Water-Triggered Photoinduced Electron Transfer in Acetonitrile-Water Binary Solvent. Solvent Microstructure-Tuned Reactivity of Hydrophobic Solutes

Anna Lewandowska-Andralojc[*a,b], *Gordon L. Hug*[c], *Bronislaw Marciniak*[a,b], *Gerald Hörner*[d], *Dorota Swiatla-Wojcik*[*e]

[a]Faculty of Chemistry, Adam Mickiewicz University, Uniwersytetu Poznanskiego 8, 61-614, Poznan, Poland, alewand@amu.edu.pl

[b]Center for Advanced Technology, Adam Mickiewicz University, Uniwersytetu Poznanskiego 10, 61-614 Poznan, Poland

[c]Radiation Laboratory, University of Notre Dame, Notre Dame, USA

[d]Institut für Anorganische Chemie IV, Universität Bayreuth Universitätsstraße 30, NW I, 95540 Bayreuth, Germany

[e]Institute of Applied Radiation Chemistry, Faculty of Chemistry, Lodz University of Technology, Zeromskiego 116, 90-924 Lodz, Poland

swiatlad@p.lodz.pl

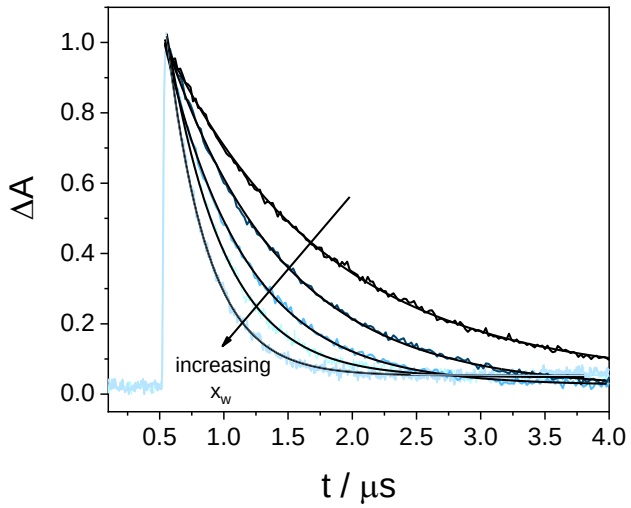

Figure S1. Normalized decay profiles at 520 nm obtained during laser flash photolysis at 355 nm of deoxygenated solutions of benzophenone (2.5×10^{-3} M) and anisole (0.006 M) in different ACN-H_2O mixtures (x_w from 0.34 to 0.81).

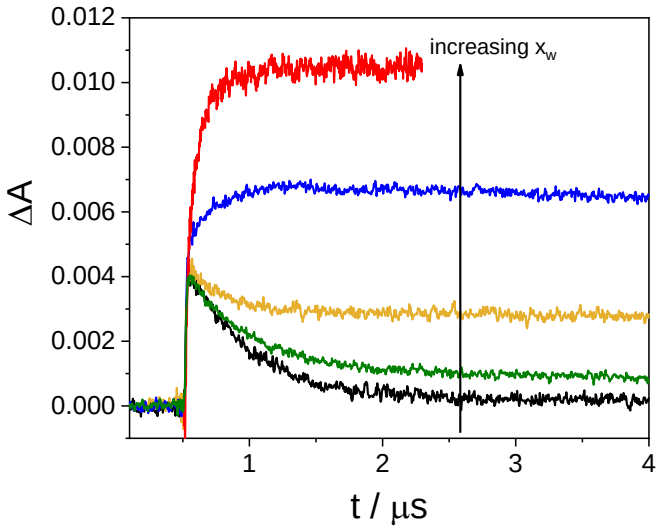

Figure S2. Decay profiles at 600 nm obtained during laser flash photolysis at 355 nm of deoxygenated solutions of benzophenone (2.5×10^{-3} M) and anisole (concentration for 90% of quenching) in different ACN-H_2O mixtures, x_w = 0.66 black symbols; x_w = 0.74 green symbols; x_w = 0.81 yellow symbols; x_w = 0.89 blue symbols; x_w = 0.92 red symbols.

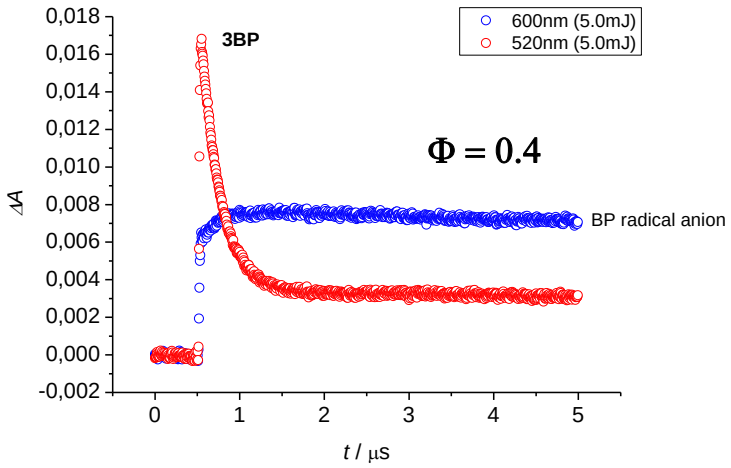

Figure S3. Decay profiles obtained during laser flash photolysis at 355 nm of deoxygenated solutions of benzophenone (2.5×10^{-3} M) and anisole (4.6×10^{-3} M anisole) in ACN-H_2O (1:4 v/v), (520 nm (red), 600 nm (blue).

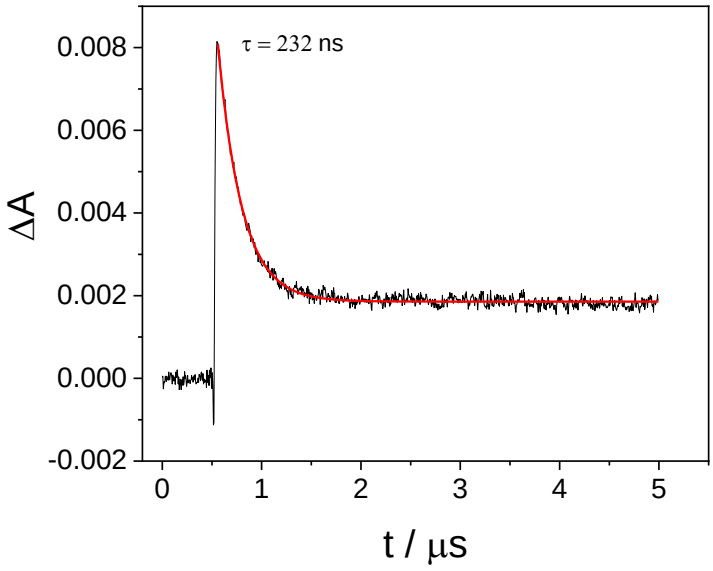

Figure S4. Decay profiles at 480 nm obtained during laser flash photolysis at 355 nm of deoxygenated solutions of benzophenone (2.5×10^{-3} M) and anisole (4.6×10^{-3} M anisole) in ACN-H_2O (1:4 v/v). Solid curve is the monoexponential fit, the number represents the value obtained from the fit to kinetic profile.

Collins-Kimball model adopted for rationalization of kinetics model

The estimates of the following are based on the Collins-Kimball solution to contact diffusion-reactions with $u(r) = 0$, adopted from literature [1]:

$$k(t) = k\left[1 + \frac{k_0}{k_D} e^{\alpha^2 t} erfc(\alpha\sqrt{t})\right] = \begin{matrix} k_0 & at & t = 0 \\ k & at & t = \infty \end{matrix} \quad (Eq.S1)$$

$$k_D = 4\pi\sigma D \quad (Eq.S2)$$

$$\alpha = \sqrt{\frac{D}{\sigma^2}\left[1 + \frac{k_0}{k_D}\right]} \quad (Eq.S3)$$

$$k = \frac{k_0 k_D}{k_0 + k_D} \quad (Eq.S4)$$

or

$$\frac{1}{k} = \frac{1}{k_0} + \frac{1}{k_D} \quad (Eq.S5)$$

At 25 °C the diffusion constants of acetonitrile and water are 3.18×10^{-5} cm^2s^{-1} and about 2×10^{-5} cm^2s^{-1}, respectively. Putting these diffusion constants into the equation for α along with σ of the order of 7 Å and $\frac{k_0}{k_D}$ the order of 1 or smaller, the factor $e^{\alpha^2 t} erfc(\alpha\sqrt{t})$ goes to zero very rapidly with time. This is illustrated in the simulation presented in Figure S5.

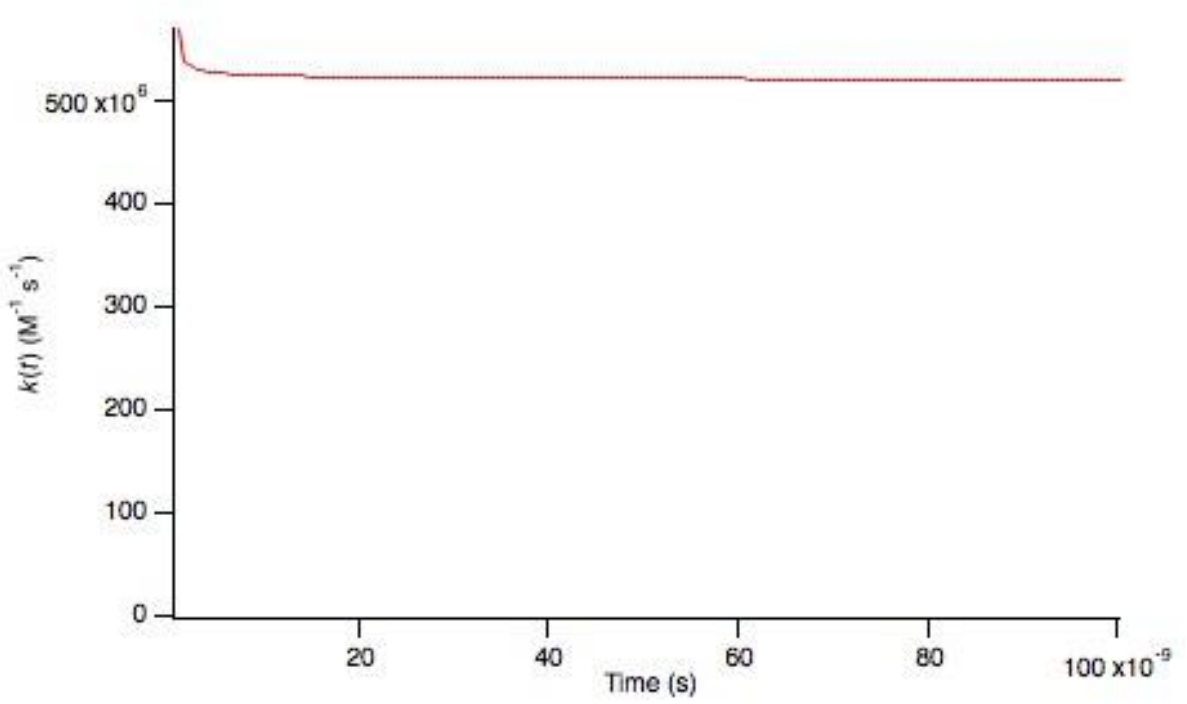

Figure S5. Collins-Kimball solution to diffusion quenching in free space.

The contact reaction rate constant was chosen k_0 = 5.96 × 10^8 M^{-1} s^{-1} to be consistent with the steady-state equation, $\frac{1}{k} = \frac{1}{k_0} + \frac{1}{k_D}$, using k = 5.4 × 10^8 M^{-1} s^{-1} which is the largest empirical k_q (plotting k(obs) vs [Q]) measured at $\chi_w = 0.92$. k_D was taken to be $5.79 \times 10^9 M^{-1}$ s^{-1} (using the viscosity interpolated to the value at $\chi_w = 0.92$ from ref. [2]) in computing k_0 used in the Figure S5. In particular, we computed $\frac{1}{k_0} = \frac{1}{k_q} - \frac{1}{k_D}$. This simulation shows that on the time scale used in the experiments performed in this study, namely measuring triplet quenching, it is not expected to see the transient in a time-dependent quenching rate constant. Single exponential decays were observed in all of kinetic traces, and, empirically, all pseudo-first order plots, namely dependence of reciprocal lifetimes vs quencher concentration were linear.

In addition, in Burshtein's "kinetic limit"[1], the generally time-dependent rate constant, $k(t)$, becomes a time-independent rate constant, k_0. In the Figure S5, the time-dependent Collins-

Kimball rate constant reaches a plateau as it just gets into the nanosecond range. In summary, the steady-state Collins-Kimball solution

$$\frac{1}{k_q} = \frac{1}{k_0} + \frac{1}{k_D} \quad (Eq.S6)$$

can be used for the analysis of the second-order quenching rate, k_q.

Rational for viscosity not accounting for the observations

Viscosity considered as the sole factor for our observed variation in k_q cannot account for the quantitative behavior of the empirical quenching rate constant as a function of solvent composition in this case. Viscosity (η) would come into the equation for k_q as $k_D = k_B T/(6\pi\eta\sigma)$. This cannot explain the change in k_q from 4.6×10^6 M^{-1} s^{-1} at $\chi_w = 0$ to 5.4×10^8 M^{-1} s^{-1} at $\chi_w = 0.92$ (a change in quenching rate constant by factor of 100) because the viscosity at the extremes changes only by a factor of 0.38 mPa s to 1.1 mPa s going from $\chi_w = 0$ to $\chi_w = 0.92$[2]. Because of the relationship between diffusion constant and viscosity being reciprocal, this relationship is even in the wrong direction for viscosity to account for our observations.

Continuous solvent model in the Marcus-theory

The values for the squared refractive index (n_D^2) and the static dielectric constant (ε_s) for the ACN-water mixtures where extrapolated from the refs. [2-4] and plotted in Figure S6 and Figure S7, respectively.

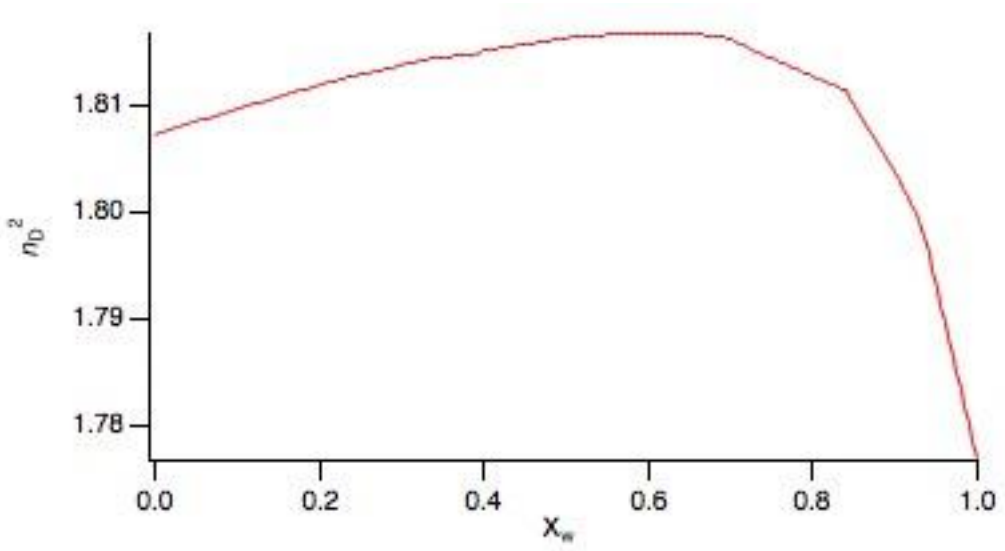

Figure S6. Squared refractive indexes as a function mole fraction of water interpolated from the refs. [2, 4].

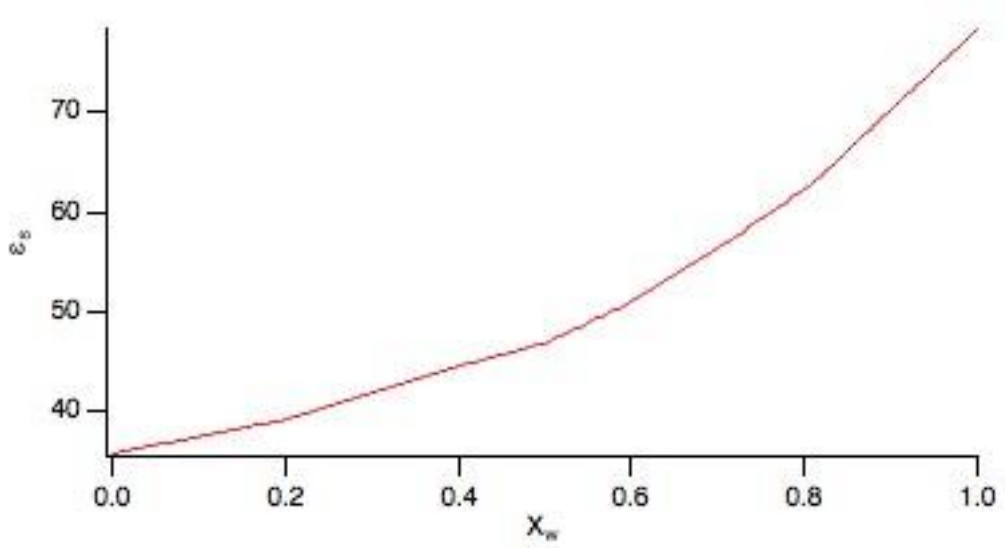

Figure S7. Interpolated static dielectric constants as a function of x_w from the ref. [3]

Based on the data plotted on Figure S6 and Figure S7 solvent reorganization energies for various ACN-H_2O mixtures were calculated using the Born formula for the free energies of ions in solution:

$$\lambda = e^2\left(\frac{1}{2r_B}+\frac{1}{2r_Q}-\frac{1}{r_{BQ}}\right)\left(\frac{1}{n_D^2}-\frac{1}{\varepsilon_s}\right) \quad (Eq.S7)$$

Where: r_B – is the radius of the BP anion (3.5 x 10^{-8} cm), r_Q – is the radius of anisole cation (3.5 x 10^{-8} cm) and r_{BQ} – is center-to-center separation of radical ions at contact (7 x 10^{-8} cm). The dependence of the solvent reorganization energies on the ACN-H_2O mixture composition is depicted in Figure S8.

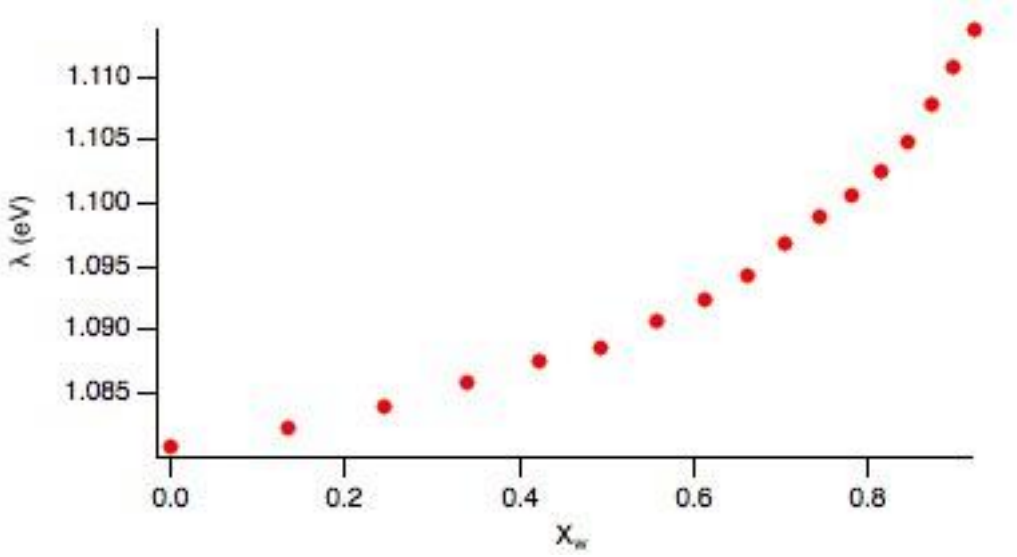

Figure S8. Solvent reorganization energies as function of x_w calculated using the Born formula (Eq. S7).

Subsequently, the ΔG_{ET}^0 for electron transfer process was computed based on the Eq. S8:

$$(\Delta G_{ET}^0)_{\chi w} = (E_{\text{ox}} - E_{\text{red}})_{\chi w} - \frac{e^2}{(\varepsilon_s)_{\chi w} r_{\text{BQ}}} - E_T \quad (Eq.S8)$$

Where: $\frac{e^2}{(\varepsilon_s)_{\chi w} r_{\text{BQ}}}$ is the energy of interaction of the radical ions at contact, E_T is the benzophenone triplet energy (3.0 eV), $(E_{ox} - E_{red})_{\chi w}$ is the value taken from ref. [5] equal 3.59 eV for pure ACN and 3.29 eV for all other molar fractions.

In the next step, Marcus activation energy was computed according to Eq. S9

$$E_{\text{A}} = \frac{(\Delta G_{ET}^0 + \lambda)^2}{4\lambda} \quad (Eq.S9)$$

Finally, the rate constants as a function of water mole fractions based on the classical Marcus theory was computed from Eq. S10 and plotted in Figure S9

$$k_{ET} = \frac{2\pi}{\hbar} V_{BQ}^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{E_A}{k_B T}\right) \quad (Eq. S10)$$

Where: V_{BQ} – is the exchange interaction at contact between excited B and Q (0.01 eV)

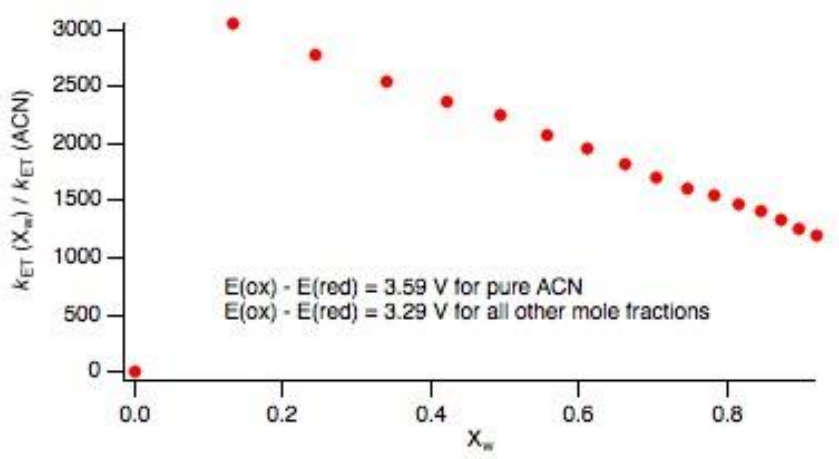

Figure S9. Ratio of the classical rate constant for electron transfer for various ACN-H_2O mixtures to rate constant for electron transfer in ACN as a function of x_w calculated from Marcus theory (Eq. S10).

Figure S9 shows that using continuum-solvent model as a function of refractive index, static dielectric constant and hydrogen bonding interactions that affect the (E_{ox} -E_{red}) one obtains the variation of electron-transfer rate constants that doesn't match our experimental data.

References

[1] A. I. Burshtein, *Adv. Chem. Phys.*, **2004**, *129*, 105-418.
[2] A.-L. Vierk, *Z. Anorg. Chem.*, **1950**, *261*, 283-296.
[3] R. Jellema, J. Bulthuis, G. van der Zwan, *J. Mol. Liq.*, **1997**, *73-74*, 179-193.
[4] J. E. Bertie, Z. Lan, *J. Phys. Chem. B*, **1997**, *101*, 4111-4119.
[5] A. Lewandowska, G. L. Hug, G. Hörner, T. Pedzinski, P. Filipiak, B. Marciniak, *ChemPhysChem*, **2010**, *11*, 2108-2117.