

Micellar Radii and High Aggregation Numbers in a 0.6 M NaCl Sodium Dodecylsulfate Solution Determined through Positron Annihilation Lifetime Spectroscopy

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The equations related to a recently published method to measure both the micellar average radius (R_{mic}) and aggregation number (N_{ag}) using a single technique, positron annihilation lifetime spectroscopy (PALS), are extended and applied to a 0.25 M sodium dodecylsulfate (SDS) aqueous solution in the presence of large amounts of NaCl (0.6 M) as a function of temperature (T). The analysis of the PALS spectra confirms that the triplet state of positronium, o -Ps, originally formed in the aqueous subphase (o -Ps^{aq}) becomes trapped inside the organic core of the micelles (o -Ps^{org}). The equations take into account the variety of o -Ps^{org} lifetimes promoted when introducing a Ps oxidizer (duroquinone) into the solution, which distributes into the micelles according to Poisson's law. The variation with T of R_{mic} derived from PALS agrees well with two sets of values previously published, showing an important decrease upon heating, from about 5.8 nm at 305 K down to 2.3 nm at 343 K. By contrast, although all three sets of data agree on the concomitant decrease in N_{ag} with T , toward values denoting a nearly spherical shape of the micelles at high T , large differences are found at the lowest T studied, the PALS data giving much higher values than those previously published. However, our data show good agreement with the variation of N_{ag} with T , calculated from the measured R_{mic} and the volume of the SDS molecules on the assumption that the micelles display a prolate ellipsoid shape.

Introduction

In a previous work, a new method was developed allowing one to determine quantitatively both the average radius (R_{mic})¹ and the aggregation number (N_{ag})² of a micellar system through a single technique, positron annihilation lifetime spectroscopy (PALS), by using the long-lived triplet state (o -Ps) of positronium (Ps, the bound state of an electron with a positron) as a probe. This was possible by taking advantage of the fact that Ps becomes trapped from the water bulk (Ps^{aq}) into the organic core of the micelles (Ps^{org}) through a purely diffusion-controlled process, thereby modifying its decay profile; at concentration C_{mic} of micelles, the lifetime of o -Ps^{aq} decaying in water becomes shorter than it is in the absence of micelles, τ_3^0 , and a new component appears, with a lifetime of τ_4^0 , arising from o -Ps^{org} decay in the micellar core.

In a first step, the equations relevant to the concomitant Ps^{aq} decay and trapping processes were established, taking account of both the existence of a bubble state for Ps in the aqueous solution and of the time dependence of the trapping rate coefficient.¹ The equation of the o -Ps decay curve includes two parameters related to the micelles that appear to be correlated: R_{mic} , from the diffusion equations; N_{ag} , from the definition of the micelle concentration as the ratio of the surfactant concentration, C_{surf} , to N_{ag} . It was successfully applied in the case of an aqueous solution of sodium dodecylsulfate (SDS)¹ and extended to some other systems,^{3–5} yielding the expected values of R_{mic} with N_{ag} set at a previously determined value.

Next, to unravel the correlation between R_{mic} and N_{ag} and determine these two parameters in a completely independent

way, a method was proposed based on what is done in fluorescence probing experiments.² Once added to the system, a solute (quencher) known to react effectively with Ps and soluble only in the organic core of the micelles will distribute over the micelles according to Poisson's law.^{6,7} In those micelles which happen to contain no quencher molecules, the o -Ps lifetime remains the same as in the absence of quencher, τ_4^0 . The intensity of this component obeys a simple exponential whose argument depends only on the quencher concentration, C_Q , and on $C_{\text{mic}} = C_{\text{surf}}/N_{\text{ag}}$. Because of the efficiency of the reaction of the quencher with o -Ps, it was expected that all other o -Ps^{org} lifetimes, for those micelles containing one or more quencher molecule, would be very short as compared to τ_4^0 . In this way, measuring the intensity associated to the longest-lived o -Ps^{org} component as a function of C_Q would yield an exponential decrease with N_{ag} as the only fitting parameter. This method was successfully applied in the case of a simple SDS aqueous solution.² However, the o -Ps^{org} lifetime of those micelles containing one or more molecules of quencher was found to be not as short, as compared to τ_4^0 , as one would have expected from its high reaction rate constant with Ps measured in pure dodecane; this was attributed to some localization of the quencher molecules near the water/micelle interface.²

The aim of the present paper is to extend and further establish the usefulness of our method based on PALS to determine both R_{mic} and N_{ag} by selecting cases where other, more conventional techniques have shown limitations. To this end, we have undergone the study of aqueous SDS solutions in the presence of large amounts (0.6 M) of NaCl, as a function of temperature

(*T*). In a previous study,³ we had shown that PALS could deliver the expected size of the micelles in 0.28 M SDS aqueous solutions as a function of NaCl concentration up to moderate micellar radii: about 2.3 nm for the micellar core radius at 303 K, corresponding to 0.35 M NaCl. However, at higher NaCl concentrations, the micellar radius has been shown to increase drastically^{8–11} with a concomitant change from spherical to prolate ellipsoidal.⁸ Upon heating, the micelles would progressively return to a smaller size, regaining the spherical shape they have in the absence of NaCl.^{8,9,11–14}

Most generally, all previous studies, based on light-scattering experiments, have produced reasonably concordant values as regards the micelle radii. Thus, for a (0.069 M SDS + 0.6 M NaCl) aqueous solution at 298 K, published values for the micellar mean hydrodynamic radius are in the range of 7.5–8.0 nm;^{11,13,14} however, values up to 11.3 and 13 nm have also been reported.^{8,12} Regarding the aggregation number in the same micellar system, measured through fluorescence quenching methods, the agreement is not as good, with values ranging from 153⁹ to 400¹⁰ and 920,⁸ the latter being calculated from the measured hydrodynamic radius on the assumption of a prolate ellipsoid for the micellar shape.

Because of the rather short lifetime of *o*-Ps in water, about 1.8 ns, this probe might not be effective enough in a dilute system in which the probability for Ps to get trapped into the organic subphase would be too low. Therefore, on the basis of our previous work, convenient conditions have been chosen hopefully by studying a 0.25 M SDS aqueous solution; the *o*-Ps quenching agent was duroquinone, which has been shown to react very effectively with Ps in dodecane² and is not soluble in water.

Experimental Section

The chemicals, SDS and duroquinone from Aldrich, were used as received. The SDS concentration was 0.25 M, whereas duroquinone was added to the micellar aqueous solution at concentrations ranging from 0.25 up to 1 mM.

The source of positrons was a 5×10^5 Bq carrier-free ²²Na droplet directly introduced into the solution. The latter was placed in a Pyrex tube, degassed through the conventional freeze–thaw technique, and then sealed.

The PALS apparatus consisted of BaF₂ and Pilot U scintillators used in a fast–fast coincidence mode. The temperature range (305–343 K) was investigated by using a thermostatically controlled copper cylinder (3 cm diameter) in which the Pyrex tube was introduced, with a thermal stability of 0.2 K. To avoid heating of the detectors, these were separated from the cylinder by a copper plate radiator. This arrangement resulted in a time resolution of 330 ps.

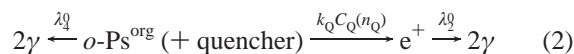
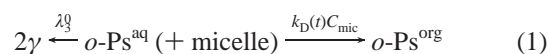
Besides the (0.25 SDS + 0.6M NaCl) solutions, pure water and a 0.6M NaCl solution were also studied as references. For a better definition of the PALS parameters, each sample was counted repeatedly (typically, 3 times) with an integral of counts kept at about 10⁶. The experimental error on the PALS parameters, intensities and lifetimes of the various components, was about 1%.

Theoretical Expression of the Decay Profiles of the *o*-Ps Components

On developing a specific method to determine the micelle aggregation number,² it was hoped that the latter could be obtained directly, through a model-independent procedure, from the measurement of the intensity of the longest-lived PALS component, related to *o*-Ps^{org} trapped inside the micelles. This

would have been the case provided that the lifetime of any of the *o*-Ps^{org} atoms happening to be present in a micelle containing a number $n_Q \geq 1$ of quencher molecules would have a lifetime, τ_4 , much shorter than τ_4^0 . However, it soon appeared that this condition would not be fulfilled, at least at the lowest *T* studied. Therefore, a set of equations descriptive of the decay of the *o*-Ps^{aq} and *o*-Ps^{org} components was established to fit the experimental PALS spectra, following the procedure of our previous work.^{1,2}

The trapping process and the oxidation of *o*-Ps^{org} by the quencher (duroquinone) may be described by the following schemes



Here, $\lambda_3^0 = 1/\tau_3^0$ is the *o*-Ps^{aq} decay rate constant in the absence of SDS, λ_4^0 is the *o*-Ps^{org} decay rate constant in the absence of quencher, and λ_2^0 is the free positron decay rate constant; $C_{\text{mic}} = C_{\text{surf}}/N_{\text{ag}}$ is the micelle concentration and $C_Q(n_Q)$ is the quencher concentration, inside the micelle, when n_Q quencher molecules are present

$$C_Q(n_Q) = n_Q/(V_{\text{core}}N_{\text{Av}}) \quad (3)$$

where V_{core} is the volume of the micellar organic core and N_{Av} is Avogadro's number. The expression of the diffusion-controlled, time-dependent trapping rate coefficient, $k_D(t)$, has been given previously.^{1,2} For the sake of simplicity, the time dependence of k_Q is ignored; this is physically sound, since, for the reaction of small solutes (0.3–0.6 nm) with Ps, the error induced on the value of k_Q should not exceed 10%.

Fitting the PALS spectra was thus carried out by considering the Ps singlet state (*p*-Ps) and free e^+ components as normal exponentially decaying components, in a conventional way, whereas specific expressions were derived from the kinetic schemes 1 and 2 for the *o*-Ps components. Solving the corresponding equations allows two different solutions to appear, according to whether a certain parameter, $\Delta = \alpha - \lambda_4$, is positive or negative. Although the final equations do not consist in a sum of simple decaying exponentials, allowing one to define discrete lifetimes, the expressions for α and λ_4 are equivalent to those obtained for the *o*-Ps^{aq} and *o*-Ps^{org} decay rate constants, respectively, in case of quenching with no time dependence of the reaction rate coefficients

$$\alpha = \lambda_3^0 + k_D C_{\text{mic}} \quad (4)$$

$$\lambda_4 = \lambda_4^0 + k_Q C_Q(n_Q) \quad (5)$$

Here, k_D is the time-independent trapping rate constant, whose expression takes into account both the reaction radius (R_{core}) and the hydrodynamic radius (R_{mic}) of the micelles, appearing in the Smoluchowski equation for a purely diffusion-controlled reaction rate constant¹

$$k_D = 2N_{\text{Av}}k_B T(R_{\text{core}} + R_{\text{Ps}})(1/R_{\text{mic}} + 1/R_{\text{Ps}})/(3000\eta) \quad (6)$$

where k_B is Boltzmann's constant, T is the absolute temperature, η is the viscosity of the medium, and R_{Ps} is the Ps (bubble) radius. The difference between the R_{core} and R_{mic} amounts to the diameter of the SDS polar heads, set at $d_{\text{head}} = 0.506$ nm.¹ Note that changing this latter value in a reasonable range (about

0.4 to 0.6 nm) was found to have no significant effect on the experimental results to come.

Thus, the equations of the continuous PALS spectrum for the *o*-Ps components arising from an initial amount (I_3) created in water, when n_Q molecules of quencher are present in a micelle, $S_{o-Ps}(n_Q, t)$, are as follows:

For $\Delta = (\alpha - \lambda_4)$, $\Delta > 0$

$$S_{o-Ps}(n_Q, t)/I_3 = A \exp(-\alpha t - \beta t^{1/2}) + [B - CD_1 \operatorname{erf}(\beta/2\Delta^{1/2})] \exp(-\lambda_4 t) + CD_1 \exp(-\lambda_4 t) \operatorname{erf}[(\Delta t)^{1/2} + \beta/2\Delta^{1/2}] + E \exp(-\lambda_2^0 t) + F_2 \exp(-\lambda_2^0 t) \int_0^{(\delta_3 t)^{1/2} - \beta/(2\delta_3^{1/2})} e^{x^2} dx \quad (7)$$

For $\Delta = (\lambda_4 - \alpha)$, $\Delta > 0$

$$S_{o-Ps}(n_Q, t)/I_3 = A \exp(-\alpha t - \beta t^{1/2}) + [B - CD_2 \int_0^{\beta/(2\Delta^{1/2})} e^{x^2} dx] \exp(-\lambda_4 t) + CD_2 \exp(-\lambda_4 t) \int_0^{\beta/(2\Delta^{1/2})} e^{x^2} dx \int_0^{(\Delta t)^{1/2} - \beta/(2\Delta^{1/2})} e^{x^2} dx + E \exp(-\lambda_2^0 t) + F_2 \exp(-\lambda_2^0 t) \int_0^{(\delta_3 t)^{1/2} - \beta/(2\delta_3^{1/2})} e^{x^2} dx \quad (8)$$

The various symbols used read as follows

$$\beta = 2k_D C_{\text{mic}} (R_{Ps} + R_{\text{core}})^{1/2} (R_{\text{mic}} + R_{Ps})^{1/2} (6\eta/k_B T)^{1/2} (R_{\text{mic}} R_{Ps})^{1/2}$$

$$\delta_1 = \lambda_4 - \lambda_4^0$$

$$\delta_2 = \lambda_2^0 - \lambda_4$$

$$\delta_3 = \lambda_2^0 - \alpha$$

$$A = \lambda_3^0 - \lambda_4^0 (\alpha - \lambda_3^0)/\Delta - \lambda_2^0 \delta_1 (\alpha - \lambda_3^0)/(\Delta \delta_3)$$

$$B = \lambda_4 (\alpha - \lambda_3^0) (\lambda_2^0 - \lambda_4^0)/(\Delta \delta_2)$$

$$C = \beta \lambda_4 (\lambda_2^0 - \lambda_4^0) (\lambda_3^0 - \lambda_4)/(\Delta^{3/2} \delta_2)$$

$$D_1 = (\pi^{1/2}/2) \exp(\beta^2/4\Delta)$$

$$D_2 = \exp(-\beta^2/4\Delta)$$

$$F_1 = \lambda_2^0 \delta_1 (\alpha - \lambda_3^0)/(\delta_2 \delta_3)$$

$$F_2 = \lambda_2^0 \delta_1 \beta (\lambda_2^0 - \lambda_3^0) \exp(-\beta^2/4\delta_3)/(\delta_2 \delta_3^{3/2})$$

$$E = F_1 + F_2$$

The final expression of the *o*-Ps decay profile, including all probabilities of having n_Q molecules of quencher per micelle, $P(n_Q)$, for an initial intensity of *o*-Ps formed I_3 , is

$$S_{o-Ps}(t) = I_3 \sum_{n_Q=0}^{\infty} P(n_Q) S_{o-Ps}(n_Q, t) \quad (9)$$

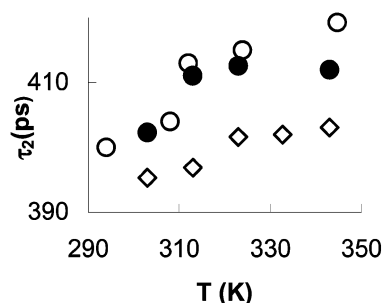


Figure 1. Variation of the e^+ lifetime, τ_2 (ps), with temperature, T (K), in (○) pure water, (●) 0.6 M NaCl, and (◇) 0.6 M NaCl + 0.25 M SDS aqueous solutions. Experimental errors: 4 ps.

$P(n_Q)$ is ruled by the Poisson distribution as

$$P(n_Q) = (N^n/n_Q!) \exp(-N) \quad (10)$$

where N is the average number of molecules per micelles, given by

$$N = N_{\text{ag}} C_Q / C_{\text{surf}} \quad (11)$$

In the fitting program,^{1,2} eq 9 was duly convoluted by the resolution function of the apparatus, in the form of a sum of Gaussians, and discretized over channels. For the sake of space, the final equation is not given but can be deduced from the treatments developed in our previous work.^{1,2} The P_s radius, R_{Ps} in eq 6, was calculated on the basis of one of the simplest bubble models:¹⁵ in the T range explored, R_{Ps} varies very smoothly, from 0.312 to 0.315 nm between 305 and 343 K, respectively; it was verified that moderate changes in these values would not affect significantly the results to come. The viscosity of the (SDS + NaCl) solutions, η in eq 6, was calculated from the viscosity of pure water, η_w , at each T , and the NaCl concentration, C_{NaCl} , according to¹⁶

$$\eta = \eta_w + 0.0989 C_{\text{NaCl}} \quad (12)$$

The only physically meaningful fitting parameters left in eq 9 were thus those related to the micelles, R_{mic} and N_{ag} , plus the duroquinone reaction rate constant, k_Q . Typically, at specified T , about 15 spectra for various duroquinone concentrations were fitted simultaneously.

Results and Discussion

A. PALS Parameters. In all solutions, the shortest lifetime, τ_1 , was in the range 110–130 ps, denoting *p*-Ps annihilation. Figure 1 shows the smooth increase^{17,18} in the free e^+ lifetime, τ_2 , with T in all cases. The values are slightly lower in the NaCl solution, possibly denoting the presence of the $P_s\text{Cl}$ bound state,¹⁷ and still lower in the (SDS + NaCl) solutions, most probably denoting the formation of an additional e^+ bound state with the sulfate heads of the surfactants. For the (SDS + NaCl) solutions, no significant differences were found in τ_2 in the absence or presence of duroquinone at each T .

Figure 2 shows the smooth decrease of the *o*-Ps lifetime, τ_3 , with T in water and the 0.6 M NaCl solution. The values are slightly lower in the latter case, due to an increased pick-off decay rate arising from the increase in the (electron) density of the medium; they were set as the *o*-Ps^{aq} lifetime values in the absence of SDS (τ_3^0 in eqs 1 and 4) in the fitting program.

The changes in the initially formed *o*-Ps^{aq} intensity, I_3 , are shown in Figure 3. In water, there is a smooth increase with T , whereas there is hardly any change in both the NaCl and (SDS

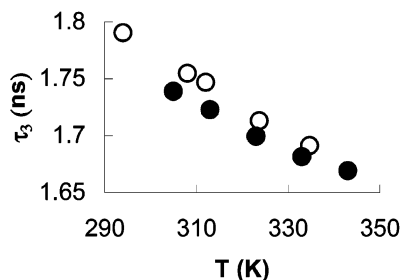


Figure 2. Variation of the *o*-Ps lifetime, τ_3 (ns), with temperature, T (K), in (○) pure water and (●) 0.6 M NaCl aqueous solution. Experimental errors: 20 ps.

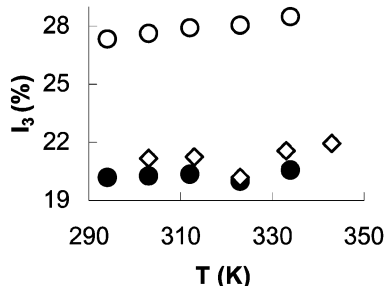


Figure 3. Variation of the initially formed *o*-Ps intensity, I_3 (%), with temperature, T (K), in (○) pure water, (●) 0.6 M NaCl, and (◇) 0.6 M NaCl + 0.25 M SDS aqueous solutions. Experimental errors: 0.2%.

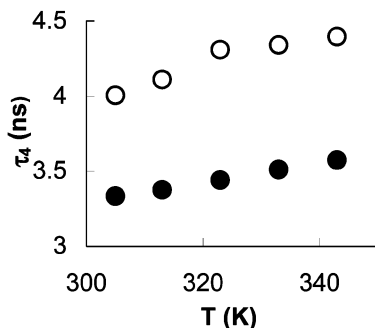


Figure 4. Variation of the *o*-Ps^{org} lifetime, τ_4 (ns), with temperature, T (K): (○) experimental values for the 0.6 M NaCl + 0.25 M SDS aqueous solution; (●) values calculated from eq 12 for pure dodecane. Experimental errors: 30 ps.

+ NaCl) solutions, in agreement with previous findings.¹⁷ The halide ions have been shown to promote a limited inhibition of Ps formation in polar solvents, ascribed to localized e^+ capture, by which I_3 would reach a plateau value, I_{3p} , with increasing halide concentration; upon heating, the total Ps yield (I_3) would increase, while I_{3p} , ascribed to Ps formation through the reaction of quasifree e^+ and e^- , would remain constant.^{17,19,20} Adding SDS to the NaCl solution results in a small increase in I_{3p} ; the additional presence of duroquinone does not bring in any significant change.

Figure 4 shows the smooth increase with T of the *o*-Ps^{org} lifetime in the (SDS + NaCl) solution, τ_4 , together with that expected in dodecane according to the following equation

$$\tau \text{ (ns)} = 1/(0.061\gamma^{1/2}) \quad (13)$$

Equation 13 arises from the Ps bubble model^{15,21} applied to the specific case of alkanes.²² The values of the surface tension, γ (dyn/cm), were derived by extrapolating a selection of data on long-chained alkanes.²³ The experimental and calculated plots are parallel, with higher values of τ_4 for the former, indicating a lower surface tension of the organic tails forming the micellar

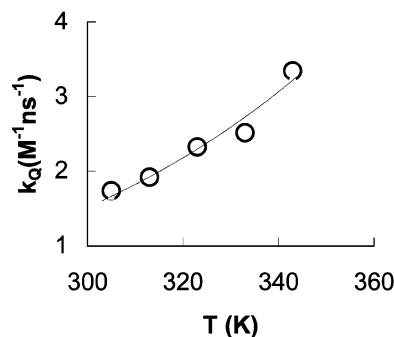


Figure 5. Variation of the duroquinone quenching rate constant, k_Q ($M^{-1} \text{ ns}^{-1}$), with temperature, T (K), in a 0.6 M NaCl + 0.25 M SDS aqueous solution. The solid line is a fit for a diffusion-controlled reaction (see text). Experimental errors: $0.1 M^{-1} \text{ ns}^{-1}$.

core than in bulk dodecane; in the 305–343 K range, γ inside the micelles would change from 16.8 to 13.9 dyn/cm as compared to 24.3–21.0 dyn/cm in pure dodecane.

As in our previous work, fitting the PALS spectra indicates no initial Ps formation in the micelles. Besides the fact that these occupy a low-volume fraction in the solutions, about 8% from the volume of the surfactant molecules,²⁴ this is most probably due to the existence of mixed spurs, previously shown to result in a greatly enhanced probability for Ps to be formed in water, in the case of reverse micelles.²⁵ In essence, an e^+/e^- pair that would happen to be initially on either side of the water/alkane interface has much larger chances to react and form Ps in the aqueous subphase because of the much larger Onsager radius (the distance between two charged particles at which the thermal energy overcomes the Coulomb attractive energy)²⁶ and particle mobility in the alkane. Consequently, all Ps^{org} ending up inside the micelles originates from the trapping of *o*-Ps^{aq}. From eq 1, the total amount of trapped *o*-Ps^{org}, I_4 , is thus given by

$$I_4 = I_3 - \lambda_3^0 \int_0^\infty o\text{-Ps}^{\text{aq}} dt = I_3 - \lambda_3^0 I_3 \int_0^\infty \exp(-\alpha t - \beta t^{1/2}) dt$$

$$I_4 = I_3 - \lambda_3^0 I_3 [1 - \rho(\pi^{1/2}/2) \exp(\rho^2) \text{erfc}(\rho)]/\alpha \quad (14)$$

where $\rho = \beta/(2\alpha^{1/2})$ and erfc is the complementary error function. From the fitting parameters, the I_4 values increase from 2.3% (11% of the initially formed *o*-Ps) up to 5.8% (27% of *o*-Ps) between 305 and 343 K, respectively.

Figure 5 shows the smooth variation of the duroquinone quenching rate constant, k_Q , as a function of T . Assuming k_Q to be proportional to $T \exp(-E/k_B T)$ as expected for a diffusion-controlled reaction (essentially because of the T dependence of the viscosity, see eq 6) leads to $E = 0.13$ eV, which coincides with the activation energy of viscosity in dodecane, $E_\eta = 0.13$ eV,²³ showing that the reaction of *o*-Ps with duroquinone is controlled by diffusion. However, the absolute values of k_Q are much lower than what is expected from measurements in pure dodecane ($16.2 M^{-1} \text{ ns}^{-1}$ at 294 K),² denoting some geometrical hindrance; as previously found,² the duroquinone molecules are most probably confined in a rather small volume at the micelle surface.

B. Micellar Parameters. Figure 6 shows the variation with T of the average micellar radius, R_{mic} , derived from the PALS spectra together with data from two previous works.^{13,14} Our values agree well with these latter, despite the difference in the SDS concentrations (0.25 M in our case, 0.069 M for the two

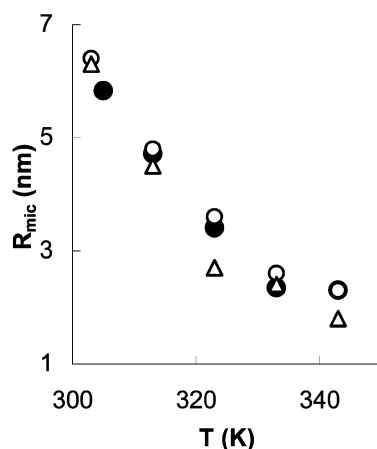


Figure 6. Variation of the average micellar radius, R_{mic} (nm) with temperature, T (K), in a 0.6 M NaCl + SDS aqueous solution: (●) this work (0.25 M SDS), (○) from ref 13 (0.069 M SDS), and (△) from ref 14 (0.069 M SDS). Relative experimental errors: 5%.

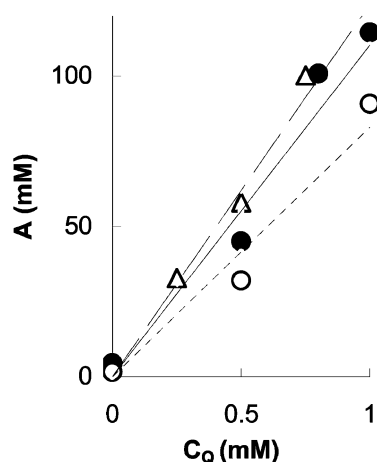


Figure 7. Variation of A_w (mM) (see eq 15) with duroquinone concentration, C_Q (mM) in a (0.6 M NaCl + 0.25 M SDS) aqueous solution at: (△, broken line) 305 K, (●, solid line) 333 K, and (○, dotted line) 343 K. The slope of the lines is N_{ag} .

other works); this confirms that the micellar radius is a little dependent on the nominal SDS concentration^{27–29} and further establishes the quantitative reliability of our method.

In a first step, we tried to deduce N_{ag} directly from the PALS spectra, by examining the normalized integrals at concentration C_Q of quencher, $I_w(C_Q)$, in a time window chosen far enough from the origin to include only the contribution from the unquenched $o\text{-Ps}^{\text{org}}$ component (τ_4^0), so that (see eq 10)²

$$A_w = \ln[I_w(0)/I_w(C_Q)]C_{\text{surf}} = N_{\text{ag}}C_Q \quad (15)$$

Figure 7 shows that this expectation is possibly met at the highest T studied, 333 K and 343 K, for which eq 15 yields $N_{\text{ag}} = (110 \pm 5)$ and (83 ± 3) , respectively, which are consistent with previously published values, around 60.^{13,14} However, much too low values were obtained below 333 K, giving, for example, $N_{\text{ag}} = (124 \pm 15)$ at 305 K (broken line in Figure 7), whereas previous determinations would give values above 220.^{13,14} In all cases, the integral $I_w(C_Q)$ was taken between 13.7 and 16 ns. The lower time threshold should be high enough to allow for the complete disappearance of the $o\text{-Ps}^{\text{aq}}$ component ($\tau_3 < 1.8$ ns) but, as it seems from the results at 305 K, might not be sufficient to allow the complete disappearance of those $o\text{-Ps}^{\text{org}}$ components having a lifetime shorter than τ_4^0 (see eqs 3 and 5).

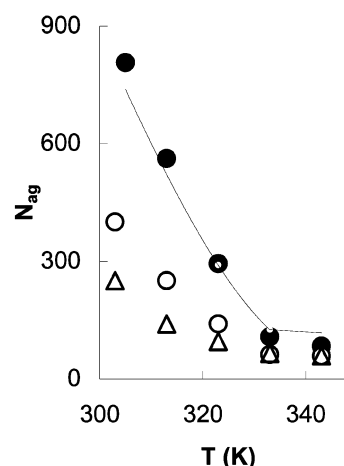


Figure 8. Variation of the aggregation number, N_{ag} , with temperature, T (K), in a 0.6 M NaCl + SDS aqueous solution: (●) this work (0.25 M SDS), (○) from ref 13 (0.069 M SDS), and (△) from ref 14 (0.069 M SDS). The solid line is calculated for prolate ellipsoid micelles of radius R_{mic} taken from Figure 6 (see text). Relative experimental errors: 5%.

No improvement was found when changing the window times in a reasonable range.

Figure 8 shows the decrease in the aggregation number, N_{ag} , derived from fitting the PALS spectra on the basis of eq 9, together with previously published data.^{13,14} Although agreeing on the convergence toward low values characteristic of (nearly) spherical micelles at high T , the three sets of data are rather divergent in the low T range, the present values being highest. The figure also includes N_{ag} values calculated from the measured micellar radii and from the volume of the SDS molecules (solid line in the Figure) according to the following method.

The volume of the SDS molecule can be estimated at each T as²⁴

$$v_{\text{SDS}} = v(\text{CH}_3) + (n_c - 1)v(\text{CH}_2) + v_{\text{head}} \quad (16)$$

In eq 16, n_c is the number of carbons (12 for SDS) and $v(\text{CH}_3)$ and $v(\text{CH}_2)$ are the volumes of the methyl and methylene groups, respectively, varying with T as (units of 10^{-3} nm^3)²⁴

$$v(\text{CH}_3) = 54.6 + 0.124(T - 298) \quad (17)$$

$$v(\text{CH}_2) = 26.9 + 0.0146(T - 298) \quad (18)$$

The volume of the polar head, v_{head} , was calculated from its diameter, $d_{\text{head}} = 0.506 \text{ nm}$.^{1,30}

For prolate ellipsoids, N_{ag} can be calculated from the following expression¹³

$$N_{\text{ag}} = N_{\text{ag}}^0 a/b \quad (19)$$

where a and b are the semimajor and semiminor axes of the ellipsoid, respectively, and N_{ag}^0 is the aggregation number for spherical micelles of radius b . The latter was estimated from the length of the stretched SDS molecule at 298 K, as (units of nm)³¹

$$b = 0.15 + 0.1265n_c + d_{\text{head}} \quad (20)$$

Some slight variation with T was allowed for b , to the extent of the cubic root of the variation of the SDS molecule volume from a given T to another; in this way, N_{ag}^0 is T independent (see eq 22).

TABLE 1: Parameters Calculated for Micellar Prolate Ellipsoids as a Function of Temperature, T (K): SDS Molecular Volume, v_{SDS} , from Eq 16; Semimajor Axis, a , from Eq 21; Semiminor Axis, b , from Eq 20; N_{ag} , from Eq 19

T (K)	v_{SDS} (nm ³)	b (nm)	a (nm)	N_{ag}
305	0.4203	2.178	15.7	741
313	0.4226	2.182	11.1	524
323	0.4254	2.187	6.20	292
333	0.4283	2.192	2.66	125
343	0.4311	2.196	2.51	118

TABLE 2: Lifetimes, τ_4 (ns), and Relative Probabilities at $C_0 = 1$ mM, $P(n_Q)$, of the o -Ps^{org} Components Derived from Fitting Eq 9 to the PALS Spectra as a Function of the Number, n_Q , of Duroquinone Molecules Present in a Micelle, at 305 K (Left Hand) and 343 K (Right Hand)

n_Q	τ_4 (ns)	$P(n_Q)$	τ_4 (ns)	$P(n_Q)$
0	4.00	0.040	4.40	0.717
1	3.77	0.128	2.19	0.238
2	3.56	0.206	1.46	0.040
3	3.37	0.222		
4	3.21	0.179		
5	3.05	0.115		
6	2.92	0.062		
7	2.79	0.028		
8	2.67	0.011		

Next, the semimajor axis value, a , was calculated from the expression for the average (measured) micellar radius for a prolate ellipsoid, at each T , according to¹³

$$R_{\text{mic}} = a(1 - b^2/a^2)^{1/2} / \ln \left[\frac{1 + (1 - b^2/a^2)^{1/2}}{b/a} \right] \quad (21)$$

The aggregation number for a spherical micelle, N_{ag}^0 , was then given by

$$N_{\text{ag}}^0 = v_{\text{SDS}} / (4\pi b^3/3) \quad (22)$$

Table 1 collects the values used for v_{SDS} , a and b at each T , together with the calculated N_{ag} values. From eq 22, it comes that $N_{\text{ag}}^0 = 103$.

It may be seen that the N_{ag} values calculated from eq 19 (solid line in Figure 8) are in good agreement with our experimental values, much better so than with those previously published. As our calculations were made on the assumption that the micelles aggregate in the form of prolate ellipsoids, the present agreement gives also support to this hypothesis. However, other elongated shapes are certainly possible for the micelles, such as spherocylinders,⁵ but no expression of large enough applicability is available for R_{mic} apart from spherical or ellipsoidal geometries.

The parameters derived when eq 9 is fitted to the data allow us to understand why the model-independent method based on the experimental integrals of the PALS spectra (eq 15) fails to yield acceptable values for R_{mic} at low T . Table 2 gives two sets of values of $\tau_4(n_Q)$, the o -Ps^{org} lifetimes in the presence of n_Q molecules of quencher in a micelle (see eq 5), at 305 and 343 K, together with their relative probabilities, $P(n_Q)$, at a duroquinone concentration of 1 mM. At 343 K, the longest o -Ps^{org} lifetime, $\tau_4(0) = 4.40$ ns (see Figure 4) is distinct enough from the second-longest lifetime, $\tau_4(1) = 2.19$ ns, for the former to contribute alone in the time window chosen to derive the experimental integrals $I_w(C_Q)$ and thus for eq 15 to apply. Because of this, the two values of N_{ag} derived from the integrals, (83 ± 3) , and from the fitting with eq 9, (83 ± 3) , are the same. At 305 K, on the contrary, all o -Ps^{org} lifetimes for decreasing

values of n_Q are too close to one another to allow an efficient segregation of the longest-lived component, $\tau_4(0) = 4.00$ ns, in any time window of the PALS spectra. In such a case, eq 15 is not valid, as it applies only to $n_Q = 0$ (see eqs 10 and 15). The physical reason for the applicability of eq 15 at high T and not at low T arises merely from the fact that the micelles have a much smaller volume in the former case: this results in a much higher concentration of the quencher inside the micelle and thus in a much more efficient quenching of o -Ps^{org}, even when $n_Q = 1$ (see eq 5).

Conclusions

The present data confirm the ability of PALS to deliver quantitative information regarding various properties of micelles. (i) The values of the o -Ps^{org} lifetime in the absence of a quencher provide information on the surface tension inside the micelles, which is lower than in the corresponding bulky alkane. As compared to conventional techniques, this is information specific to PALS. (ii) The micellar radii derived from PALS agree well with some of those determined though light-scattering experiments. As stressed in the Introduction, rather discordant values have been published regarding the micellar hydrodynamic radius in a same system (0.07 M SDS + 0.6 M NaCl) by using exactly the same technique (light scattering), the highest difference amounting to almost a factor of 2.^{8,11–14} Although measured in the presence of a higher SDS concentration, the PALS results show excellent agreement with three^{11,13,14} out of five of those previous works. (iii) The aggregation numbers obtained are different from those determined in fluorescence quenching experiments. However, the latter show large discrepancies between themselves in systems, as the one here studied, where N_{ag} can reach rather high values (typically, above 200). In contrast to those previous studies, our results appear coherent with the values of N_{ag} calculated on the assumption of a prolate ellipsoid shape of the micelles. This agreement shows self-consistency and points to the capability of our method to give information on both the aggregation number and the shape of the micelles. (iv) The rather weak quenching rate constant found for duroquinone in the micellar core as compared to bulky dodecane denotes some confinement of the duroquinone molecules at the micelle/water interface, which illustrates the possibility of having information on the location of solutes. It may be expected that similar information would be obtained on other types of solutes inside the micelles, provided they could affect either the lifetime (through quenching) or the intensity (through inhibition) of o -Ps.

The above findings must be taken as mere examples of the potentialities of our method. Other properties of micellar systems have already been shown to be accessible to PALS, such as the speciation of ions, in reverse micelles; the possibility of studying opaque media might also prove useful (e.g., to study templates made out of surfactants in a solid matrix). Extending similar studies as presented here to other micellar systems is therefore quite promising. Technically, PALS appears as an interesting independent technique to develop; as compared to light diffusion or fluorescence quenching apparatuses, it is as cheap and compact and certainly more versatile with applications ranging from gases to liquids and solids; the only drawback might be the recording time per experiment, which amounts to hours.

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