Nanometer-Scale Phase Separation and Preferential Solvation in THF−Water Mixtures: Ultrafast Electron Hydration and Recombination Dynamics Following CTTS Excitation of I⁻

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Ⓢ *Supporting Information*

ABSTRACT: We use the sensitivity of the charge-transfer-to-solvent dynamics of tetrabutylammonium iodide (t−ba⁺ I⁻) to local solution environment to explore the microscopic heterogeneity of binary solutions of tetrahydrofuran (THF) with water in low mole fraction. By tracking the spectrum of the nascent solvated electron, we show that the water is not homogeneously dispersed throughout the THF but rather is "pooled" on the nanometer length scales probed by electron diffusion. The sensitivity of the electron's spectrum to the proximity of t−ba⁺ further reveals that the parent ion pair is differentially solvated, with t−ba⁺ and I⁻ preferentially solvated by THF and water, respectively. Finally, we find that the hydration environment surrounding I⁻ "turns on" geminate recombination between the electron and iodine atom, a

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process not observed in neat THF on the sub-nanosecond time scale. These findings all underscore the fact that microscopic heterogeneities direct the course of chemical transformations in mixed solution environments.

SECTION: Dynamics, Clusters, Excited States
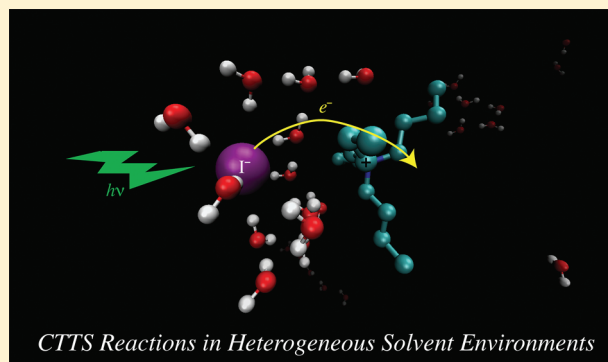
Chemists often perform reactions in mixtures of solvents to control the bulk solution properties needed to carry out a desired chemistry. Yet, even though the bulk properties of liquid mixtures, such as viscosity or polarity, typically vary smoothly as the composition is changed, the local environment experienced by any particular solute may not be reflective of the bulk. Instead, it is quite common for solutes to be preferentially solvated by one component of a liquid mixture. Of greater subtlety, a liquid mixture that is macroscopically homogeneous may have significant inhomogeneity on molecular or nanometer length scales as a result of specific local interactions between the two components.[1−3] The underlying importance of these microscopic details leads us to the questions addressed in this Letter: How can one characterize the local environment of a solute in a solvent mixture? How does this depend on the nature of heterogeneities inherent to a solvent mixture? How does the chemical identity of the solute depend on the nature of local heterogeneity? How does the local environment around a solute in a solvent mixture direct or control chemical reaction dynamics?

In this work, we focus on mixtures of tetrahydrofuran (THF) and water. THF−water mixtures have an unusual closed pressure−temperature loop on their phase diagram: At pressures (P) and temperatures (T) outside this loop (including room temperature and pressure), these solvents are macroscopically miscible in

any proportion; inside the loop, these solvents phase-separate into water-rich and THF-rich components.[4] The bulk properties of THF−water mixtures are highly tunable outside the closed P−T loop: for example, Figure 1 (blue circles) demonstrates that the static dielectric constant of room-temperature/atmospheric pressure THF−water mixtures can be varied smoothly from ∼8 (pure THF) to ∼80 (pure water) simply by changing the bulk composition.[5] Viscosity and other bulk properties change with composition in a similar fashion, but these changes in bulk properties are not linear with mixture composition (cf. Figure 1), suggesting that there are significant local interactions between THF and water that can affect the macroscopic properties of their liquid mixtures.[1,3,6]

Local solvent environment has even greater bearing on the chemistry of reactants dissolved in mixtures, as preferential solvation may significantly alter the energetic barriers for reactions between solutes. In this work, we closely examine the local environments of two particular solutes: iodide ions and solvated electrons (e_{solv}^-). The electronic excited states of both of these solutes are entirely solvent-supported.[7,8] This makes the spectroscopy of these solutes,
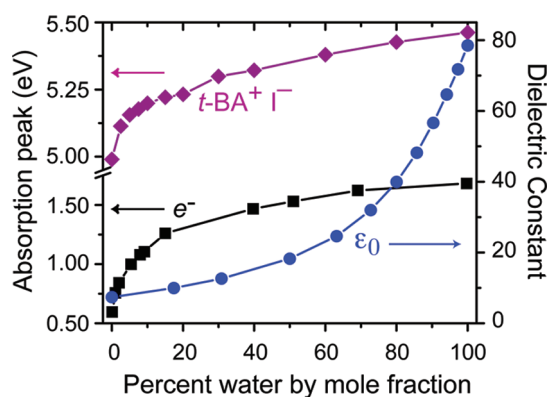
Figure 1. Dependence of the steady-state spectroscopy of the solvated electron[11,12] (black squares) and the CTTS band of t–ba$^+$ · I$^-$[13] (purple diamonds) on solvent composition in THF–water mixtures. The fact that the absorption spectra shift more rapidly at low mole fractions of water than bulk properties such as the dielectric constant[5] (blue circles) indicates that both solutes are preferentially hydrated in the mixtures.

the UV charge-transfer-to-solvent (CTTS) absorption of I$^-$ and the near-IR absorption of the solvated electron, extraordinarily sensitive reporters of each solute's local solution environment.[9,10] Figure 1 compares the peak wavelength of the absorption bands of both tetrabutylammonium (t–ba$^+$) I$^-$ and e_{solv}^- in THF–water mixtures, plotted with purple diamonds and black squares, respectively, across the full range of bulk composition.[11–13] Both of these solutes show dramatic absorption shifts upon the addition of very low mole fractions of water, a composition range over which the bulk properties of the mixtures hardly differ from those of pure THF. Therefore, Figure 1 clearly suggests that both I$^-$ and e_{solv}^- are preferentially solvated by water in mixtures with low water mole-fraction.

Given the spectroscopic sensitivity these solutes have to their local environment, we have performed a series of experiments that interrogate the influence of solvent heterogeneity on the ultrafast charge-transfer dynamics that follow excitation of I$^-$ in a series of THF–water mixtures. By watching how the solvated electron's absorption band shifts with time following CTTS ejection, we have been able to probe the local inhomogeneity of mixtures with low water mole-fractions. We find that electrons are initially ejected into local environments that are essentially indistinguishable from that of pure THF. The electrons subsequently become preferentially hydrated, but they do so with nearly two-state kinetics. This suggests that the electrons simply diffuse until they find a pre-existing "pool" of water in the THF-rich mixtures rather than continuously "gathering" water molecules around themselves one at a time. This implies that THF–water mixtures are not homogeneous on the length scales probed by the initial electron injection and subsequent electron diffusion; rather, these mixtures must be phase-separated on nanometer length scales.

We also have studied the way in which preferential solvation in these mixtures affects subsequent reactions of CTTS-ejected electrons. It is known that counterions play an important role in CTTS reactions in low-polarity solvents due to strong ion-pair interactions with the parent anions: counterions not only perturb the spectra of CTTS anions but also can act as attractive "traps" for electrons ejected into the liquid.[9,14] Our data show that CTTS-generated electrons are "captured" by the proximal t–ba$^+$

cations in mixed solvent environments and that the spectra of these cation-electron pairs exhibit no influence from the water component of the mixtures immediately after electron capture. Therefore, our results show that even though I$^-$ is preferentially solvated by water in these mixtures, its nearby t–ba$^+$ counterion, which is close enough to perturb the I$^-$ CTTS spectrum, must be primarily solvated by THF because the electron initially lands in a pure-THF-like environment. Furthermore, even though the t–ba$^+$ cation does not facilitate electron-iodine recombination in pure THF,[9] we observe that even a small amount of water in the vicinity of the ion pair greatly influences the likelihood for electrons to recombine geminately to reform I$^-$ in these mixtures. All of these findings have important implications for the dynamics of electron transfer and related reactions in mixed solvent environments.

The conclusions we draw from the measurements described here are facilitated by our understanding of the CTTS dynamics of iodide salts in neat THF. In previous work, we demonstrated that the population of electrons generated through CTTS excitation of "counterion-free" I$^-$ in pure THF appears on a ~500 fs time scale.[15] We observed no wavelength-dependent variation in the transient spectral dynamics like those that accompany electron solvation in other solvents, such as water.[16] This is consistent with the lack of electron solvation observed following both multiphoton ionization (MPI) of pure THF[17] and CTTS electron ejection from sodide (Na$^-$).[18] We have attributed this lack of dynamic solvation to the structural properties of liquid THF: our simulations predicted[19] and neutron diffraction experiments by others later confirmed[20] that the structure of room-temperature liquid THF is characterized by large voids. The orientation of the THF molecules around these naturally occurring cavities gives them a net positive electrostatic potential so that they readily can accommodate a newly created solvated electron with very little structural rearrangement. Of prime importance to the discussion below, the lack of spectral dynamics following electron ejection from "counterion-free" I$^-$ in pure THF means that any spectral dynamics of electrons injected into mixtures can be attributed directly to interactions with counterions, cosolvents, or both.

The spectroscopic methods we employed in our current investigation were similar to those in our previous work studying the CTTS ejection dynamics of I$^-$ in pure THF,[9,15,21] and are described in detail in the Supporting Information.[13] Figure 2 presents single-wavelength absorption transients that we collected at various probe wavelengths in the near-IR following 266 nm CTTS excitation of t–ba$^+$ I$^-$ solutions made with (a) neat THF and THF–water mixtures containing (b) 2.5% and (c) 5% water by mole-fraction. The amplitudes of the transients have been normalized, and we have offset the members of each series for clarity. For the transients in neat THF, we observe a subtle wavelength dependence of the e_{solv}^- absorption over the first ~10 ps following CTTS excitation consisting of a slight decay at long wavelengths and a corresponding slight rise at shorter wavelengths.[9] Because the only difference between the data shown here and the counterion-free case we previously explored[15] is the presence of t–ba$^+$, this spectral blue-shifting must reflect dynamics of ion–pair interactions between the ejected electrons and t–ba$^+$.[9] We previously modeled this spectral shift as resulting from the formation of so-called "loose" electron-cation pairs following CTTS ejection.[9] Regardless of whether they pair with counterions in solution, the data in Figure 2a and our previous work show that e_{solv}^- generated in neat THF from both "counterion-free" I$^-$ and t–ba$^+$ I$^-$ negligibly
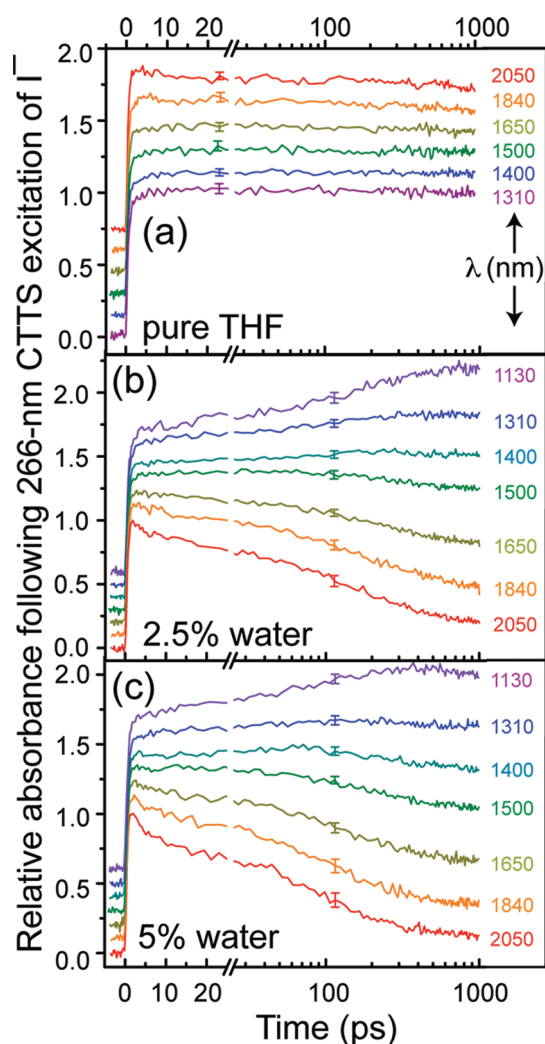
Figure 2. Single-wavelength transient absorption of solvated electrons generated by the 263 nm CTTS excitation of $t-ba^+\, I^-$ in (a) neat THF, (b) a 2.5% mole fraction water/97.5% mole fraction THF solvent mixture, and (c) a 5% mole fraction water/95% mole fraction THF solvent mixture. The slight wavelength dependence of transients during the first 10 ps in neat THF (and presumably also in the mixtures) reflects the process of ion pairing between the nascent solvated electron and the tetrabutylammonium cation.[9] The much more dramatic slower spectral dynamics on the hundreds of picoseconds time scale in the mixtures reflects the subsequent preferential hydration of the ejected electrons.

recombine with their geminate iodine atom partners on sub-nanosecond time scales.

Although the $t-ba^+$ counterion's influence on the spectroscopy and kinetics of e_{solv}^- in pure THF is fairly subtle, Figure 2b,c shows that the addition of a small amount of water dramatically changes the dynamics of CTTS-generated electrons. In solutions containing 2.5% water by mole fraction, the transient absorption at 2050 nm, the wavelength of peak absorbance for e_{solv}^- in pure THF, decays significantly during the first nanosecond following excitation. Concomitantly, the absorption intensity increases at 1130 nm, a wavelength slightly blue of the absorption maximum for an equilibrated electron in a THF—water mixture of this composition (cf. Figure 1). This trend is magnified when the water concentration is increased to 5% mole-fraction, with the 2050 nm absorbance decaying by >75% of its initial value and the

1130 nm absorbance increasing by >50%. Therefore, the presence of small amounts of water leads to a slow but substantial dynamic blue shift of the solvated electron's spectrum following CTTS injection into mixtures of THF and water.

The spectral changes seen in Figures 2b,c are quite different from the rapid spectral blue shifts seen following CTTS ejection from I^- in pure water and short-chain alcohols.[16] Those shifts are associated with the translation and reorientation of solvent molecules nearby the parent I^- as they accommodate the new charge distribution of the $I{:}e^-$ pair. In contrast, the hundreds-of-picoseconds time scale of the blue shifts observed here is much slower than the characteristic reorientational and translational motions of both water and THF in neat solutions (typically a few hundreds of femtoseconds to a few picoseconds)[22−24] and thus must reflect a change in the local solvent composition around the solute.[25−27] Therefore, the data in Figure 2b suggest that electrons initially localize in water-deficient regions of the mixture following CTTS ejection but subsequently become preferentially hydrated as water replaces THF in the vicinity of e_{solv}^-.

To better understand the dynamics of this change in the local solvent composition around the electron, it is important to reconstruct the full spectral evolution associated with the transients in Figure 2. This type of spectral reconstruction requires weighing the single-wavelength transients with their proper relative spectral intensities, which depends on knowledge of the equilibrium spectrum of the solvated electron in THF—water mixtures. Jou and Dorfman previously measured the equilibrium spectra of solvated electrons following pulsed radiolysis of water—THF mixtures.[11] Unfortunately, they reported only the peak positions (cf. Figure 1) and full widths for the absorption spectra; these two parameters alone are insufficient to determine the full spectral shape, even with an assumed Gaussian—Lorentzian form for the absorption band. In addition, we noted above that interaction of electrons with $t-ba^+$ counterions can change the e_{solv}^- spectrum in pure THF. Therefore, it would not be surprising if the counterions could also influence the electron's spectrum in water—THF mixtures with low water mole-fractions. This means that the data in Figure 2 should not be reconciled using the spectra of solvated electrons measured following pulsed radiolysis of neat (no added salt) THF—water mixtures, even if they were available.

Therefore, to sort out both the effects of the counterion and the dynamics of preferential hydration of solvated electrons in THF—water mixtures, we measured the e_{solv}^- transient absorption spectrum to ~1400 nm, the limit of our experimental apparatus, at a time 1 ns after CTTS excitation, which is long enough to ensure that the solvated electrons had reached equilibrium. The details of how we performed these broadband measurements are given in the Supporting Information,[13] and our results are shown in Figure 3a for solvated electrons generated via CTTS excitation of $t-ba^+\, I^-$ solutions in neat THF and THF—water mixtures containing 2.5, 5, and 10% water by mole-fraction (solid curves). We note that we were unable to obtain reliable measurements in the 750−850 nm region because of scatter from the 800 nm driving wavelength for the white-light generation, so we scaled the near-IR and visible sections of the spectrum by applying a simple linear spline through this spectral window. Once scaled this way, we fit each composite spectrum with the characteristic Gaussian—Lorentzian line shape commonly applied to the spectra of solvated electrons (dashed curves).[28] Our fitting procedure and best-fit parameters are summarized in the Supporting Information.[13] The peak wavelength from these fits is
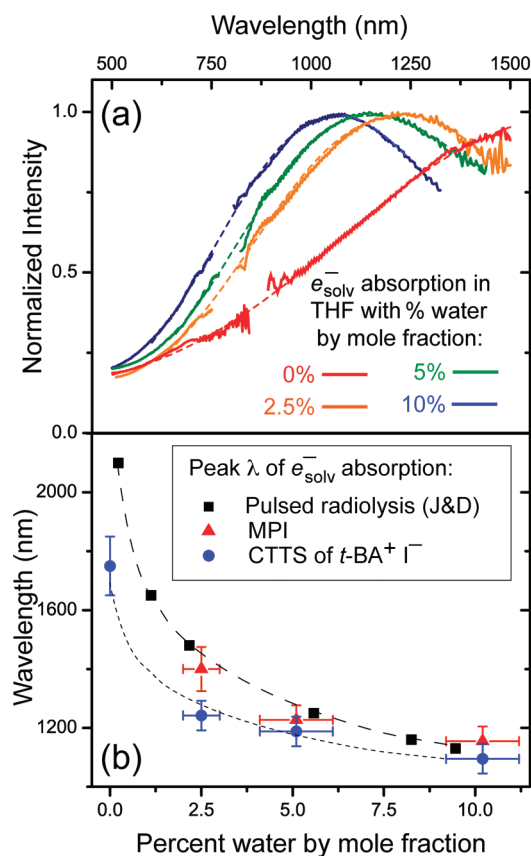
Figure 3. (a) Multichannel transient absorption spectrum of photo-generated electrons in neat THF (solid red curve) and THF mixtures containing 2.5% (solid orange curve), 5% (solid green curve), and 10% (solid blue curve) mole fraction water, measured 1 ns following CTTS excitation of $t-ba^+ I^-$. The dashed curves show best-fit Gaussian–Lorentzian line shapes whose parameters are summarized in the Supporting Information.[13] (b) Peak wavelength of the solvated electron's absorption following CTTS excitation of $t-ba^+ I^-$ (blue circles; values taken from the fits to the data in panel a) and following multiphoton ionization (MPI) of the THF–water solvent mixtures with no solute (red triangles; raw data presented in the Supporting Information[13]). The black squares mark the peak wavelengths measured by Jou and Dorfman[11] following pulse radiolysis of THF-water solvent mixtures.

Figure 4. Spectrally reconstructed transient absorption of solvated electrons generated via 263-nm CTTS excitation of $t-ba^+$-I^- in (a) neat THF, (b) a 2.5% mole fraction water/97.5% mole fraction THF solvent mixture, and (c) a 5% mole fraction water/95% mole fraction THF solvent mixture (same data as in Figure 2). The hydration dynamics in the two solvent mixtures cannot be described by a simple continuous shift but rather follow two-state kinetics, implying that the water molecules in the mixtures are phase-separated from the THF on the nanometer length scales probed by electron diffusion. (See the text for details.)

plotted in Figure 3b (blue circles), along with the peak wavelengths measured by Jou and Dorfman via pulsed radiolysis (black squares; cf. Figure 1).[11] Both data sets exhibit the solvatochromatic blue shift expected with preferential hydration of the electron with increasing water concentration. However, our measured peak absorbance values consistently fall to bluer wavelengths than those reported by Jou and Dorfman.

On the basis of our previous work that investigated electron-counterion interactions in THF,[9,14] we believe that the discrepancy between our measured peak wavelengths for the e_{solv}^- in THF–water mixtures and those of Jou and Dorfman results from the influence of the $t-ba^+$ counterion in our experiments.[29] To test this, we also measured transient absorption spectra of the THF-solvated electron produced following the MPI of neat THF and THF–water mixtures. Although MPI creates both an electron and a radical cation, we have previously shown that the MPI process in liquid THF ejects the electron many nanometers from its point of origin.[17] Therefore, the electrons generated by MPI
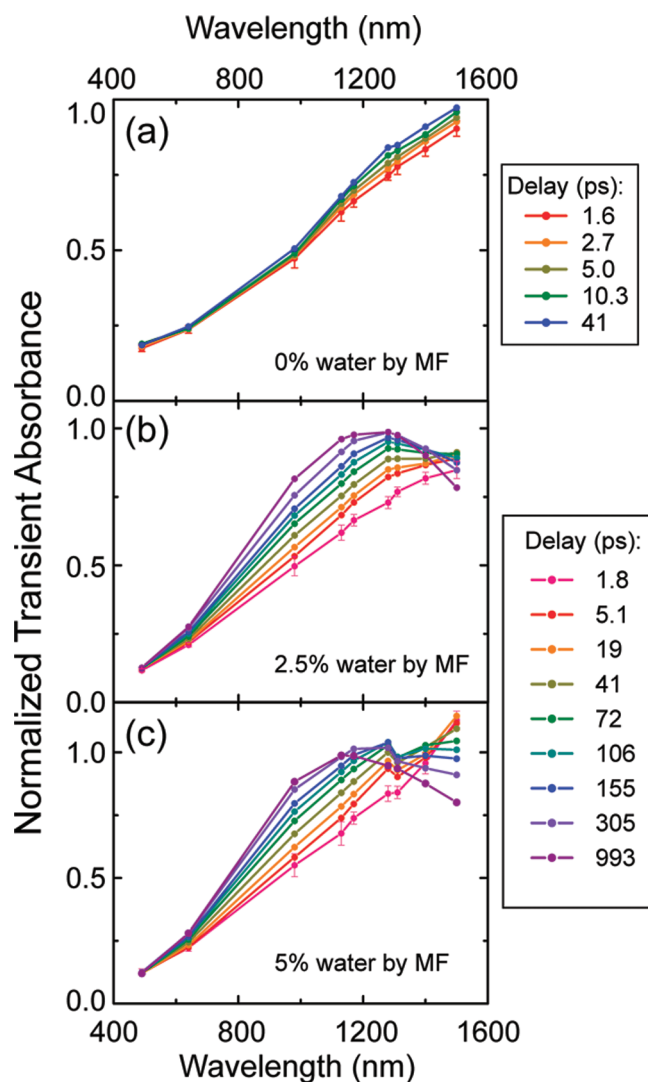
in THF-rich mixtures should be effectively "counterion-free", and their equilibrium spectrum should be identical to what is measured in pulsed radiolysis experiments.[30] The near-IR absorption spectra of solvated electrons created both via CTTS excitation of $t-ba^+ I^-$ and via direct MPI of the different THF–water mixtures measured both 5 ps after excitation and 1 ns (equilibrium) after excitation are shown in the Supporting Information.[13] The peak wavelengths of the equilibrium spectra of electrons created via MPI, which are indicated with red triangles in Figure 3b, agree within error with those reported by Jou and Dorfman.[11] This agreement suggests that the partially hydrated electrons formed after MPI of a solvent mixture are essentially identical to those formed following pulsed radiolysis. The e_{solv}^- spectra collected following CTTS excitation of $t-ba^+$

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I^-, however, are blue-shifted relative to those created from solvent MPI. This indicates that a significant fraction of electrons is able to find and interact with a $t-ba^+$ cation and that this association with the cation remains even as the electrons equilibrate with the mixed solvent environment.

Given that the cation has a clear influence on the electron's spectrum, it is reasonable to anticipate that $t-ba^+$ also should influence the preferential hydration and other dynamics that follow CTTS excitation of I^- in these mixtures. To investigate this in greater detail, we reconstructed the full spectral dynamics encoded in our single-wavelength transients (Figure 2) using the fits to our measured equilibrium transient broadband spectra, which are plotted in Figure 3a. The details of our reconstruction procedure are outlined in the Supporting Information,[13] and the reconstructed spectra are shown in Figure 4. In all cases, the reconstructed spectra 5 ps after CTTS excitation agree with those that we measured directly (see Supporting Information[13]), indicating that our reconstruction procedure is robust. The reconstructed spectra in Figure 4 show that for electrons injected into neat THF there is a slight blue shift of the e_{solv}^- spectrum over a ~10 ps time scale, which results from the formation of a loose-contact pair between the electron and the nearby $t-ba^+$.[9] This behavior persists with added water, but its effect on the spectrum becomes minor relative to the slow preferential hydration dynamics that occur over hundreds of picoseconds and that lead to the highly blue-shifted equilibrium spectra of electrons in mixtures.

Perhaps of greater interest, Figure 4 (cf. also the Supporting Information[13]) clearly shows that electrons injected into solution initially find essentially water-free environments, with spectra in the mixtures that are virtually identical to those in neat THF. Therefore, our data strongly support a picture in which the initially ejected electrons do not land in an environment reflective of the bulk composition; instead, they prefer to localize in "dry" regions of the THF in which no water resides. Once they land in the dry regions, the electrons then become preferentially hydrated, attaining their equilibrium spectrum after a few hundred picoseconds. But the most surprising feature seen in Figure 4 (cf. also the data in Figure 2) is that the spectral dynamics measured in the THF—water mixtures exhibit a quasi-isosbestic point near ~1400 nm, indicating that the spectral shift associated with preferential hydration is not continuous in nature. Therefore, our data strongly suggest that hydration does not occur through a process by which the ejected electrons continuously gather water in their first solvation shell. Instead, Figure 4 indicates that preferential hydration and equilibration occurs via a kinetic interconversion on a hundreds-of-picoseconds time scale.

Because the spectral dynamics seen in Figure 4 clearly are dominated by the disappearance and formation of two distinct states of electron hydration, we can understand the hydration process quantitatively using a simple kinetic model. Our initial attempts focused on describing the data in the mixtures with a two-species interconversion model

$$e_{dry}^- \xrightarrow{k_{hyd}} e_{wet}^- \qquad (1)$$

where e_{dry}^- has the spectrum of an electron in neat THF and e_{wet}^- has the (preferentially hydrated) equilibrium spectrum for a given THF—water mixture. This model implies a well-defined isosbestic point in the time-evolving spectrum but the data in Figure 4 show only quasi-isosbestic behavior; consequently, this model did not provide a satisfactory fit. Our attempts to describe

Table 1. Best Fit Parameters for Kinetic Hydration-Recombination Model Given by Equations 2 and 3[a]

water mole-fraction (%)	2.5	5	10
k_{hyd} (ps)	239 (25)	183 (30)	118 (25)
k_{GR} (ps)	106 (25)	71 (20)	138 (50)
f_{GR}	0.20 (0.03)	0.26 (0.04)	0.16 (0.04)

[a] Estimated parameter uncertainties are given in parentheses.

the spectral evolution with a continuous spectral shift also were met with little success.[31]

Therefore, we turned to a slightly more complex model that involves a simple two-species kinetic conversion but with some probability (f_{GR}) that one of the species disappears (and therefore no longer absorbs) due to geminate recombination with iodine with rate k_{GR}

$$e_{dry}^- \xrightarrow{k_{hyd}} e_{wet}^- \qquad (2)$$

$$e_{wet}^- + I \xrightarrow{k_{GR}, f_{GR}} I^- \qquad (3)$$

We can readily justify such a model by noting that even though there is no geminate recombination on sub-nanosecond time scales between the CTTS-ejected electron and the parent iodine atom in neat THF,[15] such recombination occurs readily in neat water, where 65—70% of the ejected electrons recombine within 200 ps.[32] Because water and THF are macroscopically miscible, it is reasonable to expect that the probability for geminate recombination in THF—water mixtures would turn on with increasing mole-fraction water. It also makes sense that recombination is much more likely to occur during an encounter of the geminate pair in a hydrated region within the mixture, with water providing a trap to hold electrons near the iodine atom, altering the Marcus curves for back-electron transfer, or both. This also fits with the data in Figure 1, which shows that I^- itself is preferentially solvated by water so that any recombination likely takes place in water-rich regions of the mixture. Finally, this type of model is highly consistent with the data: by invoking recombination only from a fraction of hydrated motifs, we can recover the slight spectral blue shift in Figure 4 between 1300 and 1500 nm that washes out a distinct isosbestic point. A model invoking disappearance of "dry" electrons would introduce a red shift around the quasi-isosbestic point, a result in contrast with the data.

We fit the data in Figure 4 to the model summarized by eqs 2 and 3 by assuming that the spectrum we measured at 5 ps is that of the "dry" electron (in its loose complex with the $t-ba^+$ counterion) and that the equilibrium "wet" spectrum is that measured 1 ns after CTTS excitation (cf. Supporting Information).[13] Our fit uses only three parameters: a hydration rate (k_{hyd}), a geminate-recombination rate (k_{GR}), and the fraction (f_{GR}) of electrons that recombine after becoming hydrated. The fits are quantitative in all mixture compositions we studied, with the residuals for each data point at every time delay falling well within 95% confidence limits. A summary of the best fit parameters is given in Table 1.

The fact that such a simple model fits the data so well has important implications for the liquid structure of THF—water mixtures: the model suggests that the water in such mixtures naturally exists in localized regions or "pools" rather than being homogeneously distributed throughout the solvent. Solvated

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electrons are initially ejected to places that on average reside a fair distance from any of the water pools. They must then diffuse through what is essentially pure THF until they encounter a pool. Because we see no evidence of a continuous solvation-induced shift of the electron spectrum, the water must then preferentially hydrate electrons on a time scale fast compared with diffusion. All of this means that THF and water in such mixtures must be phase-separated on a length scale given by the distance that electrons can diffuse on a roughly 100 ps time scale, which is at least several nanometers.[9,17] Therefore, despite their macroscopic homogeneity, our results show that THF and water are not truly miscible on microscopic length scales, an observation that is consistent with recent neutron diffraction,[3,33] dynamic light scattering,[6,34] and X-ray diffraction[2] experiments on THF—water mixtures.

It is straightforward to understand why electron injection into THF—water mixtures is a natural probe of the nanometer-scale phase segregation of the two components. We know that neat THF is characterized by the presence of electropositive voids that are naturally occurring traps for ejected electrons.[19,35] As we add small amounts of water to liquid THF, it is easy to imagine that the water might preferentially reside in the pre-existing THF cavities, creating water pools that are separated from the otherwise pure regions of THF; such an idea fits nicely with the fact that THF and water have a negative volume of mixing.[36] We can then explain the electron ejection and solvation dynamics as follows. In mixtures with low water mole-fraction, the electrons are likely to localize in a THF-rich domain simply on a statistical basis; if there is only 5% mole-fraction water and the water is pooled together, then the electron is ~20 times more likely to find a THF region of the mixture. Moreover, if there are still some empty THF cavities in the mixtures, we expect the electrons to prefer to localize into the empty cavities because we know these act as favorable traps for a newly generated electron.[19] In addition, we believe that the initially ejected electrons prefer to avoid the water in the mixtures for two reasons. First, because water—THF interactions are characterized by hydrogen bonding between the water H atoms and THF oxygen atoms,[1] small water pools in THF cannot provide the appropriate H-bond stabilization to capture newly ejected electrons.[37] Second, the change in hydrophobicity of the iodide ion upon loss of its electron dominates the H-bonding structure of the local water molecules[38] so that there is no favorable location for a small iodine-containing water pool to accept a newly generated electron. Therefore, in the absence of counterions, electrons are initially solvated entirely by THF; then, they simply diffuse until they encounter a water pool, where on a time scale fast compared with diffusion they become rapidly preferentially hydrated and reach equilibrium.

Although this simple model fits our measurements quantitatively, we must still reconcile the spectral kinetics we see — and their implications for nanometer-scale phase separation of THF—water mixtures — with the influence the counterions have on the electron-transfer dynamics in solution. The fact that $t-$ba$^+$ cations are able to modify the spectral shape and peak-wavelength of the e_{solv}^- absorption spectrum from a time ≤5 ps after ejection to beyond 1 ns (cf. Figure 3b) implies that most electrons generated via CTTS excitation of $t-$ba$^+$ I$^-$ remain in the proximity of the cation throughout the process of hydration. We observed previously that even though electrons were ejected to a distance of ~6 nm from counterion-free I$^-$ in neat THF, most of the ejected CTTS electrons landed within ~1.5 nm of a sodium cation when Na$^+$ was present.[15] This is because the
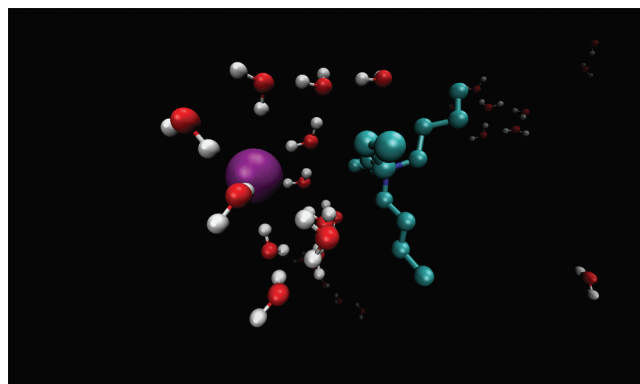

Figure 5. Representative snapshot from an equilibrium classical molecular dynamics simulation of $t-$ba$^+$-I$^-$ in a 5% mole fraction water/95% mole fraction THF liquid mixture. The THF molecules are not shown for clarity, and the size of the Figure is adjusted to encompass the entire simulation box. The "pooling" of the water molecules (red O atoms and white H atoms) in the THF can plainly be seen, as can the fact that the I$^-$ ion (purple) is preferentially hydrated by residing at the edge of a water pool. The pairing with the nearby $t-$ba$^+$ counterion (dark blue N atom, light blue united-atom CH$_2$ groups), which resides in the THF-rich region adjacent to the iodide ion's water pool, is also readily evident.

positive charge on a cation lowers the potential energy of any nearby THF cavities, making them deeper traps for newly ejected electrons. For the mixtures, given that we know the ejected electrons land in the proximity of the cation and that the e_{solv}^- initial environment is "dry", this implies that the $t-$ba$^+$ cation cannot be located in a water pool. At the same time, we know that I$^-$ is preferentially solvated by water (Figure 1) and that its CTTS band is perturbed by the presence of $t-$ba$^+$. Therefore, our data indicate that $t-$ba$^+$ is initially solvated primarily by THF but also resides close enough to an I$^-$ —containing water pool to influence the iodide's absorption spectrum. The net implication is that $t-$ba$^+$ I$^-$ is solvated differentially in nanometer phase-segregated THF—water mixtures: I$^-$ sits at the edge of a water pool and $t-$ba$^+$ resides nearby in a predominantly "dry" region of THF.

To test this picture of differential solvation, we performed classical molecular dynamics simulations of $t-$ba$^+$ I$^-$ in a liquid mixture of 5% water in THF; the details of how our simulations were carried out are given in the Supporting Information.[13] Figure 5 shows a representative snapshot from these simulations, with the THF molecules omitted for clarity. (An alternate version of this figure with the THF molecules shown is included in the Supporting Information.[13]) A quick glance at Figure 5 shows the following features: (1) rather than being homogeneously dispersed throughout the mixture, the water is indeed isolated into distinct "pools" that are separated on nanometer length scales; (2) the I$^-$ ion resides at the edge of one of the water pools and is thus preferentially hydrated; this finding is related to those of previous simulations that have shown that iodide prefers to localize at aqueous interfaces;[39] and (3) the $t-$ba$^+$ counterion is associated with the I$^-$ ion but resides in a region of the solvent composed of THF molecules just at the outside edge of the water pool containing the I$^-$ ion. All of these features strongly support the conclusions we reached from the ultrafast spectral dynamics discussed above.

In addition to the ultrafast spectral dynamics, the recombination yields extracted from our kinetic model are also affected by the local solvation environment in solvent mixtures. With only 2.5% water by mole-fraction, we already observe a 20% yield for

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recombination on a 1 ns time scale after CTTS excitation; in contrast, electrons do not recombine with their geminate iodine partners on this time scale in neat THF. It is difficult to assign this increase in recombination yield to any single factor. We expect that preferential hydration in the region of the electron-iodine pair should alter the relative stabilization and solvent coordinates of the Marcus curves for the reactants and products. This could reduce the barrier to back-electron transfer enough to compete with the diffusion that allows the electron to escape recombination. However, water may also play another important role in the recombination process: trapping the electron nearby the iodine atom via local hydration. In this sense, the water creates an energetic penalty (alternatively, an additional kinetic layer) for the electron to escape into the THF and diffuse away. Therefore, the water's ability to trap and hold the electron nearby the I atom may be a dominating factor giving rise to the increased recombination yields in these solvent mixtures.

In addition, given that the ejected electrons stay associated with $t-ba^+$, the preferential hydration dynamics we observe must involve mutual diffusion of the cation-electron pair toward a water pool. If the hydration of the cation-electron pair takes place in the same water pool with the I atom (which is likely to be the closest pool because we know that $t-ba^+$ and I^- were associated before CTTS excitation), then the cation may have a similar constraining effect as water on encounters of the geminate pair: the $t-ba^+$ cation, like the water, "tethers" e^-_{solv}, holding it close to its geminate I atom partner. Yet, even though $t-ba^+$ may promote encounters between e^-_{solv} and I, the fact that the electron is associated with $t-ba^+$ may actually hinder the probability for recombination by providing a minimum in the potential of mean force that is unfavorable for recombination. This could be the reason behind the relatively flat recombination yield with increasing water concentration seen in Table 1. Although the presence of both $t-ba^+$ and water complicate the geminate recombination process, the fact that the cation can trap an electron proximal to the iodine in both "dry" and preferentially hydrated local environments indicates that it is the water's effect on the barrier for back-electron transfer that is the dominant factor giving rise to the increased recombination yield with increasing water content.

In summary, we have used the ultrafast dynamics of preferential hydration and geminate recombination of the solvated electrons produced following CTTS excitation of I^- to probe the microscopic heterogeneity in liquid water−THF mixtures with low water mole-fractions. Steady-state spectroscopy tells us that both the I^- ion and the solvated electron are preferentially hydrated in such mixtures, yet CTTS excitation initially ejects electrons into an environment that is identical to that of dry THF. The subsequent dynamics of preferential hydration takes place with two-state kinetics, showing that macroscopically homogeneous THF−water mixtures are in fact phase-separated on the nanometer length scales probed by electron diffusion. In addition, we saw spectroscopic evidence that the ejected electrons remain associated with the counterion and that $t-ba^+ I^-$ must be differentially solvated: thus, the iodide ion resides at the edge of a water pool, and the counterion is located in an immediately adjacent region of dry THF, a picture verified by molecular dynamics simulation. Finally, we saw that the local heterogeneity also affects geminate recombination, with the presence of small amounts of water allowing geminate recombination to take place even though it does not occur in dry THF. Taken together, the results show that the nature of

local inhomogeneities in liquid mixtures critically determine the dynamics of chemical reactions in complex solution environments.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental and MD simulation details, spectral fitting parameters, and detailed comparison of spectra and dynamics of electrons produced via MPI and CTTS from I^- in THF−water mixtures. This material is available free of charge via the Internet at http://pubs.acs.org/.

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(29) We note that the peak wavelength we observe in neat THF is consistent with our previous work on t−ba⁺ I⁻ in this solvent, in which we found that CTTS excitation generates electrons that are initially "free" but then couple to the t−ba⁺ counterion over the first several picoseconds, leading to a spectral blue shift.[9] Furthermore, this peak wavelength closely matches the peak of the transiently lived Na+·e^- loose-contact pair we observed in the reaction of solvated electrons with Na+ in THF.[14]

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