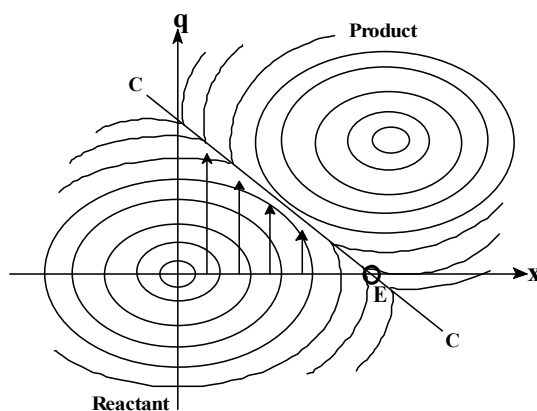


Figure 4. Plot of τ_1^{-1} vs. ΔG^0 for coumarin-DMAN systems. The ET rates are k_0 ($=\tau_{\text{fast}}^{-1}$) and k_1 ($=\tau_2^{-1}$), represented by solid and open squares, respectively.

Sumi-Marcus Model: Although a detailed theoretical formulation to incorporate all the discussed aspects together is a gigantic task and beyond the scope of the present study, yet a logical approximation of the system parameters can certainly be obtained to appreciate the insights of the ET dynamics and even to obtain a semi-quantitative correlation among the ET results in the viscous media. Following the Marcus ET theory, the rate constant k_{et} for an outer sphere ET reaction under non-adiabatic condition can be given by the following generalized quadratic equation,

Chart 2. Isoenergy contours of the potential energy surfaces drawn in a two-dimensional plane for the reactant and product states in relation to the two-dimensional ET model.⁹⁶



$$k_{et}(NA) = \frac{2\pi}{\hbar} \frac{V_{el}^2}{\sqrt{4\pi\lambda_s k_B T}} \exp\left(-\frac{\Delta G^*}{k_B T}\right) \quad (6)$$

where each term are having their usual meaning. In the 2DET model, the free energy of activation $\Delta G^*(X)$ for the ET reaction becomes a function of the non-equilibrium solvation coordinate X and would be expressed as^{10,62-66}

$$\Delta G^*(X) = \frac{[\Delta G^0(X) + \lambda_s(1-2X) + \lambda_i]^2}{4\lambda_i} \quad (7)$$

In photoinduced ET reaction, as is the present case, it is obvious that the initial X coordinate for the reactant state produced through photo-excitation, say X_g , would be quite away from the equilibrium X coordinate ($X=0$) for the reactant, as the dipolar nature of the fluorophore changes very substantially in the excited state compared to that in the ground state. Under this situation, if the solvent relaxation process is substantially slow, as would be the case in relation to the ultrafast ET component in ILs, only the $(1-2X_g)$ fraction of λ_s (i.e. λ_s^{eff}) can contribute to $\Delta G^*(X)$. Accordingly MIR would show its onset at a much lower exergonicity ($|\Delta G^0| \ll \lambda_s$) than what it would have been under conventional ET model ($|\Delta G^0| \gg \lambda_s$).

The value of X_g for the studied D-A systems can approximately be estimated from the observed differences in the Stokes shifts ($\Delta\nu$) for the coumarin dyes between the concerned IL media and a nonpolar reference solvent (e.g. hexane), where the dielectric solvation is assumed to be negligible. The $\Delta(\Delta\nu)$ and X_g values are related by the following equation,⁶²⁻⁶⁶

$$\Delta(\Delta\nu) = 2\lambda_s X_g^2 \quad (8)$$

An estimate of the average X_g parameter (*cf.* Table 2) translates the contribution of λ_s towards the free energy of activation for the initially prepared reactant state following photoexcitation as

$\lambda_s^{eff} \sim 0.42$ eV in the two ILs. The contribution of λ_s for similar coumarin-amine systems in ILs has also been reported to be around 0.4 eV by Bhattacharyya and coworkers.³⁷ The present λ_s^{eff} value is slightly lower than the effective exergonicity (~ 0.5 eV) indicated for the onset of MIR for the studied systems (*cf.* Fig. 4). This small difference, we propose is due to the contribution of the intramolecular reorganization energy λ_i . From the above considerations it is therefore quite justified to assume that the ultrafast component (τ_{fast}) of the ET process in the studied ILs is mainly governed by the 2DET mechanism where solvent reorganization contributes only partially to the effective free-energy of activation.

In the present context we would like to mention that the conventional Marcus ET model is also not able to justify the observation of MIR at largely reduced exergonicity, reported for ET between intercalated dye and nucleobases in a DNA scaffold appearing at $\Delta G^0 \sim -0.4$ eV.¹⁷ This observation can however, be easily explained by the Sumi-Marcus 2DET model. Moreover, the 2DET model, can also in principle justify the similar observations of MIR occurring at much lower exergonicity than expected from the value of solvent reorganization energy, as observed for bimolecular ET reactions in micelles, reverse micelles, vesicles, supramolecular aggregates and ionic liquids.

Table 2. 2DET parameters for coumarin-DMAN systems in ILs.

	$\langle \lambda_s \rangle, \text{cm}^{-1}$	$\Delta \langle \Delta v \rangle, \text{cm}^{-1}$	X_g	$\lambda_s^{eff}, \text{cm}^{-1}$
ILs	8067	1367	0.291	3370.7
	(1 eV)	(0.17 eV)		(0.42 eV)

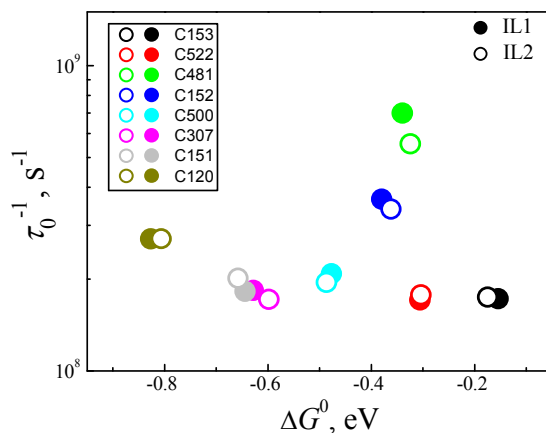


Figure 5. Plot of natural fluorescence decay rate (τ_0^{-1}) in absence of quencher as a function of reaction free energy for coumarin-DMAN systems.

Influence of differential lifetimes of probes on MIR: As stated earlier, the influence of transient (or non-stationary) contribution leading to higher k_q values for the TCSPC and SS data following simple SV analysis is certainly not unexpected. However, the extent of this overestimation will depend on the observed time-window for which the quenching interaction is measured. It is true that the range of the lifetime values for the coumarin dyes used in this study is not very narrow, spreading over $\sim 1.4 - 5.8$ ns. Consequently one may argue that a somewhat higher ET rate can be exhibited by the dyes having shorter lifetime values (e.g. C481 & C152) compared to those having a longer lifetime. To look into this aspect critically and thus to ensure that the observed MIR in viscous media is genuinely stems from the energetics of the ET reactions rather than the differences in the τ_0 values, we plotted τ_0^{-1} values against ΔG^0 values for the studied coumarin series (*cf.* Fig. 5). As observed from Figure 5 that the τ_0^{-1} vs. ΔG^0 plot lacks any resemblance to the bell-shaped Marcus correlation shown in Figure 4 while plotting the k_0 values against the ΔG^0 values. A plot of the k_q values estimated from simple SV analysis of TCSPC data,⁴³ against ΔG^0 values also show a clear bell shaped correlation (*cf.* Fig. 6), similar to

those reported by many groups in restricted reaction environment (with respect to reactant diffusion & solvent relaxation). Comparison of these plots in Fig. 4 to 6 is suggestive enough to conclude that the dominant role is played by the energetics of the ET reaction for the present observation of MIR in viscous media. Though the lifetime of C481 ($\tau_0 \approx 1.4$ ns) is much shorter than that of C500 ($\tau_0 \approx 5.0$ ns), the later shows comparable or higher values for k_q and k_0 , respectively. This is in stark contrast to the claims of differential lifetimes leading to the MIR in these media. Additionally, with a conservative approach, the k_q values from TCSPC measurements and the diffusion limited rate (k_d) are found to be in the range of about $\sim 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $\sim 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively. Thus, for one molar quencher concentration, the span of quenching times [$\tau_q = (k_q[\text{DMAN}])^{-1}$] is expected to be in the ranges of about 1-10 ns, which is well within the observation time window of ET reaction using TCSPC measurements (from ~ 100 ps to around five times of τ_0 values), even for the shortest lifetime dyes used in these studies. Therefore, the major part of the non-stationary regime will actually be monitored by all the fluorophores used giving reasonably accurate estimate of the average k_q values. The small portion of this non-stationary quenching regime monitored additionally by the long excited-state lifetime probes at the boundary of the non-stationary and stationary regimes will not be that substantial to influence the estimated average k_q values significantly. Moreover, a comparison of Fig. 6 and Fig. 5 definitely suggests that the shallow distribution of excited state lifetime of the fluorophores does not obscure the observation of Marcus inversion under restricted reaction environment. Therefore, we strongly feel that the distribution of fluorophore lifetimes (at least for the studied coumarin dyes) does not have any significant effect on the observed MIR.

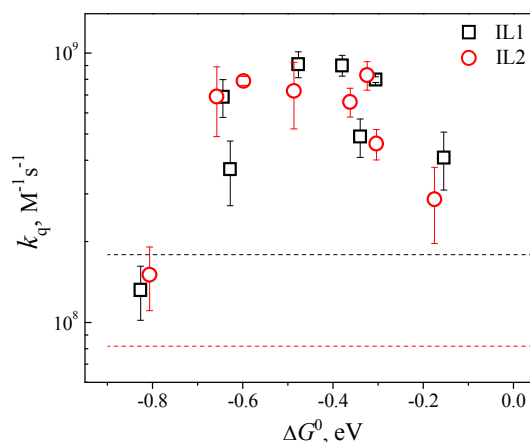


Figure 6. Plot of k_q , estimated from TCSPC data, against free energy of the reaction. The dashed lines represent the diffusion rate expected from the viscosity of the IL media.

Furthermore, the absence of any clear correlation in the plot of k_0 vs τ_0^{-1} (*cf.* Figure 7) also substantiates that the ultrafast ET component is completely independent of the fluorophore lifetimes. It is to be mentioned here that no pronounced influence of the chemical structures of the two types of coumarin dyes used, one with unsubstituted amino groups (C500, C307, C151 & C120) and the other with alkyl or julolidyl substitutions (C153, C522, C481 & C152), has been observed on the estimated quenching rates, suggesting that the observed MIR emerges from the energetic and kinetic reasons of the ET reactions studied.

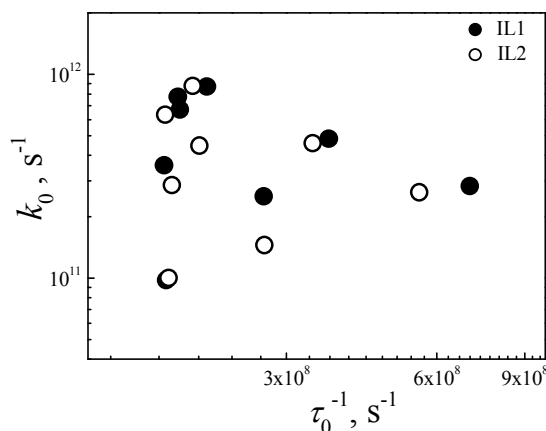


Figure 7. Plot of k_0 against τ_0^{-1} for coumarin-DMAN systems.

In the present context, the results of solvation dynamics of coumarin dyes by Ghosh & coworkers⁹⁷ and the fluorescence correlation spectroscopic study by Bhattacharya & coworkers⁹⁸ in DMSO-glycerol binary solvents are very intriguing, and certainly imposes doubt on the selection of DMSO-glycerol solvent mixtures as a substitute for neat IL media. The assumption of similar physical parameters for different DMSO/glycerol mixed solvents (with respect to dielectric constant and refractive index), as a substitute of neat ILs to study the influence of viscosity on bimolecular ET process has been found to be untrue. Instead, in these solvent mixtures, DMSO and glycerol undergoes phase segregation on the microscopic length scale (>300 nm) due to their non-cooperative association.^{97,98} The oversimplified assumption of spherically symmetric diffusion equation without considering the local microscopic structures to comprehend the diffusional quenching kinetics in these later solvent mixtures⁴² may have also resulted in the improper extraction of the kinetic parameters for the ET reactions.

It is pertinent, at this juncture, to compare one recent result on MIR for bimolecular ET interaction in a normal fast relaxing solvent, i.e. ACN,⁵⁸ with that observed in high viscosity and slow relaxing media. In the former case, the intrinsic ET rates (static quenching) were theoretically estimated from the fitting of ultrafast transients by similar diffusion assisted Marcus ET model with finite dielectric response of the solvent. However, with an average solvation time of 260 fs⁹⁹ and the derived fastest ET time of ~ 250 fs (approximately corresponding to k_0 value of $40 \times 10^{11} \text{ M}^{-1}\text{s}^{-1}$ at $\sim 1 \text{ M}$ quencher concentration⁵⁸) under non-adiabatic condition ($V_{\text{el}} \sim 72 \text{ cm}^{-1}$), the ET reaction is certainly competitive with the solvation process. Hence, Sumi-Marcus 2DET model should be the better choice to discuss such ET reaction, as mentioned earlier, than the semi-classical Marcus ET model. Besides, the inability of the model to fit the initial about 1

ps data (in the ultrafast decay transients), perhaps also points to the possibility of even faster ET rate than the solvation rate. Furthermore, a variation in the V_{el} values of more than one order of magnitude ($V_{el} \sim 100$ to ~ 1100 cm^{-1} ; adjusted to obtain a reasonable fit of the fluorescence transients) has been adopted by these authors, which will naturally influence the k_{et} values by more than two orders of magnitude because of square relation of V_{el} with ET rate (*cf.* eq. 2 & 6). Such a wide range of V_{el} for a homologous D-A pairs is very unlikely and certainly puts a doubt on extracted k_0 values. Most importantly, it is incomprehensible to treat all such D-A pairs with such a large variation in V_{el} using a single Marcus correlation. Though a weaker MIR is claimed by these authors in the fast relaxing solvent but it is far from a convincing one, as reported in slow relaxing viscous media. In spite of all these critical aspects, this report seemingly deserves appreciation for an attempt to retrieve the intrinsic ET rates involving diffusion assisted reactions in fast relaxing solvents.

CONCLUSIONS: In conclusion, we infer that (i) the observed MIR for bimolecular ET reactions in viscous media using ultrafast fluorescence up-conversion measurement, where ET rates are measured directly as the static quenching component, is a genuine observation. (ii) Though solvation dynamics in ILs are relatively faster than those observed in organized assemblies, yet the relaxation is slow enough such that the better description of ET reaction in these viscous media would be the situation where the reactants move to the product state along the nuclear vibrational coordinate from a quite non-equilibrated solvent reorganization coordinate, rather than the conventional Marcus-type description, where reactant state is always in thermal equilibrium along the solvent reorganization coordinate. A better recipe to deal with this could be a model based on spherically symmetric diffusion equation coupled with 2DET formulation along with reasonable ET parameters. The results on the ET kinetics thus obtained

would probably reproduce the experimentally observed facts in various viscous media including ILs and organized assemblies. (iii) Despite the limitations of simple SV analysis, small distribution of fluorophore lifetimes does not significantly influence the overall trend of Marcus correlation curve and the observation of MIR in viscous media. It is realized that for precise determination of ET quenching rates in viscous media, a detailed diffusion kinetics model based on 2DET incorporating the static, transient and diffusion limited conditions is the utmost necessity.

ASSOCIATED CONTENT

Supporting Information. Details of experiments and results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Email: manojk@barc.gov.in (MK) & hpal@barc.gov.in (HP)

Notes

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