J. Am. Chem. Soc. 1989, 111, 4974–4980

Femtosecond Attachment of Excess Electron to the Water Pool of Aerosol Sodium Dialkyl Sulfosuccinate Reversed Micelles

Y. Gauduel,* S. Pommeret,† N. Yamada, A. Migus, and A. Antonetti

Contribution from the Laboratoire d'Optique Appliquêe, INSERM U275, Ecole Polytechnique—ENSTA, Centre de l'Yvette, 91120 PALAISEAU, France.

Received August 17, 1988

Abstract: The primary steps of an excess electron capture in the water pool of aerosol sodium dialkyl sulfosuccinate (AOT) reversed micellar system have been investigated by using visible and infrared absorption spectroscopy at the femtosecond time scale. Electrons are photolytically generated through femtosecond ultraviolet ionization of phenothiazine at 294 K. For a molar ratio $W = [H_2O]/[AOT] = 50$, an early electron attachment $[e^- + (H_2O)_m]$ occurs following a pseudo-first-order rate of 6×10^{12} s^{-1}. This fast electron transfer within aqueous microdroplets leads to the formation of a trapped electron for which the surrounding water molecules are not in equilibrium configuration. The formation of a nonrelaxed solvated electron (presolvated state) occurs in 140 fs. This transient species absorbing in the infrared has a lifetime of 270×10^{-15} s. Changes in the H_2O/AOT ratio from 50 to 5 substantially affect the efficiency of the ultrafast excess electron attachment to AOT reversed micelles. In small water clusters ($W = 5$) where water molecules are immobilized through strong ion–dipole interactions, an ultrafast attachment of excess electron occurs at a rate (2×10^{12} s^{-1}) exceeding that of a diffusion-controlled process. These data bring strong evidence that, in reversed micelles in which there is an overall disruption of the three-dimensional hydrogen-bonded network ($W = 5$), the electron reactivity with rigid sequestered water bubbles occurs at a time that is short as compared to any solvent dipole orientation or complex motions of water molecules.

I. Introduction

Microemulsions and micellar systems have been much investigated for the last few years because these models have found numerous applications varying from chemical catalysis to biological analysis and membrane mimetic photochemistry.[1-3] Reversed micelles [water-in-oil (W/O) microemulsion] of sodium dialkyl sulfosuccinate (aerosol OT) are spheroidal aggregates of amphiphile molecules in an aliphatic solvent, which can solubilize a large amount of water molecules. On the L_2 phase diagram of a ternary system (AOT/*n*-heptane/H_2O) the number of water molecules solubilized by spheroidal aggregates of amphiphile molecules in hydrophobic solvent is determined as the $[H_2O]/[AOT]$ ratio (W). The stability of these organized assemblies is ensured by molecular interactions including ionic, steric, and hydrophobic effects.[3]

On the basis of numerous experimental studies (colorimetric measurements, fluorescence probing, neutron small angle and X-ray scattering, Na^+ and H^+ NMR spectroscopy), it is now well established that the structure and the state of micellized water bubbles are quite dependent on the water pool size (W).[4-9] The two-state model developed by Zinsli[10] describes a specific water structure close to the interface and an aqueous bulklike water inner core. More recently, several experiments on proton transfer of fluorescent probes in reversed micelles are consistent with the existence of at least two types of water in the sequestered water pool.[11,12]

At low H_2O/AOT ratio ($W = 5$), the water bubble is dramatically perturbed and corresponds to a highly structured medium in which all of the water molecules are expected to be involved in the solvation of the counterion Na^+. Compared with bulk water, the rotational correlation time (T_c) is significantly increased. With larger H_2O content ($W = 20$), the immobilization of water molecules by strong ion–dipole interaction with counterions (Na^+) decreases and the water aggregate properties become similar to those of bulk water.[6]

Previous works on the capture process of electrons by the water pool of reversed micelles were carried out by radiolysis or photolysis of chromophore or solvent molecules.[13-16] Conductivity studies demonstrated that electron attachment at high W values ($W = 30$) occurs at a rate $k[e^- + (H_2O)_m]$ exceeding that of a diffusion-controlled process.[14] However, up to now, the elucidation of the primary steps of charge separation and electron capture by the water pool (electron thermalization, localization, and solvation) was limited by instrumental resolution.

The aim of the present work is to study the dynamics of the primary steps involved in the attachment of an excess electron to aqueous microphases of reversed micelles. The resulting primary products have been investigated by femtosecond spectroscopy and analyzed in relation with the degree of organization of water molecules inside the hydrophobic core of reversed micelles. Excess electrons are generated through multiphotoionization of a chromophore (phenothiazine) solubilized in the AOT reversed micellar systems. We have chosen the reversed micelles of sodium dialkyl sulfosuccinate (AOT) in *n*-heptane because their structure and properties in the micellar phase L_2 have been extensively studied.[8,10,17-19] The nature of the sequestered water pool provides a unique aqueous medium for investigating the reactivity of a fundamental reducing species (electron) with microdroplets. The dielectric properties and the molecular motions are modified by high ionic strength. The investigation of monoelectronic transfers in these specific organized assemblies is of considerable interest in regard to the oxidation–reduction or radical reactions occurring in water pockets of bioaggregates.

II. Experimental Section

Samples of W/O microemulsions containing cosurfactant were prepared by dissolving a known quantity of sodium bis(2-ethylhexyl) sulfo-

---

† S.P. is a recipient of a grant from DRET, Paris, France.

(1) Turro, N. J.; Grätzel, M.; Braun, A. M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 679–696.
(2) O'Connor, J. C.; Comax, T. D.; Ramage, R. E. *Adv. Colloid Interface Sci.* **1984**, *20*, 21, and references therein.
(3) Fendler, J. H. *Chem. Rev.* **1987**, *87*, 877, and references therein.
(4) Eicke, H. F.; Rehak, J. *Helv. Chim. Acta* **1976**, *59*, 2883.
(5) Day, J. H. R.; Robinson, B. H.; Clarke, J. H. R.; Doherty, J. V. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 132.
(6) Thompson, K. F.; Gierasch, L. M. *J. Am. Chem. Soc.* **1984**, *196*, 3648.
(7) Keh, E.; Valeur, B. J. *J. Colloid Interface Sci.* **1981**, *79*, 465.
(8) Zulauf, M.; Eicke, H. F. *J. Phys. Chem.* **1979**, *83*, 480.
(9) Lang, J.; Jada, A.; Malliaris, A. *J. Phys. Chem.* **1988**, *92*, 1946.
(10) Zinsli, P. E. *J. Phys. Chem.* **1979**, *83*, 3223.
(11) Bardez, E.; Monnier, E.; Valeur, B. *J. Phys. Chem.* **1985**, *89*, 5031.
(12) Politi, M. J.; Chaimovich, H. *J. Phys. Chem.* **1986**, *90*, 282.
(13) Wong, M.; Grätzel, M.; Thomas, J. K. *Chem. Phys. Lett.* **1975**, *30*, 329.
(14) Bakale, G.; Beck, G.; Thomas, J. K. *J. Phys. Chem.* **1981**, *85*, 1062.
(15) Calvo-Perez, V.; Beddard, G. S.; Fendler, J. H. *J. Phys. Chem.* **1981**, *85*, 2316.
(16) Pileni, M. P.; Hickel, B.; Ferradini, C.; Pucheault, J. *Chem. Phys. Lett.* **1982**, *92*, 308.
(17) Robinson, B. H.; Toprakcioglu, C.; Dore, J. C. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 13.
(18) Maitra, A. *J. Phys. Chem.* **1984**, *88*, 5122.
(19) Martin, C. A.; Majid, L. J. *J. Phys. Chem.* **1981**, *85*, 3938.

0002-7863/89/1511-4974$01.50/0

succinate (Aerosol OT) in a measured volume of *n*-heptane. The reversed micelles with sequestered water pool were obtained by dissolving and mixing a precise volume of doubly distilled water in AOT/*n*-heptane solution. The quantity of water was calculated to obtain different H_2O/AOT ratios ($0 < W \leq 60$). Phenothiazine (PTH) was incorporated after the formation of reversed micelle solution by gently stirring PTH with the AOT/*n*-heptane/H_2O mixture at 294 K during several hours so as to obtain a complete integration of the chromophore and a clear solution. During this period care is taken to exclude light. The concentration of micellized aromatic hydrocarbon was determined by spectrophotometric measurement with a Varian 2300 spectrophotometer, assuming that one could neglect the variation of the extinction coefficient of the solution when going from a homogeneous to a micellar solution. Aerosol OT (Sigma) and *n*-heptane (Merck Puriss grade) were used as supplied. Twice deionized water was doubly distilled over permanganate in a quartz still. At 294 K, the pH was 6.5 and the resistivity greater than 19 MΩ. The reversed micelles were deoxygenated by tonometry using a gentle stream of high-purity nitrogen. Concentrated aqueous solutions of sodium chloride (6 M) were prepared by dissolving sodium chloride (alpha Produkte) of Puriss quality (99.999%) in doubly distilled water.

The photochemical generation of electrons in reversed micelles was carried out by using femtosecond pulses obtained by a passively mode-locked CW dye ring laser (CPM). The pulses generated in this laser are as short as 80 fs (8×10^{-14} s) and the wavelength is centered around 620 nm.[20,21] These pulses are amplified at a 10-Hz repetition rate in a four-stage dye amplifier pumped by a Q-switched frequency-doubled Nd-Yag laser. The results in the obtention of femtosecond pulses (E = 1 mJ, 100 fs duration). The high-intensity femtosecond pulses are used for time-resolved absorption spectroscopy using a pump-probe configuration.[22] In our particular experiments, one part of the initial pulse centered at 620 nm is focused into a KDP crystal to produce up to 5-15 μJ at 310 nm constituting the pump to initiate the primary photochemical reaction (photoionization) in reversed micellar systems. The other part of the 620-nm pulse is focused into a water cell to produce a continuum.

The transient signals obtained following femtosecond excitation of samples were monitored by photodiodes in the visible and infrared spectrum. Depending on the strength of the induced absorption, kinetics at given wavelengths must be accumulated for typically 1 h in order to get a good signal-to-noise ratio. Transient spectra are then reconstructed starting from all these kinetics. The signals are fed into an electronic chain (pulse shaping, sampling holder, and digitizer) for computer processing. All experiments were performed at 294 K in fixed-volume cells of 0.2-cm path length moved in a plane perpendicular to the propagation of the light beams. Thus, each pulse at a 10-Hz repetition rate excited a fresh region of the sample.

III. Results

(a) Transient Absorption Spectrum of Solvated Electron in Reversed Micelles. The transient absorption spectra obtained following the femtosecond ultraviolet photoionization of phenothiazine (5×10^{-4} M) in reversed micelles [AOT (0.15 M)/*n*-heptane/H_2O] at various water pool sizes [W = 0, 5, 50] are shown in Figure 1.

In reversed micelles without water (W = 0), the spectrum taken 2 ps after the excitation of the electron donor (phenothiazine) shows a continuously increasing absorption from 550 to 850 nm. The contribution of the positive ion (PTH^+) being considered as negligible, this structureless spectrum has been assigned to trapped electrons in the nonpolar phase.[23-25]

At high water content (W = 50), the transient absorption spectrum observed 2 ps after the femtosecond UV excitation of PTH shows a structureless and unsymmetrical band extending toward high energies above 2.5 eV and peaking around 1.7 eV (720-730 nm). From the available literature data on the radiation chemistry of aqueous solutions this visible band is assigned to a hydrated state of the electron in the aqueous inner core of reversed micelles.[26] Evidence for an ultrafast formation of hydrated electron (e^-_{hyd}) in reversed micelles containing a large water pool has been obtained by quenching experiments. The incorporation of an oxidized nucleotide (NAD^+) in sequestered water pools reduces the amplitude of the signal and the lifetime of absorption induced at 720 nm.[27] The picosecond spectrum also shows the existence of a hump in the lower wavelength region and peaking around 520 nm. From the available literature data, we assign this band to the cationic radical of phenothiazine (PTH^+).

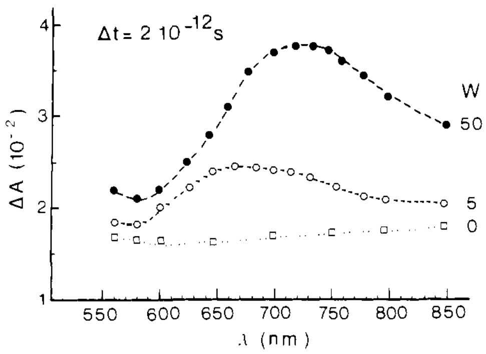


Figure 1. Transient absorption spectra recorded 2 ps after femtosecond photoionization of phenothiazine (5×10^{-4} M) in reversed micelles [AOT (0.15 M)/*n*-heptane/H_2O]: W = 50, 5, 0. The points are calculated from the experimental kinetics and the amplitude of the signal observed at different wavelengths.

When the water content of reversed micelles (W) is reduced from 50 to 5, the transient spectrum observed 2 ps after the femtosecond photoionization of PTH also shows a broad band peaking in the visible region. However, compared to the previous spectrum (W = 50), a small blue shift of ~0.12 eV is observed (Figure 1). In agreement with pulse radiolysis experiments on reversed micelles,[13,16,28] the spectroscopic properties of the hydrated electron are dependent on the size of the sequestered water pool. At low water content (W = 5), the existence of a blue shift is attributed to a change of the electron hydration energy induced by the existence of a high concentration of Na^+ counterion within the aqueous inner core of reversed micelles. A similar influence of ionic strength on spectroscopic properties of the hydrated electron has been previously described from pulse radiolysis of concentrated ionic aqueous solutions.[6,26,29]

These femtosecond spectral investigations also demonstrate that the early yield of formation of hydrated electron is dependent on the water pool size. Taking reversed micelles with W = 50 and assuming an absorption coefficient of 1.85×10^4 M^{-1} cm^{-1} for e^-_{hyd} as in homogeneous aqueous media,[16,26] we deduce that the concentration of hydrated electron after each femtosecond pulse is ~4.5 ± 0.5 μM. This transient concentration of hydrated electrons is found to decrease below 1.5 μM in reversed micelles with very low water clusters (W = 5).

(b) Dynamics of Electron Capture in the Water Pool of AOT Reversed Micelles. The time-resolved investigations of electron capture by a water pool of reversed micelles have been performed in the infrared and visible spectral region. The dynamics of electron capture and solvation in the aqueous phase of reversed micelles have been studied for different water pool sizes ($0 < W < 65$).

Figure 2 represents the apparent rise time of the induced absorption at 720 nm ($K_{obsd} = 1/T_{obsd}$) as a function of the water pool size defined as the $[H_2O]/[AOT]$ ratio. It is clear that K_{obsd} decreases when the size of the sequestered aqueous microdroplet is increased from 0 to 65.

To obtain information on the dynamics of excess electron attachment to reversed H_2O-AOT micelles, we have carefully analyzed the rise time of the induced absorption in the visible (660 or 720 nm) and the infrared (1000 or 1250 nm) with a dynamical

---

(20) Fork, R. L.; Shank, C. V.; Yen, R. T. *Appl. Phys. Lett.* **1982**, *41*, 223.

(21) Migus, A.; Antonetti, A.; Etchepare, J.; Hulin, D.; Orszag, A. *J. Opt. Soc. Am. B* **1985**, *2*, 584.

(22) Gauduel, Y.; Migus, A.; Chambaret, J. P.; Antonetti, A. *Rev. Phys. Appl.* **1987**, *22*, 1755.

(23) Richards, J. T.; Thomas, J. K. *Chem. Phys. Lett.* **1971**, *10*, 317.

(24) Baxendale, J. H.; Bell, C.; Wardman, P. *Chem. Phys. Lett.* **1971**, *12*, 347.

(25) Baxendale, J. H. *Can. J. Chem.* **1977**, *55*, 1996.

(26) Anbar, M.; Hart, E. J. *The Hydrated Electron*; Wiley: New York, 1970.

(27) Gauduel, Y.; Pommeret, S.; Antonetti, A., in preparation.

(28) Visser, A. J. W. G.; Fendler, J. H. *J. Phys. Chem.* **1982**, *86*, 947.

(29) Kreitus, I. V. *J. Phys. Chem.* **1985**, *89*, 1987.

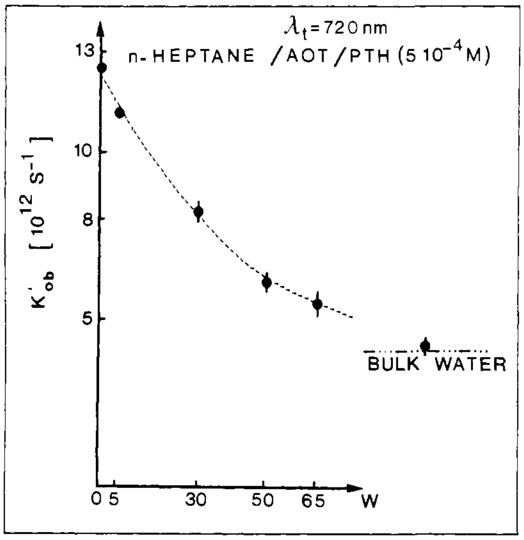
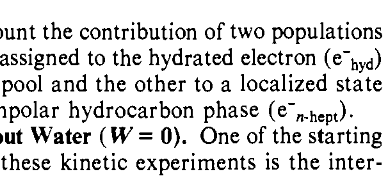


Figure 2. Variation of the apparent rise time of induced absorption at 720 nm (K_{obsd}) in reversed micelles [AOT (0.15 M)/n-heptane/H_2O] with the size of the water pool defined as the H_2O/AOT ratio. The apparent rise time ($K_{obsd} = 1/T_{obsd}$) is determined following femtosecond photoionization of PTH with a 100-fs laser pulse (λ, 310 nm; $h\nu$, 4 eV).

model that takes into account the contribution of two populations of electrons: the first one assigned to the hydrated electron (e^-_{hyd}) in the sequestered water pool and the other to a localized state of the electron in the nonpolar hydrocarbon phase ($e^-_{n\text{-hept}}$).

Reversed Micelles without Water ($W = 0$). One of the starting points of the analysis of these kinetic experiments is the interpretation of the induced absorption following femtosecond excitation of a pure solution of n-heptane with high-power laser pulses ($I > 10^{12}$ W/cm^2). The curves of Figure 3 show that the excitation of a pure n-heptane solution by a 310-nm femtosecond pulse (ΔE = 4 eV) leads to the appearance of a very weak induced absorption in the visible and the infrared (1250 nm). At 720 nm, the rise time of the signal is the fastest induced absorption we ever found in this pump–probe configuration. This signal can be assigned to a multiphotoionization of the hydrocarbon, as previously observed with n-hexane at the picosecond time scale.[30] It is well-known that, for low-intensity radiation, n-heptane is transparent in the UV spectral region up to 250 nm. However, an absorption through a multiphoton process becomes nonnegligible when we deal with ultrashort power pulses. Since the ionization threshold of n-heptane is around 8.7 eV, a multiphoton excitation by femtosecond ultraviolet laser pulses seems to be involved in a charge separation process. In this hypothesis, the early steps of the femtosecond excitation of n-heptane can be described by the following reactions:



$$\begin{array}{lr} \qquad\qquad\qquad\quad [C_7H_{16}^{+}\cdots e^{-}] \longrightarrow C_7H_{16} & \\ \qquad\qquad\qquad\qquad\qquad \uparrow & \\ (C_7H_{16}) + n\,h\nu\,(310\text{ nm}) \longrightarrow [C_7H_{16}]^{*} \longrightarrow [C_7H_{16}]^{+} + e^{-}_{qf} & (1) \\ \qquad e^{-}_{qf} + C_7H_{16} \longrightarrow C_7H_{16}^{-} \quad (e^{-}_{n\text{-hept}}) & (2) \end{array}$$

The first reaction (eq 1) corresponding to a multiphotoionization of n-heptane (C_7H_{16}) would lead to the appearance of a positive ion [$C_7H_{16}^+$] and an excess quasi-free electron (e^-_{qf}) or a geminate ion pair [$C_7H_{16}^+\cdots e^-$] with a short lifetime. In a second step (eq 2), the transient state of the electron relaxes toward a localized state of the electron [$C_7H_{16}^-$].

At 720 nm (Figure 3A) the rise time of the induced absorption can be well fitted to the convolution of the pulse profile and the expected signal rise by use of a combination of two monoexponential laws [$1 - \exp(-t/T_x)$]. In general, the deconvolution analysis of the rise time of the absorption change induced by a pulse of intensity $I_P(t)$ on a test pulse of intensity $I_T(t)$ with a time delay between the two pulses is given in our small signal case by

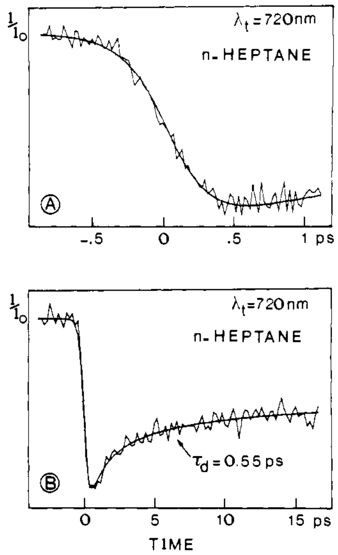


Figure 3. Rise time of induced absorption (720 nm) at 294 K following photoionization of pure n-heptane with 100-fs laser pulses (λ, 310 nm). A: the solid line represents the computed best fit of the experimental trace. It corresponds to the contribution of an instantaneous response, which takes into account the time-broadening factor due to the group velocity dispersion in the sample ($T_{x1} < 50$ fs) and a solvated electron appearance time constant $T_{x2} = 90 \pm 10$ fs. B: the decay of the induced absorption at 720 nm is well fitted to a 1D random walk form, erf $[(T_d/t)^{1/2}]$ with $T_d = 0.55 \pm 0.05$ ps.

$$\Delta\alpha(\tau) = \int_{-\infty}^{+\infty} A(\tau - \tau') \int_{-\infty}^{+\infty} I_P^2(t) I_T(t + \tau')\, dt\, d\tau' \quad (3)$$

In this expression, A is the pulse response of the molecular absorption. In the case of an instantaneous molecular response A is a constant, while in the case of a nonnull molecular response time T it becomes $A = 1 - \exp(-t/T)$ at $t = 0$. The fit of the weak induced absorption obtained following photoexcitation of a pure solution of n-heptane enables one to define the pulse shape and the position of the zero time delay, i.e., the position of the delay line for which the pump and the probe overlap exactly. The first contribution appears within the pump–probe investigation and is well fitted with "instantaneous" kinetics (T_{x1} of 50 fs), which correspond precisely to the theoretical estimate taking into account the pulse duration and the group velocity dispersion between the UV pump and the probe along the 2-mm sample path. This instantaneous component can be assigned to the formation of an early ion pair [$C_7H_{16}^+\cdots e^-$]. In the hydrocarbon phase the appearance kinetics of the second component assigned to the formation of a trapped state of the electron in the hydrocarbon phase ($e^-_{n\text{-hept}}$) can be well fitted to a time constant T_{x2} of 90 ± 10 fs.

A significant decay of the 720-nm-induced absorption is observed following the femtosecond ultraviolet excitation of a pure n-heptane solution. The curve of Figure 3B shows that the time dependence of the induced absorption decay is nonexponential. To give a physical meaning to this ultrafast relaxation we have examined the contribution of a geminate recombination. In the hypothesis where the instantaneous rise time of the 720-nm-induced absorption is assigned to the formation of an initially generated electron–cation pair (n-heptane$^+\cdots e^-$), it can be suggested that this pair executes as 1D random walk along the saturated chain of the hydrocarbon before undergoing a geminate recombination. This process can be described with an analytical solution $N_{(t)} = N^{\circ}\,\mathrm{erf}\,[(T_d/t)^{1/2}]$ in which T_d^{-1} represents the jump rate. In Figure 3 the best fit to the time dependence of the photoinduced absorbance at 2 and 20 ps gives $T_d = 0.55$ ps in pure n-heptane. This time dependence of the geminate electron–cation pair ($e^-\cdots n$-heptane$^+$) generated by femtosecond multiphotoionization of the hydrocarbon is in agreement with previous work on geminate electron–cation pairs in nonpolar solvents[31,32] and demonstrates

---

(30) Kenney-Wallace, G. A.; Jonah, C. D. *J. Phys. Chem.* **1982**, *86*, 2572.

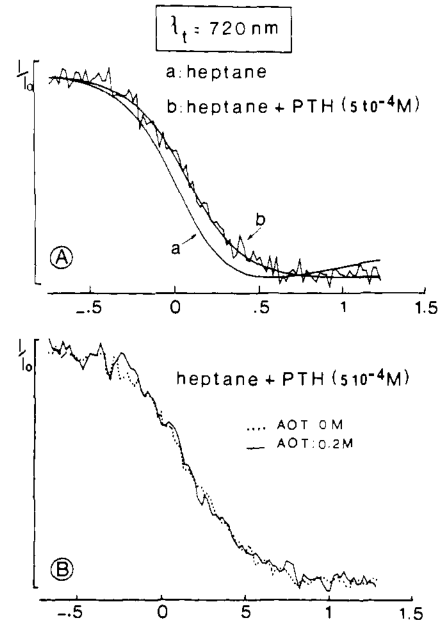


Figure 4. A: time-resolved electron solvation in *n*-heptane/PTH (5×10^{-4} M) solution at 720 nm following femtosecond UV excitation (λ, 310 nm). The curve b (—) represents the computed best fit, giving a solvated electron appearance time constant of 90 fs. The computed fit of the rise time of induced absorption in pure *n*-heptane solution is also indicated (curve a) and represents the "instantaneous" response. B: effect of aerosol OT on the rise time of induced absorption at 720 nm following excitation of PTH in *n*-heptane.

that the electron escape probability is small in *n*-heptane.

In the femtosecond photochemical experiments with reversed micelles, *n*-heptane cannot be used as an electron donor because the quantum yield of photoionization of the nonpolar medium is too low to provide an adequate signal-to-noise ratio. Therefore, the photochemical generation of an epithermal electron (ΔE = 2 eV) has been achieved by resonant two-photon ionization of a polycyclic chromophore (phenothiazine) having a low ionization potential (I_g = 6.5 eV). In the binary mixture PTH/*n*-heptane, the femtosecond photoionization of phenothiazine ([PTH] = 5 10^{-4} M) permits investigation of the electron-transfer process (eq 4):

$$\mathrm{PTH}_{S_0} \xrightarrow{h\nu} \mathrm{PTH}_{S_1} \rightarrow \mathrm{PTH}_{S_n} \rightarrow [\mathrm{PTH}^+ + e^-] \xrightarrow{\text{heptane}} \mathrm{PTH}^+ + e^-_{n\text{-hept}} \quad (4)$$

The results of the pump-probe experiments performed at 720 nm are shown in Figure 4A. The time dependence of a transient induced absorption at 720 nm following ultraviolet photoionization of PTH in *n*-heptane takes into account the position of the zero-time delay and can be well fitted to a buildup time of 90 ± 10 fs. It is interesting to note that the presence of surfactant molecules (AOT) in the concentration range 0-0.2 M does not modify the dynamics of electron trapping in the hydrocarbon phase (Figure 4B).

Reversed Micelles, W = 50. Time-resolved spectroscopy data obtained following femtosecond photoionization of (5×10^{-4} M) phenothiazine in AOT (1.5×10^{-2} M) reversed micellar solution (W = 50) are summarized in Figures 5 and 6. In AOT reversed micelles without chromophore (Figure 5A) the rise time of the induced absorption in the red spectral region (720 nm) remains similar whatever the H_2O/AOT ratio (W = 0 or 50). No detectable concentration of hydrated electron is obtained in the first 2 ps following the femtosecond photoionization of PTH. This

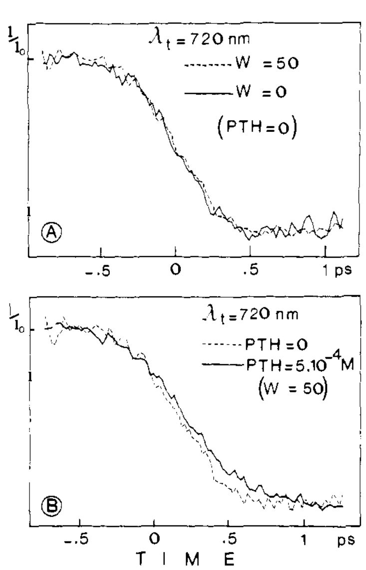


Figure 5. A: effect of H_2O/AOT ratio on the time-resolved absorption at 720 nm following femtosecond photoexcitation of reversed micelles [AOT (0.15 M)/*n*-heptane] without phenothiazine. B: influence of PTH (5×10^{-4} M) on the time-resolved absorption at 720 nm following photoexcitation of reversed micelles [AOT (0.15 M)/*n*-heptane/H_2O, W = 50].

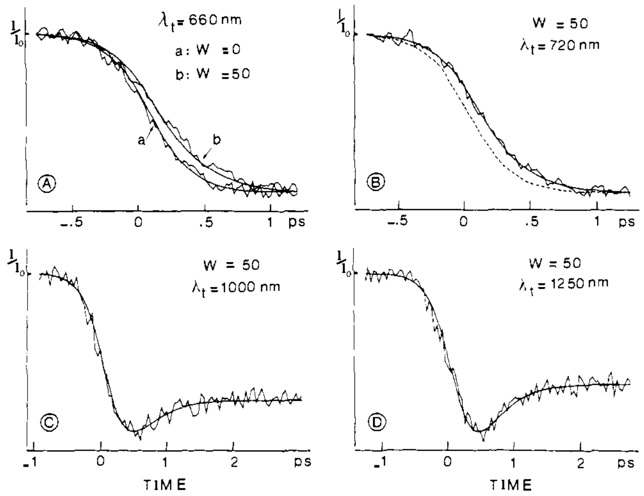


Figure 6. Time-resolved spectroscopy data at 660, 720, 1000, and 1250 nm following femtosecond photoionization of PTH (5×10^{-4} M) in AOT reversed micelles (W = 50). The smooth lines represent the computed best fits of the experimental traces. In the infrared (1000 and 1250 nm) the fits assumed the combination of an appearance time of e^-_{trap} in *n*-heptane (T_1 = 90 fs) and the rise of prehydrated electrons (e^-_{presol}) with an appearance time of 140 ± 10 fs and a lifetime of 270 ± 20 fs. The induced absorption at 660 and 720 nm includes the combination of the appearance time of e^-_{trap} and e^-_{hyd} as measured in the infrared.

result suggests that the formation of hydrated electrons occurs neither directly through a multiphotoionization of water molecules within the inner core of reversed micelles nor through an ultrafast capture of $e^-_{n\text{-hept}}$ by sequestered water clusters. In comparison with control reversed micelles (PTH = 0, W = 50), the kinetic data obtained with dissolved PTH in AOT reversed micelles (W = 50) show the existence of a time delay (Figure 5B). In reversed micelles containing large amount of sequestered water molecules and PTH, the photoejection of an electron from the chromophore involves the ultrafast attachment of the excess electron to a micelle water pool ($e^- + [H_2O]_m$). A careful analysis of the kinetic data has been performed with a model that takes into account the contribution of two populations of electrons: one considered to be an electron localized in *n*-heptane ($e^-_{n\text{-hept}}$) and the other a hydrated electron (e^-_{hyd}) in the inner core of the reversed micelles (eq 5). At 720 nm, the induced absorption $\Delta A^{\lambda}(\tau)$ is perfectly

---

(31) Hirata, Y.; Mataga, N.; Sakata, Y.; Misumi, S. *J. Phys. Chem.* **1986**, *90*, 6065.

(32) Scott, T. W.; Braun, C. L. *Can. J. Chem.* **1985**, *63*, 228, and references therein.

fitted to the convolution of the pump–probe pulse profile and a combination of the two components $e^-_{n\text{-hept}}$ and e^-_{hyd}.

$$\Delta A^{\lambda}(\tau) = \Delta A^{\lambda}_{e^-_{n\text{-hept}}}(\tau) + \Delta A^{\lambda}_{e^-_{\text{hyd}}}(\tau) \qquad (5)$$

The evolution of the populations during the pumping and probing follows the expressions

$$\Delta A^{\lambda}_{e^-_{n\text{-hept}}}(\tau) = \epsilon e^-_{n\text{-hept}} l \int_{-\infty}^{+\infty} C_1(\tau - \tau')C^{\lambda}(\tau')\, d\tau' \qquad (6)$$

$$\Delta A^{\lambda}_{e^-_{\text{hyd}}}(\tau) = \epsilon e^-_{\text{hyd}} l \int_{-\infty}^{+\infty} C_2(\tau - \tau')C^{\lambda}(\tau')\, d\tau' \qquad (7)$$

in which l is the interaction length, ϵ the molar extinction coefficient, and $C(\tau')$ the normalized third-order correlation between the probe and the pump pulse.[33] The concentrations of $e^-_{n\text{-hept}}$ and e^-_{hyd} created at a time t (C_1 and C_2) are determined by expressions 8 and 9. In these expressions T_1 represents the

$$C_1(t) = C^{\circ}_1(1 - \exp(-t/T_1)) \qquad (8)$$

$$C_2(t) = C^{\circ}_2(1 - \exp(-t/T_2)) \qquad (9)$$

dynamics of electron localization in the hydrocarbon phase and T_2 the dynamics of electron capture and solvation in the aqueous pool of reversed micelles. In reversed micelles ($W = 50$), the rise time of the 660- and 720-nm-induced absorption (Figure 6A,B) can be fitted to two monoexponential laws including the combination of the electron localization in *n*-heptane and the electron capture and solvation in water clusters. In expression 8, the best fits give $T_1 = 90$ fs as in pure *n*-heptane. In eq 9, T_2 must be determined from infrared investigations. The infrared absorption spectroscopy data in Figure 6C,D show the existence of a transient species. At 1000 and 1250 nm the time-resolved spectroscopic data are fitted to a model that takes into account the contribution of the localized electron in the hydrocarbon phase, the hydrated electron in the aqueous phase of the micelle and an infrared species.

This species appears with a time constant T'_1 and relaxes toward the solvated state with a time constant T'_2: $A_{(t)} = A_0\,[1/(T'_2 - T'_1)][\exp(-t/T'_2) - \exp(-t/T'_1)]$. As previously shown in pure liquid water and aqueous micellar solutions,[34-36] this transient infrared species must be assigned to a precursor of the hydrated electrons in the polar inner core of reversed micelles. In the present experiments, the convolution of the pulse shape with the dynamics of the different populations of electrons at 1000 and 1250 nm assumes $T'_1 = 140 \pm 10$ fs and $T'_2 = 270 \pm 20$ fs. Consequently, at 720 nm the induced absorption due to hydrated electron is perfectly fitted to the convolution of the pulse profile and the expected signal rise $A_{(t)} = A_0[1 - 1/(T'_2 - T'_1)][T'_2 \exp(-t/T'_2) - T_1 \exp(-t/T'_1)]$ by use of the same values of T'_1 and T'_2 as determined at 1000 and 1250 nm. The incomplete recovery of the signal at 1000 and 1250 nm is due to a contribution of the $e^-_{n\text{-hept}}$ and e^-_{hyd}.

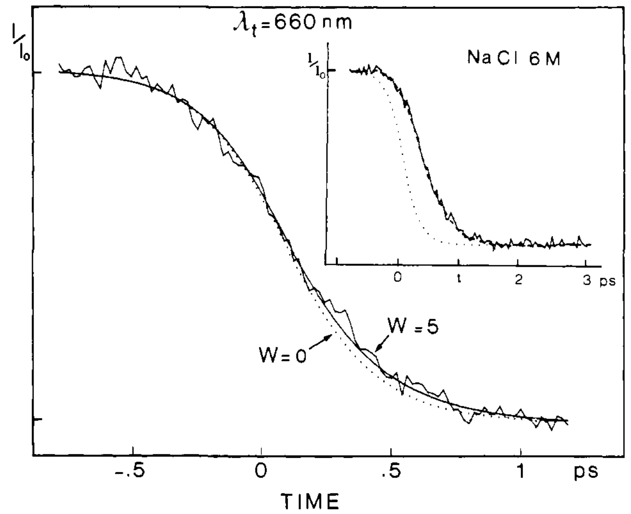


Figure 7. Kinetic results obtained at 660 nm after femtosecond laser photolysis of PTH ($5\ 10^{-4}$ M) in AOT reversed micelles [AOT (0.15 M)/*n*-heptane]. The dotted line represents computed best fit giving a time constant of 90 fs ($W = 0$). At $W = 5$, the solid line is the combination of the appearance time of $e^-_{n\text{-hept}}$ ($T_1 = 90$ fs) and the rise time of solvated electrons in the aqueous inner polar core of reversed micelles ($T_2 = 500$ fs). The inset represents the rise time of induced absorption at 660 nm following femtosecond photoexcitation (λ, 310 nm) of a concentrated aqueous solution of sodium chloride (6 M).

Reversed Micelles, $W = 5$. The femtosecond photoionization of PTH (5×10^{-4} M) in 8×10^{-2} M AOT reversed micellar solution containing small water pockets ($W = 5$) leads to the development of an early transient spectrum with an absorption maximum centered around 660–670 nm (Figure 1). This broad band is assigned to the presence of hydrated electrons in the small water clusters of reversed micelles. The study of electron capture in reversed micelles with a low $[H_2O]/[AOT]$ ratio is based on time-resolved spectroscopic data at 660 nm. The results summarized in Figure 7 show that the rise time of induced absorbance is slightly modified when the water pool size increases from 0 to 5. However in comparison with reversed micelles ($W = 0$), the time delay for the induced signal is smaller than with high W values (Figure 6A). The analysis of time-resolved absorption at 660 nm has been performed using eq 6–11. In expression 10, it cannot be assumed that the time constant T_2 assigned to electron capture in the aqueous micropocket equals the value obtained at $W = 50$. In fact, at a low water-to-surfactant ratio ($W = 5$), the counterion Na^+ and the water sequestered in AOT reversed micelles form microdroplets of very high ionic strength. The effective molar concentration of Na^+ can be estimated by the equation $[Na^+] = B.\ 55.5/W$ where B is the Na^+ dissociation coefficient;[9] $[Na^+] = 6$–7 M for $W = 5$. Femtosecond ultraviolet photoionization of concentrated aqueous solutions of sodium chloride (6 M) has been performed in order to obtain additional information on the dynamics of electron solvation in a strong ionic environment. The inset of Figure 7 represents the rise time of the induced absorption due to the appearance of solvated electrons following the femtosecond photolysis of aqueous solutions of sodium chloride. The induced absorption rise time is perfectly fitted to the convolution of the pulse profile and a monoexponential signal rise giving a time constant T_2 of 500 fs. This value has been introduced into eq 10 and 11. Under these conditions, the time-resolved absorption curve shown in Figure 7 can be well fitted to a combination of a fast component due to the appearance of e^-_{trap} in *n*-heptane ($T_1 = 90$ fs) and a slower component assigned to the formation of e^-_{hyd} in the sequestered water pool of reversed micelles $W = 5$ ($T_2 = 500$ fs).

(c) Efficiency of Excess Electron Attachment to the Water Pool. Our femtosecond spectroscopic investigations on AOT reversed micellar systems show that the primary events occurring after the photoionization of PTH correspond either to an electron trapping in the hydrocarbon phase or to an ultrafast electron capture by the sequestered aqueous microdroplets. In order to fully understand the dependence of electron capture and solvation efficiency on water pool size, we have determined the percentage of electron population that reacts with either the hydrocarbon phase or the sequestered water clusters. The analysis of the normalized kinetic data obtained at 660 and 720 nm has permitted the determination of the proportion $x_1(x_2)$ of $e^-_{n\text{-hept}}(e^-_{\text{hyd}})$ generated after each femtosecond pulse:

$$\Delta A^{\lambda}(t_{\infty}) = x_1 + x_2 = \Delta A^{\lambda}_{e^-_{n\text{-hept}}}(t_{\infty}) + \Delta A^{\lambda}_{e^-_{\text{hyd}}}(t_{\infty}) \qquad (10)$$

with $x_1 + x_2 = 1$. For $t > T_1$ or T_2, the identification of the coefficients x_1, x_2 in expressions 6–10 permits the determination

---

[33] Gauduel, Y.; Migus, A.; Antonetti, A. In *Chemical Reactivity in Liquids, Fundamental Aspects*; Moreau, M., Turcq, P., Eds.; Plenum Press: New York, 1988; p 15.

[34] Gauduel, Y.; Martin, J. L.; Migus, A.; Yamada, N.; Antonetti, A. In *Ultrafast Phenomena V*; Fleming, G. R., Siegman, A. E., Eds.; Springer Verlag: New York, 1986; p 308.

[35] Migus, A.; Gauduel, Y.; Martin, J. L.; Antonetti, A. *Phys. Rev. Lett.* **1987**, *58*, 1559.

[36] Gauduel, Y.; Berrod, S.; Migus, A.; Yamada, N.; Antonetti, A. *Biochemistry* **1988**, *27*, 2509.

Table I. Effect of the Size of Water Cluster (*W*) on the Efficiency of Excess Electron Attachment to the Water Pool of AOT Reversed Micelles

W	[AOT], M	$[e^-_{H_2O}]/([e^-_{H_2O}] + [e^-_{n\text{-hept}}])$	x_1/x_2	r_w,[a] Å	n[b]	S_w, 10^{23} Å^2
5	0.15	0.038	0.15	7.3	41	14.2
30	0.08	0.085	0.3	46.9	600	20.9
50	0.08	0.116	0.4	78.9	1400	23.3
50	0.15	0.160	0.65	74.3	1400	39.2

[a] The radii of the water pool (r_w) have been calculated by eq 1 of ref 4. [b] *n* aggregation numbers of AOT are based on data presented in ref 18.

of the percentage of excess electron that react with the sequestered water pool of AOT micelles.

$$\epsilon_1 C^\circ{}_1/\epsilon_2 C^\circ{}_2 = x_1/x_2 \qquad (11)$$

In expression 11, ϵ_1 and ϵ_2 correspond to the molecular extinction coefficients of $e^-_{n\text{-hept}}$ and e^-_{hyd}, respectively. At 720 nm, $\epsilon e^-_{hyd}(\epsilon_2)$ is taken as 18 500 M^{-1} cm^{-1} and $\epsilon e^-_{n\text{-hept}}$ (ϵ_1 = 7600 M^{-1} cm^{-1}) has been determined from Baxendale's experiments performed in *n*-hexane.[23,25]

Table I summarizes the results obtained for different values of *W* and AOT concentrations. The results of this table show that the electron capture probability defined as $[e^-_{hyd}]/[e^-_{hyd} + e^-_{n\text{-hept}}]$ is dependent on the water content of the microemulsion, i.e., on the structure of the water/surfactant interface. The efficiency of excess electron attachment to the water pool of AOT reversed micelles remains low for low $[H_2O]/[AOT]$ ratios. This means that the probability of electron capture in sequestered microbubbles follows the concentration of water pools in micellar systems. Table I also reports the estimate of the aqueous microdroplet surface (S_w) defined as $(N\pi r^2{}_w)([AOT]/n$. In this expression, r_w is the radius of the water pool and *n* the mean aggregation number per micelle. The values of the average aggregation number of AOT are based on data established by Eicke and Rehak.[4] The radius of the water pool (r_w) is calculated by the equation $r_w = 36.65\ \mu/g$, in which μ and *g* are the volume and weight percentage of water and AOT, respectively.[37] The data summarized in Table I clearly establish that the probability of an ultrafast electron capture by the water pool of reversed micelles increases as S_w.

The efficiency of the early electron–micelle attachment is enhanced in large water clusters (*W* = 50) and the probability of electron capture by water clusters is ~0.16. These results are in agreement with previous experiments that used pulse radiolysis of the hydrocarbon phase[16,38] to generate solvated electrons in reversed micelles. It is worth noting that, at constant H_2O/AOT ratio (*W* = 50), the increase of AOT concentration results in the increase of electron capture by water droplets. Owing to the fact that in this concentration range (0.08–0.15 M) the influence of AOT concentration on *n* (mean aggregation number) remains small at ambient temperature,[9] it can be concluded that the main effect of AOT is to increase the solubilization of PTH near the aqueous bubble and to favor an ultrafast electron transfer between PTH and the sequestered aqueous phase.

IV. Discussion

In AOT/PTH reversed micelles, the electron capture mechanism by the water droplet is highly dependent on the solubilization of PTH in the reversed micellar system. In agreement with earlier experimental work showing that the solubility of PTH in *n*-heptane is significantly increased by the alkyl chains in AOT[15] our static absorption spectra of PTH in AOT reversed micelles suggest that this chromophore is preferentially localized near the interfacial water (Figure 8). From the available literature data, it can be assumed that the structure of AOT reversed micelle (hydrodynamic radius) is not significantly perturbed by the presence of small hydrophobic species.[8,39] Since phenothiazine is almost insoluble in water, the chromophore will be preferentially associated with the surfactant aggregate and with the solvent. This preferential localization of PTH near the interfacial aqueous phase of reversed micelles would favor an ultrafast electron capture by the surfactant-solubilized water pool following the photoionization of PTH. This ultrafast electron capture can be understood either by the photochemical generation of an excess electron and its ultrafast reactivity in the vicinity of a water droplet or through the existence of a tunneling process between an excited state of phenothiazine and unoccupied levels of the system aq/e^-_{hyd} inside the aqueous inner core.

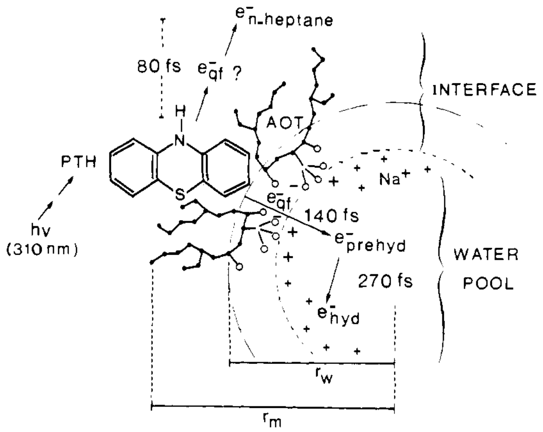


Figure 8. Sequence of primary photochemical events involved in the charge separation and electron capture by reversed micelle water pool (*W* = 50). e^-_{qf}, quasi-free electron (dry electron); $e^-_{n\text{-heptane}}$, localized electron in *n*-heptane; e^-_{prehyd}, infrared prehydrated electron; e^-_{hyd}, hydrated electron.

One of the main results obtained in the present study is the direct observation of a transient infrared species following electron transfer from phenothiazine to large water clusters. The infrared time-resolved data obtained with AOT reversed micelles (*W* = 50) clearly show that the electron capture of photoelectron by a water cluster does not proceed in a single step. The attachment of the excess electron to a sequestered water pool occurs through a transient state assigned to a precursor of the fully solvated electron (localized or presolvated electron). The rise time T_1 of this infrared tail (140 ± 10 fs) includes both thermalization of the electron and its localization inside the aqueous micellized cluster. Earlier studies led to an estimation of the thermalization distance of an epithermal electron with excess kinetic energy around 1 eV at ~40 Å.[37] Such a distance is smaller than the mean radius (r_w) of the aqueous microphase measured from small-angle neutron scattering, X-ray scattering, fluorescence polarization, or photon-correlation spectroscopy:[4,7,8,17] r_w = 60 Å for *W* = 50. This would suggest that when a photoelectron is ejected through the charged interface and captured by a bulklike water cluster, its localization and solvation probably occur in the inner polar aqueous phase of the water droplet containing no specific structure imposed by the interfacial layer (nonbound water). RMN spectroscopy of AOT micellized water clusters has shown that the sodium counterion (≃70%) is preferentially localized near the micellar solubilized water interface and that the unbound water molecules remain localized in the inner core of the aqueous cluster.[38] Additional investigations[10,38,39] have shown the existence of an inhomogeneous polar interior of AOT reversed micelles including a viscous polar boundary layer of ~6 Å and an inner layer of unbound water molecules. The similarity of the picosecond absorption spectrum of solvated electrons in AOT reversed micelles

---

(37) Wong, M.; Thomas, J. K.; Grätzel, M. *J. Am. Chem. Soc.* **1976**, *98*, 2391.

(38) Thomas, J. K.; Grieser, F.; Wong, M. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 937.

(39) Pileni, M. P.; Brochette, P.; Hickel, B.; Lerebours, B. *J. Colloid Interface Sci.* **1984**, *98*, 549, and references therein.

(40) Neff, H.; Sass, J. K.; Lewerenz, H.; Ibach, H. *J. Phys. Chem.* **1980**, *84*, 1350.

(41) Kjellander, R.; Marceja, S. *Chem. Phys. Lett.* **1985**, *120*, 393.

(42) Mallace, F.; Migliardo, P.; Vasi, C.; Wanderlingh, F. *Phys. Chem. Liq.* **1981**, *11*, 47.

($W = 50$) with that in pure aqueous solution also argues for an ultrafast capture of the excess electron within the nonperturbed water cluster. It is interesting to note that in large water droplets, the appearance time and the lifetime of the primary species (prehydrated electron) are similar to experimental values obtained in pure liquid water.[34,35]

These femtosecond spectroscopic data on electron capture by large sequestered clusters ($W = 50$) suggest that the primary events involved in the localization and solvation of the electron are not influenced by the properties of the sequestered water bubble. The time-resolved appearance of an early nonfully hydrated electron absorbing in the infrared rules out the assumption of a predominant role of a high density of preexisting deep traps involving an ultrafast electron capture after the charge separation from PTH.

In large water droplets ($W = 50$, $H_2O = 6\%$, micelle concentration = 8×10^{-5} M) excess electron capture in the water bubble occurs with a pseudo-first-order rate of 7.1×10^{12} s^{-1}. Earlier experiments have established that the rate of attachment of excess electrons to micellar water $k(e^- + [H_2O]_m)$ was faster than a diffusion-controlled rate ($\simeq 10^{15}$ M^{-1} s^{-1}) at a larger water concentration ($W > 30$).[14] Our femtosecond results on the primary electron attachment to water clusters ($e^- + nH_2O$), giving a rate constant $k(e^- + (H_2O)_m)$ of 7×10^{17} M^{-1} s^{-1}, cannot be interpreted in terms of a simple diffusion-controlled reaction.

At small H_2O cluster size ($W = 5$), the amount of solubilized water approaches the limit for solvation of Na^+ counterion and the hydration shell corresponds to tightly bound water. The solvation shell of Na^+ ($[H_2O]/[Na^+] = 5$) is characterized by high activation energies for the ^{23}Na relaxation process (6.85 kcal/mol with $W = 5$) and for the rotational correlation time of the sequestered water molecules, by decrease of the water pool fluidity, and by an increase of the microviscosity.[7,37] In this favorable distribution of ionic clusters $[Na(H_2O)_n{}^+]$ there is a disruption of the usual hydrogen-bonded structure generally observed in liquid water (regular tetrahedral structure). This results in a marked ^{1}H NMR chemical shift of the H_2O bubble in the reversed micelle at a very low $(H_2O)/(AOT)$ ratio.[6] The rotational correlation time (T_c), obtained by ^{1}H NMR relaxation, is longer than in bulk water,[43,44] whereas the ^{1}H NMR relaxation time T is significantly reduced by slow motions of water molecules.[44] Significant conclusions on the dynamical behavior of water molecules in small water bubbles have been obtained from quasielastic neutron scattering experiments.[45] Different molecular movements inside the water clusters have also been emphasized with the aid of a theoretical two-state stochastic model of sequestered water clusters in reversed micelles.[47] The correct molecular time ratio for reversed micelles and for pure liquid water is ~4.6 for $W = 5$.

Our femtosecond photochemical investigations on AOT reversed micelles directly demonstrate that the dynamics of epithermal electron capture by small water clusters containing a core of mixed polar heads and a high concentration of counterion (Na^+) is faster than the correlation time of the water–polar head interaction (T = 500 ps), the NMR relaxation rate of highly bound water around the Na^+ counterion, or the formation time of the Na^+ atmosphere around the solvated electron. The time of this epithermal electron capture can be estimated by the equation of Coyle et al.:[46] $T_r = 3.55 \times 10^{-9} \sum Z_i/\sum \mu\Lambda_i = 5$ ps for $[Na^+] = 6$ M. In this expression, Λ is the equivalent conductance of each type of ion in the solution. By use of the limiting equivalent conductance of e^-_{sol} (170 cm^2 Ω^{-1} equiv^{-1}) and of Na^+ (45 cm^2 Ω^{-1} equiv^{-1}), the estimate of the relaxation time of the ionic atmosphere of e^-_{sol} is found to be around 5 ps for $[Na^+] = 6$ M. This would suggest that in sequestered microdroplets containing highly immobilized water molecules ($W = 5$) electron solvation does not involve considerable molecular dynamics because the time-resolved spectroscopy data give a time constant of 500 fs for electron hydration in concentrated ionic solutions. However, it cannot be excluded that in small water droplets some few free water molecules remain the predominant site of electron hydration. The very low transient concentration of solvated electrons obtained after each femtosecond pulse (less than 1.5 μM) did not permit up to now a direct identification of the primary step of electron solvation in small water bubbles. Nevertheless, considering that the individual motions of interfacial water molecules have been shown to be very similar to those in concentrated ionic solutions,[47] it is instructive to underline that in very concentrated aqueous ionic solutions (NaCl, 6 M), where the static dielectric constant (ϵ_0) is ~45,[48] electron solvation occurs through at least one intermediate step. This step has been identified in the infrared as a localization process (presolvated state) of the electron (e^-_{prehyd}). The configurational stability of the presolvated electron would be achieved by rearrangement energy of the medium in the first solvation shell. These recent studies will be discussed at length in a forthcoming paper. The time-resolved delayed appearence of the initially localized state rule out the assumption of a predominant role of a high density of preexisting potential wells into which the electron would fall directly after electron capture by the water bubble. However, for small sequestered water pools, the femtosecond infrared experiments do not exclude a redistribution of the electrons among the traps by tunneling from trap to trap, a local rearrangement of the electronic cloud of water molecules, or a vibrational motion of one water molecule.

In conclusion, a photochemical monoelectronic transfer leading to the hydration process in sequestered pools of water within reversed micelles has been observed at the femtosecond time scale. The dynamics of an early electron reactivity $[e^- + n(H_2O)]$ with large water clusters ($W = 50$) has been determined by near-infrared spectroscopy. The electron capture and trapping in the sequestered water pools occurs through the formation of a transient species (presolvated state). Once the electron gets trapped inside the water bubble, its final stabilization toward the fully solvated state occurs in 270 fs. The formation of hydrated electron in the small sequestered water pool size ($W = 5$) occurs in 2×10^{12} s^{-1}. Changes in the water pool size from 50 to 5 decrease the efficiency of the femtosecond attachment to excess electron to the water pool of AOT reversed micelles.

Acknowledgment. We gratefully acknowledge the help of G. Hamoniaux, E. Maillard, and J. Bottu with laser spectroscopy and data processing. We thank Prof. C. Jonah for fruitful discussions before the preparation of the manuscript and Dr. F. Kieffer for a critical reading of the text.

---

(43) Wong, M.; Thomas, J. K.; Nowak, T. *J. Am. Chem. Soc.* **1977**, *99*, 4730.

(44) Cooke, R.; Kuntz, I. P. *Annu. Rev. Biophys. Bioeng.* **1975**, *4*, 267.

(45) Tabony, J.; Llor, A.; Drifford, M. *J. Colloid Polym. Sci.* **1983**, *261*, 938.

(46) Coyle, P. J.; Dainton, F. S.; Logan, S. R. *Proc. Chem. Soc., London* **1964**.

(47) Llor, A.; Rigny, P. *J. Am. Chem. Soc.* **1986**, *108*, 7533.

(48) Hasted, J. B.; Ritson, M.; Collie, C. H. *J. Chem. Phys.* **1948**, *16*, 1.