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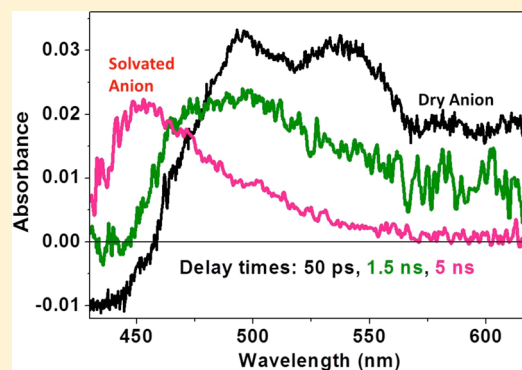
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**S** Supporting Information

**ABSTRACT:** We have studied the dynamics of solvation of electron injected directly into primary alcohols as well as that of fluorenone anion using pulse radiolysis technique with the time resolution of about 15 ps. Unlike in the previous reports, we observe nonexponential dynamics of both electron and anion solvation. While the ultrafast component,  $\tau_1$  (<15 ps) representing the inertial time scale of the dynamics is faster than the time resolution of the spectrometer, the slower component,  $\tau_2$ , has been assigned to the translational motion leading to structural changes of the hydrogen bonding network of the solvent in the inner solvation cell or alcohol cluster.  $\tau_2$  agrees well with the electron solvation times reported by the earlier authors.  $\tau_3$  is associated with the restructuring of the hydrogen bond network structure of the solvent in the region outside the solvation cell. Nonexponential solvation dynamics of the fluorenone anion has been described well by a two-component process. The most important observation in this work is that the lifetime of the shorter component,  $\tau_1$ , determined in four alcoholic solvents, is much longer than the electron solvation time in the corresponding solvents determined in this work or anion solvation time reported earlier. The lifetime of this component is nearly comparable with the average dipolar solvation time but shorter than the longitudinal relaxation time of the solvent. In the case of anion,  $\tau_1$  has been assigned to the restructuring of the first solvation shell by breakage of solvent hydrogen bonds of the fluorenone molecule and formation of hydrogen bonds with the anion. In this case, too, the longer component,  $\tau_2$ , with the lifetime of a few nanoseconds, has been assigned to reorganization of hydrogen bonds in the solvent hydrogen bond network structure.



## 1. INTRODUCTION

Radiation chemistry is mainly concerned with the reactivities of primary radicals and ionic species, which are generated in liquids or solutions following irradiation using ionizing radiations.<sup>1,2</sup> Solvent plays an important role in altering their chemical reactivities by confining them in a solvent cage via dipolar and/or any kind of specific interactions, such as hydrogen bonding, which is popularly known as solvation.<sup>3–5</sup> Solvation lowers the energy and hence the mobility as well as the reactivity of these reagents. In addition, both the energetics and the kinetics of solvation influence the chemical reactivity.

Electron solvation in hydrogen bonding solvents, e.g. water, ammonia and alcohols, has been the subject of immense interest during the past five decades, and the fact has been well established that the process is complete within a few tens of femtoseconds to picoseconds depending on the structure of the solvent.<sup>6–31</sup>

In the 1960s and 1970s, it was realized that dynamics of electron solvation process could only be studied in matrices at low temperature (4 or 77 K).<sup>6–12</sup> For example, in ethanol at 4 K, an absorption band was observed in the IR at 1500 nm, but at 77 K, it was possible to follow the continuous shift of this band from 1500 to 500–600 nm within 30 min. This shift was

assigned to the process by which the quasi-localized electron was stabilized from “swallow” to “deep” traps. Dynamics of solvation in liquids was first observed in alcohol at low temperature just above the freezing point following the time evolution in the microsecond time range using pulse radiolysis technique.<sup>7,8</sup> Experiments at room temperature could only be performed when picosecond pulse radiolysis was available and with a better time resolution in photoionization or photo-detachment experiments using picosecond and femtosecond laser photolysis (vide infra).

In numerous works dealing with the dynamics of electron solvation in polar liquids, we find two types of interpretation. The first one insists in a stepwise model, in which the IR band is transformed into the visible one.<sup>7,10,13,28</sup> However, no real isosbestic point between the two overlapped absorption bands was observed (Jonah called this model the *phenomenological “two-state” model of solvation*<sup>18</sup>). Two absorption bands were assigned to the quasi-localized electrons at “shallow” and “deep” traps, respectively.<sup>10</sup> It was also explained that the visible

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absorbing electrons were associated with the hydroxyl group, while the IR absorbing electrons were localized in the alkyl group region. In ethanol, about 40% of the IR absorbing electron was transformed into the visible absorbing electron, and the rest underwent geminate recombination.<sup>10</sup>

This model of electron solvation was disputed by Gilles, who considered the time evolution of the absorption spectra of electron as a continuous shift due to relaxation of the solvent or the trapping sites because of various molecular motions.<sup>8</sup> Two possible mechanisms, namely “digging” (reorientation of solvent molecules) and “seeking” (redistribution to the pre-existing deeper trapping sites), which were proposed for the relaxation of localized electrons, were not exclusive to each other, but both the mechanisms contributed to the total evolution of the spectra.

On the other hand, Pepin et al. found that solvation of electrons in liquid methanol as well as in aqueous media involved more than a strictly stepwise transition between the weakly bound (or infrared absorbing at 1500 nm) and the strongly bound (or visible absorbing, 800 nm) electrons, and the collection of kinetics revealed a continuous blue-shift of the absorbing species taking place concurrently (though at a slower rate) to the stepwise transition between them. A set of kinetic traces were successfully fitted with a model that was called “hybrid” owing to the fact that it involved those two types of relaxation of the electron–solvent configurations.<sup>25</sup>

Although the pattern of evolution of the transient spectra in other alcohol matrices was very similar to that in ethanol and 1-propanol, spectra of solvated electron were not the same in all the alcohols (for example, secondary and tertiary alcohols), suggesting the role of structure and close packing of the solvent matrix.<sup>2</sup> Moreover, it appears from numerous reports in the literature that the process is kinetically different in matrices and liquids. For example, in liquid phase, the decay of the IR absorption is similar to the rise of that in the visible, but the former is faster in matrices.<sup>6–12</sup>

During the end of the past century, both the femtosecond laser spectroscopic and picosecond pulse radiolytic techniques were extensively used to monitor the solvation of electrons in aqueous and alcoholic solvents at room temperature in real time.<sup>13–31</sup> Femtosecond studies of electron solvation in a series of neat linear alcohols by Eisenthal and co-workers show deuterium isotope effect as well as the chain length effects in slowing down the solvation dynamics attributed to hydroxyl librational and translational motions of the alcohol molecules that form the electron cavity.<sup>28,29</sup> A correlation between the electron solvation time and the Debye relaxation time,  $\tau_D(2)$ , led to predict the correlation between electron solvation and the dielectric relaxation of the solvent. Additionally, a slower process in methanol with the lifetime of about 40 ps was attributed to the cooling of the solvated electron by vibrational relaxation in the ground electron state.<sup>28</sup>

However, Kenney-Wallace and Jonah emphasized that the method of electron injection may affect the mechanism of electron solvation.<sup>19</sup> Thus, a high energy (3–7 MeV) electron injected in a pure liquid may not solvate in the same way as does an electron (energy is about a few eV) arising from photodetachment or photoionization of a solute molecule as guest in the same liquid. The main differences lie (i) in the energy of the electrons, which govern the whole process undergone by the electron from the ionization to the thermalization, (ii) in the reactivity of the parent cation, and (iii) in the distribution (inhomogeneous in radiolysis) of the

species, which influence the geminate recombination taking place concurrently with the localization and the solvation process.

Looking at the overall view of the various interpretations and types of experiments, it appears that the solvation process of electrons in hydrogen bonding solvent is not fully understood. A theoretical investigation of Abrahamczyk and co-workers on electron solvation in the glass matrices of hydrogen bonding solvents at 77 K revealed that hydrogen-bonding interactions played an important role in the first stage (i.e., localization) of the dynamics of excess electron migration.<sup>32</sup> Clark and Illing suggested that the major interaction, apart from the spin-polarization, was hydrogen bonding with the localized electron as a donor to the antibonding  $\sigma^*(\text{OH})$  or  $\sigma^*(\text{NH})$  orbitals in water and  $\text{NH}_3$ , respectively. However, in alcohols, the hydrogen bond was ignored in creating the dipole oriented cavity.<sup>33</sup>

Like in the case of electron solvation, studies of anion solvation too were initiated in matrices at low temperature due to insufficient time resolution of the absorption spectrometers. The very first experiment was due to Hoshino et al., who observed a slow (in a few hundred microseconds time scale) blue-shift of the absorption spectra of the anion radicals of benzophenone, acetophenone, and other derivatives, which was attributed to the solvation process, in ethanol at 100 K. Solvation of benzophenone anion radical proceeded with an initial stage faster than the later one. This result was interpreted by predicting rapid formation of the solvent sphere around the anion, which shielded the Coulombic field and reduced the rate of reorientation in the outer shell. In the case of fluorenone anion, no shift of the absorption spectrum of the anion was observed in these conditions.

Subsequently, Huddleston and Miller studied the spectral relaxation of benzophenone anion in methanol and ethanol glasses at 4 and 77 K. At 4 K, no spectral shift was observed in ethanol, but a very slow blue-shift in methanol (only 70 nm from 810 to 740 nm within 100 s).<sup>35,36</sup> However, at 77 K, a larger blue-shift was observed in either of these alcohols (from 810 to 625 nm within 100 s). Similarities between the spectral shifts observed in the case of benzophenone anion and that of trapped electrons ( $e^-_t$ ) in the same matrices led the authors to rule out a hopping process for  $e^-_t$ .

Marignier and Hickel performed the first experiment on benzophenone anion solvation in liquid, i.e., in *n*-propanol at 146 K (just above the melting point).<sup>37,38</sup> They too observed a fast process responsible for the most important part of the shift followed by a slower one. Both these processes obeyed a first-order decay law that allowed determining the characteristic time constants. These two processes in liquid phase were found to be in correlation with the data on dielectric relaxation. Comparison of the solvation time of benzophenone anion with the one of electron in the same condition reveals a difference of 1 order of magnitude less for the anion. The same authors also studied the effect of temperature on the spectral shift in the range 133 to 180 K in order to determine the activation energy of the two processes involved in the solvation of benzophenone anion, which revealed the breaking of hydrogen bond as the primary step. In addition, experiments on benzophenone solution in methanol–MTHF mixtures<sup>39,40</sup> and in ethanol–MTHF mixtures<sup>41</sup> also allowed to observe the spectral shift of the anion solvated in alcohol clusters.

Works of Marignier and Hickel<sup>37,38</sup> inspired Jonah and co-workers to further investigate solvation of benzophenone anion in

alcohols at room temperature using picosecond pulse radiolysis techniques. This led Jonah to publish an important series of papers from 1992 to 2003 mainly about benzophenone anion solvation and its comparison with that of electron as well as dipoles.<sup>18,21,22,35,42–46</sup> For alcohols such as 1-propanol and 2-propanol, it was necessary to lower the temperature in the range 263–223 K to slow down the process, which was too rapid at room temperature to be measured.<sup>45</sup> For larger alcohols, such as 1-butanol, 1-decanol, or 1-octanol, measurements could be achieved at room temperature.<sup>42,43</sup> Their works proposed that the spectral shift obey unambiguously to a continuous process and that the rotational motion of the C–OH bond influencing it. They also revealed that while electron solvation times were a little faster than anion solvation times, in a particular solvent, these two times were much faster than the dipolar solvation times.<sup>18,21,42–44</sup> However, this observation was in contradiction to that of Tominaga and Walker, who found that solvation time of anion created in its excited state was very similar to that of a dipole.<sup>47</sup> Jonah and co-workers pointed out that the activation energy for electron solvation was lower than the hydrogen bond energy in 1-propanol, whereas in 2-propanol the two energies were similar.<sup>18,21</sup> On this basis, they concluded that the solvation process in the former liquid did not require breaking of the hydrogen bonds between solvent molecules to allow the molecules to reorganize around the electron. Further, in 1-propanol, contrary to 2-propanol, the quasi-free electron could easily meet a deep pre-existing trap with the structure similar to that of an occupied and relaxed trap. In addition, the activation energy for anion solvation was found to be equal to the hydrogen-bond energy for the liquids, which suggested the requirement solvent reorganization by breaking the hydrogen bonds between solvent molecules. These results revealed the importance of the microscopic liquid structure in the solvation process.

Because of much better time resolution (a few tens of femtoseconds), laser spectroscopic techniques have been widely employed to study the solvation dynamics of quasi-free electrons in water using the photoionization technique. Antonetti and co-workers and Hertwig et al. determined that the characteristic time constant of electron solvation in water was about 300 fs and was completed within about 5 ps.<sup>23,26,30</sup> However, alcohols form an interesting class of liquids for investigation of the factors influencing the formation and stabilization of electrons in fluids. Essentially superimposable optical absorption spectra of solvated electrons in methanol to 1-hexadecanol with an absorption maximum at  $1.8 \pm 0.6$  eV as well as similarities in the absorption coefficients of the solvated electron strongly imply that the electron is bound in similar discrete molecular trapping sites in all.<sup>24,48</sup> However, the dynamics of the alcohol molecules should vary considerably as a result of the torque exerted by the hydrocarbon chain attached to each OH dipole. The molecular dipole moments of the liquids appear relatively constant at 1.9 D despite a 5-fold change in the macroscopic (or static) dielectric constant ( $\epsilon_s$ ) and considerable variation in the extent of hydrogen bonding.<sup>3,49</sup> In addition, dielectric relaxation studies identified three distinct time regions of dielectric loss usually associated with the dynamics of the multimer formation ( $\tau_{D1}$ ), with monomer reorientation ( $\tau_{D2}$ ) and –OH bond rotation ( $\tau_{D3}$ ) (vide infra).<sup>50</sup> While these assignments are not definitive but dependent on any strong local fields, the relaxation times nevertheless serve as a useful framework within which to

separate the relatively *slow* from the *fast* molecular motions in the solvation process.

We have studied the dynamics of solvation of high energy (7 MeV) electrons injected directly into the solvent from an electron accelerator as well as several anionic species generated via direct capture of dry electron in linear alcohols having alkane chain lengths longer than five carbon atoms, i.e. 1-pentanol and higher alcohols, using picosecond pulse radiolysis technique with about 15 ps time resolution. One of our motivation was focused on the solvation times of the fluorenone anion in the context of the earlier works of Jonah and co-workers, which report solvation times for electrons and benzophenone anion much faster than that for dipoles.<sup>19,42–45</sup> in the present work, we find that both electron and anion solvation processes are multiexponential in alcohols and the time scales are widely different.

## 2. EXPERIMENTAL SECTION

All the solvents, namely the alcohols, were of spectroscopic grade, and the solutes, namely fluorenone, biphenyl, benzophenone, and pyrene, were of puris grade procured from Aldrich-Sigma and were used without further purification.

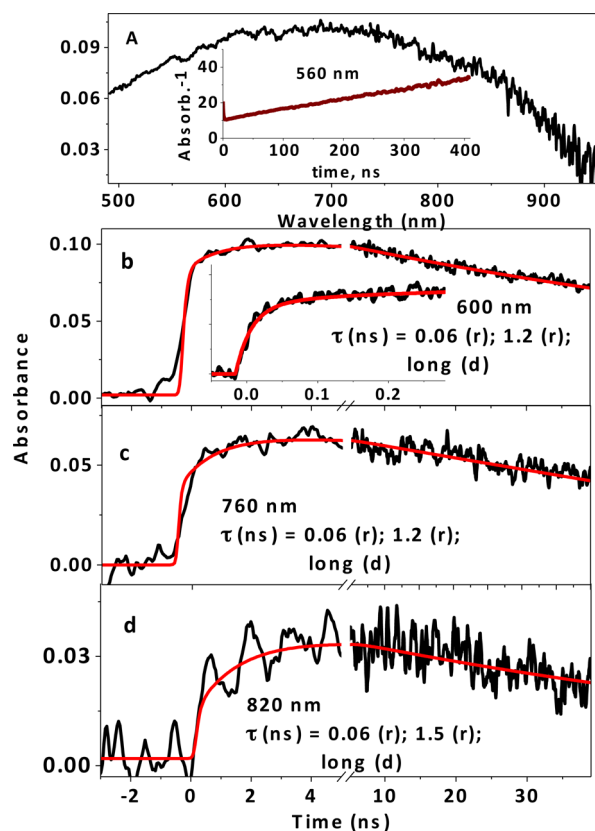
Details of the picosecond pulse radiolysis facility (ELYSE in Laboratoire de Chimie Physique, University of Paris-Sud, Orsay) have been described earlier.<sup>51</sup> Briefly, ELYSE is a femtosecond laser-driven electron accelerator. The facility is composed of two main units: (1) a femtosecond amplified Ti:sapphire laser and (2) the electron accelerator itself. The laser from Amplitude Technologies, France, delivers at 1 kHz, 100 fs pulse at 785 nm with an energy of 1.1 mJ/pulse. The major part of the pulse energy is used to generate UV pulses at 263 nm by third harmonic generation and seeded into the RF gun to extract the electron bunches from the Cs<sub>2</sub>Te photocathode. The photoelectrons are then accelerated up to 7.5 MeV kinetic energy by the 3 GHz RF field provided by a TH2130 Klystron (Thomson-CSF, 20 MW, 4  $\mu$ s). On the experimental area we used, transient absorption (TA) spectra and decay kinetics in the 450–900 nm region have been recorded using the white light beam from a homemade xenon flash lamp focused through the cell collinearly with the electron beam. The light was then focused on the entrance slit of a flat field spectrograph which disperses it on the entrance optics of a streak camera (model C-7700 from Hamamatsu). The images provided by the streak camera show the variation of light intensity into the cell due to absorption of light by transient species generated by the pulse radiolysis. Generally, a few hundred images corresponding to the same numbers of electron pulses were acquired by the streak camera and then averaged in a unique one used for the calculation of the optical density by reference to the similar image obtained on the averaging of the same number of images of the flashes of the analyzing light alone. The time resolution of the streak camera was 5 ps, and the time range used was from a few picoseconds to 1 ms and the spectral range from 250 to 850 nm. All the kinetics data and the absorption spectra were extracted from the resulting images.

For the present experiments, we have used electron pulses of about 15 ps duration, 7.5 MeV energy, and about 6.5 nC bunch charge to irradiate the deaerated liquid samples flowing through a quartz cell of path length 5 or 10 mm. The overall time resolution of the transient absorption detection was about 15 ps using a 5 mm cell and 50 ps using a 10 mm cell.



### 3. RESULTS

**3.1. Electron Solvation.** Transient absorption spectra of the fully solvated electron in 1-pentanol, 1-hexanol, 1-octanol, and 1-decanol have been recorded after about 30 ns of electron pulse irradiation of the pure solvents. The solvated electron spectrum recorded in each of these liquids was found to be very similar and extending over the broad 500–900 nm region. This is in agreement with the earlier observations.<sup>19,48</sup> The typical one recorded in 1-hexanol has been shown in Figure 1a.



**Figure 1.** (a) Solvated electron spectrum recorded in 1-hexanol at 30 ns. (b, c, d) Temporal dynamics of electron absorption in the same solvent recorded at 600, 760, and 820 nm along with the multiexponential best-fit functions. Lifetimes associated with each of the best-fit functions are given in the corresponding insets. Second-order decay of the solvated electron due to electron–electron annihilation reaction has been shown in the inset of (a).

Measurements of TA on shorter time scale (say 20 ps to 5 ns) using our streak camera requires a high intensity of analyzing light, which generates an additional background noise in the streak tube if the range of wavelength received is too large. For example, on the 1 ns time scale used in this paper it is necessary to limit the wavelength range from 50 to 150 nm depending on the analyzing light intensity in the spectral region investigated (UV or Vis). Even if the temporal profiles have been recorded in the entire 500–850 nm region, we have not made an attempt to construct the time-resolved spectra of solvated electron in the ps and ns time domain because the dynamics have been found to be very similar in this time domain. Figures 1b–d show the results of the measurements at three different wavelengths, namely 600, 760, and 820 nm in 1-hexanol, and Figure S1 (in Supporting Information) shows the electron absorption dynamics recorded at 760 nm in 1-octanol.

The most important aspect of the present investigation is that each of the temporal profiles of the TA signals recorded in the entire wavelength region of the solvated electron spectrum and in each of the four alcoholic solvents studied here could be fitted with a three-exponential function—two exponentially rising and one decay components. Lifetimes of these components are more or less wavelength independent in the 500–850 nm region.

The long-lived decay component is assigned to the decay of solvated electron and could be better fitted by using second-order decay rate equation (inset of Figure 1a), and the solvated electron decay rate constant has been determined as  $5.64 \times 10^7 \text{ s}^{-1}/\epsilon$  (where  $\epsilon$  is the extinction coefficient of the solvated electron at the monitoring wavelength), and the perfect second-order decay of the solvated electron can be assigned to electron–electron annihilation reaction.

It is a common practice to measure the solvation times using a time-correlation function of the dynamic red- or blue-shift of the maximum of the transient (fluorescence or absorption, respectively) spectra.<sup>52</sup> However, as we mentioned earlier, our detection system does not allow us to record the time-resolved absorption spectrum of the dry or unsolvated electron in the broad wavelength region of electron absorption spectrum with reasonable accuracy, and hence the time-correlation function of the dynamic blue-shift of the electron absorption maximum could not be determined. Therefore, we adopted the “single wavelength” approach, as suggested by Barbara and co-workers, to determine the solvation times by monitoring the decay or rise of the transient at the red or blue edge of the absorption spectrum, respectively.<sup>53</sup> This method has also been employed by Jonah and co-workers for determining the solvation times for electron and benzophenone anion.<sup>21</sup>

In the present case, we observed the nonexponential growth of transient absorption for solvated electron in the 500–800 nm region. Three rising components, including an instrument response time limited rising component,  $\tau_1$  (not shown in the insets of Figures 1 and S1), have been used to fit the truly nonexponential electron solvation process, and the values of these lifetimes ( $\tau_1$ ,  $\tau_2$ , and  $\tau_3$ ) are given in Table 1. These values

**Table 1. Lifetimes of Three Components of Electron Solvation Process in Alcohols and of the Dielectric Relaxation Times**

alcohols	$\tau_1^a$ (ps)	$\tau_2$ (ps)	$\tau_3$ (ps)	dielectric relaxation times <sup>b</sup>			$\tau_{\text{solv}}^c$ (ps)
				$\tau_{D3}$ (ps)	$\tau_{D2}$ (ps)	$\tau_{D1}$ (ps)	
1-pentanol	<15	35					34
1-hexanol	<15	60	1350	2.9	31	1210	52
1-octanol	<15	75	1500	3.23	38.7	1780	45
1-decanol	<15	72	1800	3.87	47.5	2019	51

<sup>a</sup>Lifetime of this component is instrument response time limited.

<sup>b</sup>Reference 50. <sup>c</sup>Electron solvation times reported earlier (ref 19).

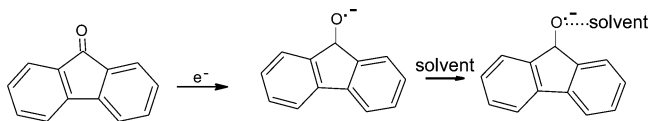
have been compared with the dielectric relaxation times measured by Garg and Smyth<sup>50</sup> and also the lifetimes of electron solvation ( $\tau_{\text{solv}}^e$ ) determined by the earlier authors using the technique of photoionization as well as stroboscopic picosecond pulse radiolysis techniques.<sup>19</sup> Bernas et al. reviewed the results on the measurements of the lifetimes of electron solvation in linear alcohols reported by different groups of workers, and a comparison revealed that the values reported by

other groups are comparable or a little shorter than those reported by Kenny-Wallace and Jonah.<sup>19,54</sup> We find that the value of  $\tau_{\text{solv}}^e$  agrees quite well with the value of  $\tau_2$  determined in the present work. Therefore, the earlier authors reporting the single-exponential dynamics of electron solvation missed both the ultrafast component,  $\tau_1$ , and the slower component,  $\tau_3$ . The ultrafast component was missed obviously because of limitation of the time resolution of the pulse radiolysis setup used, whereas the reason for missing the slower component was possibly the limitation in recording the transient decay up to sufficiently longer delay time (for example, in the case of stroboscopic pulse radiolysis technique, the limitation of the delay time is only 400 ps) and/or poor dynamic range of the detector used in recording the transient decay, resulting in poor signal-to-noise ratio. It is important to note that the multiexponential electron solvation process is being reported here for the first time using pulse radiolysis technique. In 1-pentanol, however, we could not determine the lifetime of  $\tau_3$  with good accuracy because of very small amplitude of this component.

Comparison of the lifetimes of three components of electron solvation with those of dielectric relaxation process reveals that we have not been able to resolve the ultrafast component ( $\tau_{\text{D}3}$ ), which has a lifetime of nearly about 3 ps in all four alcoholic solvents used here due to limitation of the time resolution of the pulse radiolysis set up ( $\sim 15$  ps). While we find a reasonably good agreement between the experimentally determined values of  $\tau_3$  and the lifetime of the longest-lived component of the dielectric relaxation process,  $\tau_{\text{D}1}$ , the experimentally determined values of  $\tau_2$  are longer than those of  $\tau_{\text{D}2}$  (vide infra).

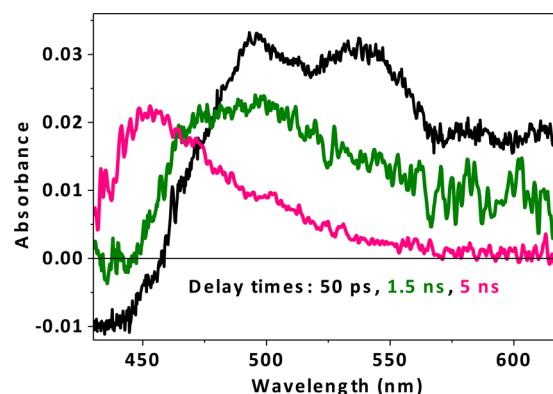
**3.2. Anion Solvation.** Use of a high concentration of a solute (say,  $>0.15$  mol dm<sup>-3</sup>) in alcoholic solution ensures that the solute captures the dry or quasi-localized electron before the solvation of the electron is complete (Scheme 1) and hence

**Scheme 1.** At 0.16 mol dm<sup>-3</sup> of Concentration of Fluorenone in Alcohol Solution, the Dry Electron Is Captured by Fluorenone To Form Unsolvated Anion, Which Is Followed by Solvent Reorganization Process To Solvate the Anion



does not put any limitation on the reaction time of the electron with the solute, so that electron solvation process cannot compete with the process of formation of fluorenone anion. It has been shown earlier that less than 5% of the total number of electrons remains unreactive in the presence of 0.05 M of an aromatic solute (say benzophenone) at room temperature, and the concentration of solvated electron decreases exponentially as the solute concentration is increased.<sup>35</sup> It has also been shown that the ratio of the yield of solvated electron at the solute concentration of 0.15 mol dm<sup>-3</sup> to that in the absence of the solute would be expected to be  $(0.05)^3$  or  $1.25 \times 10^{-4}$ .<sup>35</sup>

In Figure 2, we have presented the time-resolved TA spectra recorded following electron beam irradiation of the deaerated solution of 0.16 mol dm<sup>-3</sup> of fluorenone in 1-hexanol, which was flowing through a quartz cell of 5 mm path length. Since at this concentration of fluorenone, the rate of the dry electron capture reaction becomes faster as compared to that of electron



**Figure 2.** Time-resolved spectra of fluorenone anion generated in 1-hexanol using the picosecond pulse radiolysis technique.

solvation and the yield of solvated electron becomes negligibly small, the TA spectrum recorded immediately after the electron pulse (duration 15 ps) can be assigned to the dry fluorenone anion, which is characterized by two absorption bands with the maxima at ca. 500 and 540 nm. This spectrum is also associated with the bleaching band appearing below 460 nm. With increase in delay time, the time evolution of the TA spectrum is associated with the decay of both the absorption bands in the red region and a gradual shift of the absorption maximum. Following this time evolution of the TA spectra, the spectrum recorded at 5 ns delay time is characterized by a single band with the maximum at ca. 450 nm. This kind of time evolution of the TA spectra has earlier been shown to be associated with the dipolar or anion solvation process, which is a consequence of lowering the free energy of the dipole or anion because of reorganization of the solvent molecules around it.<sup>20,40–45</sup>

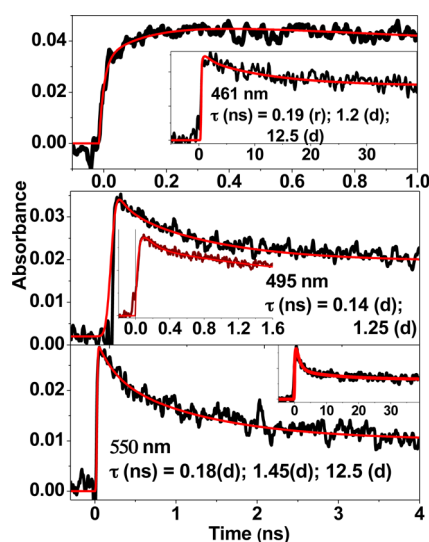
Fluorenone has been shown to form 1:1 and 1:2 hydrogen-bonded complexes with the alcoholic solvent molecules and free fluorenone molecules remain in equilibrium with the complexes in solution.<sup>55,56</sup> Following electron attachment to the fluorenone molecule, the solvent dipole configurations and hydrogen bond geometries in the complexes were not appropriate for the fluorenone radical anion thus formed. Therefore, solvent molecules reorient and/or translate with respect to that of the anion and also the coupling between the anion and the solvent changes, thus lowering the total energy of the system, causing a blue-shift of the anion absorption spectrum. Since the fluorenone or its anion has a rigid structure, no other mechanism, such as bond rotation or torsion, may be held responsible for the change in the spectrum, but only the reorganizations of the solvent molecules. Therefore, we assign the time evolution of the TA spectra presented in Figure 2 to solvation of the fluorenone anion.

Hoshino et al. reported the time-resolved absorption spectra of the fluorenone anion generated in ethanol glass matrix at 173 K.<sup>34</sup> The spectrum recorded immediately after the electron pulse of a few nanoseconds duration was characterized by two absorption maxima at ca. 520 and 560 nm, and the intensity of the absorption band with the maximum at 560 nm was about one and a half times more intense than that with the maximum at 520 nm. However, the rate of decay of the 560 nm band was seen to be faster than that of the band with the maximum at 520 nm, and the relative intensities of these two bands in the spectrum recorded at a long delay time were very similar. The spectrum of the fluorenone anion recorded in acetonitrile or dimethylformamide at room temperature following pulse

radiolysis also shows a maximum at 545 nm with a shoulder at 520 nm.<sup>34,57</sup> Therefore, comparing the shapes of the TA spectra and their time evolution presented in Figure 2 and those reported by Hoshino et al. and Samant et al. suggest that the spectrum recorded at 50 ps delay time after the electron pulse in this work cannot be assigned to a purely dry anion but the partially solvated anion.

Significant changes in the shape accompanied by the blue-shift of the absorption spectrum of the fluorenone anion with increasing delay time can be correlated with the solvent reorganization process, which strongly influences the electronic structure of the solute anion. It is also important to note that the maximum of the absorption band of the solvated fluorenone anion in 1-hexanol, a hydrogen bonding solvent, shows significantly larger blue-shift as compared to that recorded in acetonitrile or dimethylformamide, which is an aprotic solvent of larger polarity than 1-hexanol.<sup>34,57</sup> Therefore, it is quite evident that the mechanism of the solvation process is not simply via dipole orientation but via formation of intermolecular hydrogen bond between the anion and the solvent molecules and subsequent hydrogen bond reorganization process.<sup>55,56</sup>

We observe that the absorption spectrum of the dry or unsolvated fluorenone anion consists of two distinct bands, while the absorption spectrum of the fully solvated anion is characterized by a single absorption band, which is significantly blue-shifted as compared to that of the dry anion, and hence the dynamic blue-shift could not be defined well. Therefore, like in the case of electron solvation, the dynamics of solvation of the fluorenone anion has been investigated by monitoring the wavelength dependent kinetics of the time-dependent absorption of the anion. In Figure 3, we have shown a few of



**Figure 3.** Wavelength-dependent transient absorption dynamics of fluorenone anion in 1-hexanol.

the temporal profiles recorded in the 460–550 nm region. Following the characteristics of a typical dipolar solvation process investigated using the TA spectroscopic technique, we expect to observe the decay of the dry or partially solvated anion at 550 nm and formation of the fully solvated anion at 450 nm.

The temporal profile recorded at 550 nm shows the instrument response time limited rise of the TA signal, which

is followed by a triexponential decay with the lifetimes of 180 ps, 1450 ps, and 12.5 ns leading to formation of a long-lived species, which is evident from the residual absorption surviving even beyond 50 ns. Since weak absorption of the fluorenone ketyl radical extends up to this wavelength region, the decay component with the lifetime of 12.5 ns can be assigned to the hydrogen abstraction reaction by the fluorenone anion from the solvent molecules.<sup>57</sup> However, the other two decay components with the lifetimes of about 180 and 1450 ps should be associated with the solvent reorganization process around the fluorenone anion.

Because of overlapping of the absorption spectrum of the fluorenone anion and that of the ground state of fluorenone, the intensity of the probe light after transmission through the sample was very weak in the wavelength region below 460 nm, and the temporal profiles could not be monitored in this region in ultrafast time scale (e.g., <5 ns time domain) with reasonably good signal-to-noise ratio. Therefore, in Figure 3, we have presented the temporal profile recorded at 461 nm. The TA signal recorded at 461 nm could be fitted with a triexponential function consisting of two rising components with the lifetimes of <15 and 190 ps and two decay components with the lifetimes of 1.2 and 12.5 ns. As expected from the time evolution of the transient spectra presented in Figure 2, the amplitude of the longer component of solvation (with the lifetime of 1.2 ns) has been seen to be negligibly small in the fitting function of the temporal profile recorded at 461 nm.

At intermediate wavelengths, we observe that the lifetimes of these three components are wavelength dependent due to the obvious reason that the TA signals recorded at these wavelengths are associated with the formation and decay of partially solvated fluorenone anion. Therefore, we infer that the solvation process of the fluorenone anion in 1-hexanol follows nonexponential dynamics, which could be well represented by two components with the lifetimes of 180 and 1450 ps.

We have investigated the solvation dynamics of the fluorenone anion in three other normal alcohols, namely, 1-pentanol, 1-octanol, and 1-decanol. It is an important observation that the amount of the blue-shift of the absorption maximum of the fluorenone anion due to solvation does not depend on the length of the alkane chain of the alcohol. For example, in all four alcohols studied here, the TA spectrum recorded at 50 ps delay time exhibits two maxima at ca. 500 and 540 nm and the maximum of the solvated anion appears at around 450 nm. Characteristics of time evolution of the TA spectra are very similar in four alcohols. To corroborate our arguments, we have shown the time-resolved TA spectra of the fluorenone radical anion in 1-octanol and the temporal dynamics recorded at two wavelengths in Figure S2 and wavelength-dependent dynamics of fluorenone anion in 1-octanol due to solvation has been presented in Figure S3. These observations suggest that short-range interactions, rather than long-range interactions, dominate the spectral shifts of the anion. In addition, possibly the time scale for short-range interactions is faster than the time resolution (about 15 ps) of our equipment.

In each of the alcohols studied here, we find that the anion solvation process investigated with the limited time resolution of 20 ps follows nonexponential dynamics, which could be described well using biexponential kinetics. The lifetimes of the components show a regular increase with increase in the alkane chain length, which also follows the same trend for viscosity or solvation time of the alcohols. The associated lifetimes of these



two components are given in Table 2 and have been compared with the longitudinal relaxation times ( $\tau_L$ ) and the average

**Table 2. Solvent Parameters and Solvation Times of Fluorenone Radical Anion in Linear Alcoholic Solvents**

solvent	$\tau_L^a$ (ps)	$\langle\tau_{\text{sol}}\rangle^b$ (ps)	solvation times of fluorenone radical anion <sup>c</sup>	
			$\tau_1$ (ps)	$\tau_2$ (ps)
1-pentanol	147	103	105	
1-hexanol	200		185	1450
1-octanol	406		320	1800
1-decanol	565	245	350	1750

<sup>a</sup>Reference 58. <sup>b</sup>Reference 52. <sup>c</sup>This work.

solvation times ( $\langle\tau_{\text{sol}}\rangle$ ) of the solvents.<sup>52,59</sup> It is to note that the solvation times of the fluorenone anion in 1-hexanol and 1-octanol have not yet been reported. However, the general trend is that  $\langle\tau_{\text{sol}}\rangle$  of the primary alcohols increases with the increase in the size of the solvent molecules. We find that the same trend is followed by the solvation times (Table 2) determined using the fluorenone anion as the probe.

We have also investigated the solvation dynamics of benzophenone and biphenyl anions in 1-decanol, and the results are given in the Supporting Information (Figures S4 and S5). In these two cases, too, we find biexponential solvation process with similar lifetimes as determined in the same solvent using fluorenone anion as the probe (Table 2).

### 3. DISCUSSION

Since the electron can be regarded as the simplest possible charged solute, examination of electron solvation is expected to provide useful information in understanding the molecular details underlying the solvation process of a charged particle. Furthermore, the solvated electron system is an ideal probe for theoretical investigations of solvation dynamics. Several approaches have been put forth for the theoretical treatment of the dynamics of polar fluid that differ in the sophistication with which the solvent is modeled. The so-called “simple continuum model” treats the solvent as a continuous, homogeneous medium whose only relevant property is its bulk, frequency-dependent dielectric response.<sup>60</sup> This model describes the dynamics related to long-range interactions but fail to account for the intimate details of the solute–solvent interactions. The continuum model predicts that solvation should proceed on the time scale that is approximately equal to the longitudinal relaxation time of the solvent,  $\tau_L$ . However, this model does not predict nonexponential character of solvation. In addition, the activation energy for solvation calculated using this model does not agree with the experimental value in alcohol.

Rossky and co-workers employed quantum classical molecular dynamics computer simulation approach to explore the multiple time scales and associated processes manifested in electron solvation in methanol.<sup>61</sup> A relation has been established between the localization of the excess electron and the solvent relaxation and between solvation dynamics and the dynamics of hydrogen-bonding interactions. The localization of the excess electron coincides mainly with the inertial time scale of the dynamics, and the response functions evolve approximately in a biexponential manner (100 fs and 1–2 ps time scales) and are associated with an abrupt radial collapse. This localization process corresponds to a minor component of

energy relaxation. However, this process is not accessible with our experimental time resolution. While librational motions of the solvent are responsible for the ultrafast relaxation, molecular translation and solvent structural changes are responsible for the slower portion of the energy relaxation occurring in the picoseconds time scale. This relatively long time scale relaxation involves both adjustment in coordination number and disruption of the solvent–solvent hydrogen bonds, resulting in the generation of additional dangling hydrogen bonds beyond the statistical number present in the pure solvent and the initial localization sites. In another paper, the authors also pointed out that the presence of electron in the solvent bath results in slowly relaxing fluctuations on the 20 ps time scale in methanol.<sup>62</sup>

The theoretical formalism of Abramczyk describes that the band broadening mechanisms are very similar in both the IR absorption spectrometry of hydrogen-bonded complexes and near-IR and visible absorption of an excess electron in hydrogen-bonding solvents.<sup>63</sup> He suggests that the vibrational dynamics of H-bonds play an important role in localization, electron attachment, stabilization, and solvation of an excess electron generated by radiolysis or photoionization in H-bonded solvents.

Garg and Smith have found that the dielectric relaxation process in primary alcohols follows nonexponential dynamics, which could be well described by three-exponential kinetics.<sup>50</sup> They attributed three dielectric relaxation times of alcohols to contributions of the three processes; namely,  $\tau_{D3}$  is the relaxation time for the rotational orientation of the OH group and depends only on the viscosity and not on the chain length of the alcohol,  $\tau_{D2}$  is correlated with the reorientational motion of the monomeric alcohol molecules and depends on the chain length and viscosity of the alcohol, and  $\tau_{D1}$  is associated with the restructuring of the hydrogen bond network structure as determined by the time required for a monomeric solvent molecule to break off from a complex and forming a new one.

The discussion presented in the preceding paragraphs confirms the impression that picture for electron solvation is not yet very clear. However, it becomes obvious that hydrogen bonding interactions play an important role in electron solvation in alcoholic solvents. To explain the results presented in this work, due consideration of the following experimental observations reported earlier should be given to explain the electron solvation in alcohols. First, Chase and Hunt reported that activation energy of electron solvation ( $\sim 14.5$  kJ mol<sup>-1</sup>) is lower than that for H-bond breakage ( $\sim 22$  kJ mol<sup>-1</sup>).<sup>64</sup> Second, Kenney-Wallace and Jonah reported that the solvation times did not correlate well with the rotational time of the solvent molecules.<sup>19</sup> Third, Kenney-Wallace and Jonah predicted that alcohol clusters were important for electron solvation in alcohols. If the electron is initially presolvated in cyclic tetramer or pentamer structures in primary alcohols, then it is not necessary for the closest alcohol molecule to rotate and break hydrogen bonds because the alcohol molecules in the inner shell are already close to the correct configuration.<sup>19</sup> This also explains the lower activation energy. Finally, Schwartz and Rossky suggested that conventional rotational mechanism does not hold for electron solvation but through translational motion.<sup>65</sup> They suggested that creation of the electron pushes the solvent molecules away and the solvation occurs through the translation of the solvation molecules.



This discussion leads us to make the possible assignments of the three components of electron solvation (Table 1) in four primary alcohols observed here as follows:  $\tau_1$  represents the localization of the excess electron occurring in the inertial time scale of the dynamics (<15 ps). Librational motions of the solvent are responsible for this component of ultrafast relaxation. However, this process is not accessible with the time resolution of our equipment. Translational motion leading to structural changes of the hydrogen-bonding network of the solvent in the region close to the presolvated electron (i.e., in the inner solvation cell or alcohol cluster) is responsible for the slower portion of the energy relaxation occurring in the picosecond time scale, and  $\tau_2$  may be assigned to this process. In addition,  $\tau_3$  is associated with the restructuring of the hydrogen bond network structure of the solvent in the region outside the solvation cell.

Like in the case of electron solvation, solvation of the radical anion too is nonexponential, but in the present case, it could be described well by two kinds of processes. Possibly, due to limitation of the time resolution of our spectrometer, we have missed a faster component, which may arise due to inertial or librational motions of the solvents. Physically, these different time scales arise because the solvent responds at different rates, depending on the distance from the charged solute, electronic coupling, and specific interactions, such as intermolecular hydrogen bonding. If fluorenone was already hydrogen bonded with the alcohol molecules, the formation of negative anion would only strengthen and shorten the hydrogen bond.<sup>66</sup> A significant blue-shift of the solvated anion spectrum as compared to that in acetonitrile suggests that the solvation process indeed represents the formation or reorganization of the hydrogen bond as well as restructuring the hydrogen bond network structure of the solvent. The longest component,  $\tau_2$  in Table 2, with the lifetime of a few nanoseconds, like in the case of electron solvation, can be assigned to the restructuring of the hydrogen bond network structure of the solvent in the region outside of the solvation cell.

The most important observation in this work is that the lifetime of the shorter component,  $\tau_1$ , determined in four alcoholic solvents (Table 2), is much longer than the electron solvation time in the corresponding solvent determined in this work or reported earlier.<sup>19</sup> In addition, the lifetime of this component is also longer than the single component solvation time of benzophenone radical anion reported by Jonah and co-workers.<sup>42–44</sup> Table 2 also reveals that the lifetimes of this component determined in four alcohols are nearly comparable with the average dipolar solvation times of the alcoholic solvents but shorter than the longitudinal relaxation time of the solvents,  $\tau_L$ . Hydrogen bonds influence the dielectric relaxation times, and Maroncelli et al. showed that solvation times become about 2 times faster in the case of hydrogen bonding between the solute and the solvent.<sup>63</sup> Jonah and co-workers as well as Chase and Hunt showed that the activation energy of anion solvation in an alcoholic solvent is larger than that of the electron solvation but comparable to the hydrogen bond energy of the solvent.<sup>45,67</sup> It was also interesting to note that the hydrogen bond energies of the different primary alcohols are nearly similar ( $\sim 25$  kJ mol<sup>-1</sup>).<sup>2</sup> These data suggest that breakage of hydrogen bonds of the solvents in the solvent network structure to create dangling hydrogen bonds and hydrogen bond formation between the solute anion and the solvent may be the dominant processes during solvation of the

anion radical, and  $\tau_1$  may be assigned to the restructuring of the first solvation shell.

In conclusion, in the solvation processes of both the electron and radical anion in linear alcohols, the solvent reorganization process is faster for the shorter alcohol chain. However, the final spectral position and widths are very similar for different linear alcohols. This indicates that the short-range interactions dominate the spectral shifts of the solvated electron or anion instead of the long-range interactions. Because of the different solvent–solute coupling mechanisms, the time for anion solvation is longer than that for the electron solvation in the same solvent. In the case of electron solvation, since the quasi-free electron is already trapped inside a predefined alcohol cluster and hence the electron solvation is faster, because it begins from a configuration that is particularly favorable for the electron. In the case of anion solvation, the process requires the breaking of the hydrogen bonds of the solvent network and formation of hydrogen bond between the anion and the solvent, which takes place in the time scale of longitudinal relaxation time of the solvent. The longest component (a few nanoseconds), which has been observed in both these cases, has been assigned to hydrogen bond reorganization of the solvent in the outer solvation shell.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Temporal dynamics of electron absorption recorded at 760 nm in 1-octanol using a cell of 5 mm path length (Figure S1); transient absorption dynamics of fluorenone anion in 1-octanol (Figure S2); wavelength-dependent dynamics of fluorenone anion in 1-octanol due to solvation (Figure S3); temporal dynamics monitored at two selective wavelengths following pulse radiolysis of benzophenone in 1-decanol (Figure S4); time-resolved spectra recorded following picosecond pulse radiolysis of biphenyl in 1-decanol and the temporal profile recorded at 422 nm (Figure S5); the complete author list of ref 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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