Shape and Position of 4-Aminophthalimide (4-AP) Time-Resolved Emission Spectra (TRES) versus Sodium Dodecyl Sulfate SDS Concentration in Micellar Solutions: The Partitioning of 4-AP in the Micellar Phase and in Water Surrounding the Micelles

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Time-resolved emission spectra (TRES) of 4-aminophthalimide (4-AP) dissolved in water solutions of sodium dodecyl sulfate (SDS) for three surfactant concentrations (0.05, 0.15, and 0.45 M) have been determined. The fraction of 4-AP dissolved in the water phase surrounding the micelles has been shown to increase with decreasing concentration of the surfactant. To obtain TRES of 4-AP present exclusively in micelles, a method of subtraction of the contribution of the emission originating from 4-AP present in the water phase surrounding the micelles from the total emission of the probe dissolved in SDS solution has been proposed. The consequences of failing to take into account the partitioning of 4-AP between the water and micellar phases are illustrated by some exemplary TRES results, taken before and after the subtraction of the emission originating from 4-AP present in the water phase. Together with the time of appearance and presence of isoemissive points in the time-resolved area-normalized emission spectra (TRANES), these results have shown a clear dependence of the rate and character of the 4-AP TRES changes on the SDS concentration. In connection with our earlier results and literature data, it has been concluded that the concentration of the water solubilized in micelles is the main factor determining the rate and character of these changes.

1. Introduction

Micellar systems, formed as a result of the aggregation of surfactant molecules dissolved in water, have been used by many authors as model systems for the investigation of phenomena taking place in complex biological systems.[1] Although micelles have been studied for a few decades, many of their properties have not yet been fully resolved. One of them is a relationship between the micelles' structure (i.e., their shape, size, aggregation number (N), hydration, etc.) and the surfactant concentration (c_S).[2] At a surfactant concentration slightly above the critical micellar concentration (cmc), the micelles have a spherical shape. An increase in the surfactant concentration leads to an increase in their size.[1] Such a situation also takes place in the system studied (i.e., in the sodium dodecyl sulfate micelle (M-SDS)). This micelle is a well-known representative of anion micelles used by many authors as indicated in ref 3. The aggregation number N in M-SDS increases from ∼50 to ∼100 in the concentration range from $c_S \approx 8 \times 10^{-3}$ to 0.5 M.[3,4] This change is accompanied by a change in the micelle radius (R_M) from ∼23 to ∼25 Å and a change in the micelle hydration which has been observed by Bales et al. in M-SDS[5] and when Na^+ has been replaced by Li^+.[6] These authors have shown that the number of water molecules present inside micelles, per one surfactant molecule of M-SDS, decreases with increasing concentration of the surfactant. They have drawn their conclusions from an experimental observation of a dependence of the polarity index H on the aggregation number N. For micelles, this index introduced by Mukerjee et al.[7] is defined as the ratio of the O−H dipole concentration inside the micelles to the concentration in bulk water. On the basis of this ratio, Bales et al. have estimated that the micellar hydration has changed from ∼10 to ∼6 water molecules per single SDS molecule, with N increasing from 50 to 130.[5] Their results imply that the mean polarity of the micelles depends on their size and therefore on the surfactant concentration. However, the mean polarity and especially the polarity of the surface layer of the micelles depend mainly on the number of water molecules solubilized inside the micelles.

The dependence of the mean polarity of the micelles on the surfactant concentration must affect the magnitude and rate of processes related to intermolecular interactions occurring in micelles of different sizes. Such a process is solvation, which has been studied by both steady-state and time-resolved methods.[8] In optical spectroscopy methods used in solvation investigation, one needs a probe whose excitation changes the energy of its interactions with the surrounding molecules.[9] One such probe is 4-aminophthalimide (4-AP), whose excitation leads to an increase in the dipole moment from ∼3 to ∼6.5 D because of an intramolecular charge transfer from the amino group to the carbonyl groups of the probe.[10] As a result of changes in the energy of nonspecific interactions of 4-AP and the solvent, the absorption and emission spectra of the probe are bathochromically shifted to a degree depending on the polarity of the solvent.[11] 4-AP can also interact specifically with solvent molecules through hydrogen bond formation. It has been shown by steady-state and time-resolved methods that 4-AP can act both as an acceptor or a donor in hydrogen bond formation.[10−13] This process may involve the electrons of the lone electron pairs of the oxygen atoms of two carbonyl groups

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in 4-AP, the hydrogen atoms of the amino and imino group, and the lone electron pair of the nitrogen atoms of these groups. As shown by Suppan et al.,[11] Ware et al.,[12] Aramendia et al.,[13] and Maciejewski et al.,[10] the energy of the hydrogen bonds formed with the involvement of electrons of the lone electron pairs of the oxygen atoms of 4-AP carbonyl groups has a significant effect on the position of the steady-state fluorescence spectrum (FS). In protic solvents, the bathochromic shift of these spectra is much greater than in the aprotic ones. The greatest bathochromic shift of 4-AP FS is observed in water. In this solvent, the long-wavelength band of the 4-AP absorption spectrum, corresponding to the excitation of 4-AP from the S_0 state to the locally excited state, S_1-LE, has a maximum at wavelength $\lambda_{max}^{abs} = 369$ nm. Meanwhile, in the same solvent, the maximum of the FS from the excited singlet intramolecular charge-transfer state, S_1-ICT, to the ground state, S_0, is localized at wavelength $\lambda_{max}^{em} = 564$ nm. The corresponding values for 4-AP dissolved in acetonitrile (ACN) i.e., in an aprotic solvent of the polarity function, $f(D, n)$,[14] similar to that of water, are $\lambda_{max}^{abs} = 359$ nm and $\lambda_{max}^{em} = 464$ nm, respectively. Such a pronounced dependence of λ_{max}^{em} on the properties of the solvent was the main argument for the use of 4-AP as a probe in solvation studies.

4-AP occurs in micelles in two emissive species (4-AP in the S_1-ICT state and S_1-exciplex (S_1-exc)), the latter appearing as a result of the formation of one or several hydrogen bonds between 4-AP in the S_1-ICT state and the water molecules.[10] The probe in the S_1-ICT state tends to form an exciplex, which results in changes in the concentration of both species in the system. This leads to the emergence of an isoemissive point in the time-resolved area-normalized emission spectra (TRANES),[15] from which it is possible to estimate the time of the process of S_1-exc creation.[10]

According to Bales et al.,[5] the concentration of water in the micelles can be modified by changing the surfactant concentration in the solution. However, this decrease in the water concentration may cause an increase in the time needed by 4-AP and water molecules to approach each other and assume the positions needed to minimize the energy of the nonspecific interactions or/and create a hydrogen bond. To verify these observations, we have recorded FS and we have determined TRES of 4-AP dissolved in a water solution of SDS for three surfactant concentrations. The results presented in section 3.3 are in agreement with Bales et al.'s observation.[5] It has also been shown that at a low concentration of the surfactant one must take into account the fact that the probe is localized both in the micellar phase and the water phase. The procedure for the determination of the partition ratio of the probe molecules into the micellar phase and the whole solution is presented in section 3.1. Section 3.2 describes the method of determination of the contribution of the emission originating from 4-AP present in the water phase surrounding the micelles (SW) to the total emission of the probe dissolved in SDS solution (M + SW). The results are discussed at the end of the article.

2. Experimental Section

2.1. Materials. 4-AP (Aldrich) was purified by recrystallization from methanol; SDS (Sigma, Merck) was used as received. Absorption spectra (AS) and FS of 4-AP crystallized one and two times were the same. The solutions were not deoxygenated and did not contain impurities emitting in the spectral range in which the emission of 4-AP was studied. Three SDS concentrations were used (0.05, 0.15, and 0.45 M), whereas the 4-AP concentration was $\sim 10^{-4}$ M. Such 4-AP and SDS concentrations ensured that on average 1 micelle in 10 was occupied and that the probability of occupation of the same micelle by more than 1 4-AP molecule was negligent.

2.2. Experimental Setup. The measuring systems applied were the same as described in ref 10. The steady-state AS were measured on a Jasco V-550 spectrophotometer. The time-resolved fluorescence measurements were made using a time-correlated single-photon counting (TCSPC) system. The full width at half-maximum (fwhm) of the instrument response function (IRF) was of about 35 ps. The steady-state FS used for TRES generation were measured with almost the same experimental system as used for fluorescence decay measurements. In the case of steady-state measurements, instead of the time to the amplitude converter (TAC) and multichannel analyzer (MCA) a single-photon counting module was used. The wavelength of the exciting beam (λ_{exc}) was set at 400 nm, and the fluorescence decays were measured in the spectral range covering the largest possible fragment of the steady-state emission spectrum. The spectral resolution of the emission monochromator was equal to about 9 nm, and the spectral width of the excitation beam was less than 1 nm. The exciting beam of the vertical polarization was applied to excite the fluorescence collected at the magic angle. The decays were analyzed by homemade software based on the Simplex optimization algorithm. A detailed description of the experimental system is given in ref 16, and its possibilities are presented in ref 17.

3. Results

3.1. Partitioning of 4-AP between the Micellar and Water Phases. For each surfactant concentration, it was necessary to establish the partitioning of the 4-AP molecules into those solubilized inside micelles (M) and those dissolved in the water phase surrounding the micelles. Furthermore, it was necessary to determine if the emission coming from the probe molecules dissolved in the water phase could be neglected relative to that from the whole solution. To do this, a simple method was developed for the determination of the ratio (S) of the number of probe molecules solubilized in micelles to the total number of probe molecules in the micellar solution.

The problem of S determination was taken up inter alia by Carr et al.[18] and by Dale et al.[19] Carr et al. presented a method of S determination based on measurements of the steady-state AS of the probe molecule dissolved in water and in the micellar solution. This method, employing the single-value decomposition (SVD) procedure, assumes the homogeneous structure of the micelles and the independence of the micelles' structure, and thus also that of the absorption spectra of the probe molecules solubilized in the micelles (AS_M), with respect to the surfactant concentration. It requires measurements of AS of the probe molecule for several surfactant concentrations. The method proposed here does not need such assumptions and seems to be easier to use, permitting S value determination in the ground state of the probe that is similar to the method proposed by Carr et al. In the emission measurements for the probe in the excited state, the necessity of taking into account the effects investigated by Dale et al.[19] should be considered. These authors studied the transfer of naphthalene in an SDS system between the water and micellar phases after an excitation. They have shown that naphthalene emission decay is biexponential and that the decay times and the contribution of each component depend on the rate coefficient for the entry of excited-state naphthalene from the water phase into the micelles (k_{in}) and the rate coefficient for the departure of excited-state naphthalene from the micelles to the water phase (k_{out}). The

values of k_{in} ($\sim 10^9$ $M^{-1}s^{-1}$) and k_{out} ($\sim 10^6$ s^{-1}) obtained by them are in agreement with those determined by fluorescence quenching methods by several other groups.[20] Assuming that for 4-AP the values of k_{in} and k_{out} are similar and taking into account the micelle concentrations used by us ($\sim 10^{-3}$ M), it is clear that the entry rate multiplied by the micelle concentration (10^{-3} M), $k_{in} \times 10^{-3}$ M, and the departure rate, k_{out}, are too small ($\sim 10^6$ s^{-1}) to influence 4-AP deactivation, whose lifetime (τ) is equal to about 1 ns in bulk water and ~3.2 ns in SDS solution.[10] Therefore, it was assumed that 4-AP both in the ground and excited states remains at the stationary equilibrium between the micelle and water phases. Therefore, it was possible to use *S* values determined for the probe in the ground state in the emission measurements.

Moderately polar 4-AP molecules are relatively well dissolved in water. The maximum concentration of 4-AP in bulk water (c_W^{max}) is equal to 4.2×10^{-4} M. The addition of surfactant molecules at concentrations below cmc to water does not increase the solubility of 4-AP relative to that in bulk water. When the surfactant concentration exceeds cmc, 4-AP molecules are mainly solubilized in micelles, which increases the 4-AP solubility. The procedure of *S* determination required measurements of steady-state AS of the saturated 4-AP micellar solutions studied (for surfactant concentration exceeding the cmc) and AS of the saturated 4-AP solution in bulk water. In respect to the fact that the micelles are surrounded not by bulk water but by a water solution of surfactant monomers (dimers, etc.) not aggregated into micelles, the AS of the saturated 4-AP solution for SDS concentrations about 2 and 5 times smaller than the cmc was measured. The measurements have shown that the AS of 4-AP dissolved in bulk water is, within experimental error, the same (the same shape and molar absorption coefficient) as the absorption spectra obtained for the surfactant concentration below the cmc. Therefore, the saturation concentration of 4-AP in the water phase surrounding the micelles (c_{SW}^{max}) was assumed to be equal to that obtained in bulk water ($c_{SW}^{max} \equiv c_W^{max}$). However, one should keep in mind that this assumption can lead to some over/underestimations of *S*.

The molar absorption coefficients (for the maximum of the long-wavelength absorption band) of 4-AP dissolved in micellar solution (ϵ_{M+SW}) and in water solution (ϵ_W) were determined. With the obtained ϵ_{M+SW} and ϵ_W values, the saturation concentration of 4-AP in SDS solution, for a surfactant concentration above the cmc, c_{M+SW}^{max}, and in bulk water, c_W^{max}, could be determined. The *S* value was calculated from the simple relation

$$S = \frac{c_{M+SW}^{max} - (\varsigma \times c_W^{max})}{c_{M+SW}^{max}} \quad (1)$$

where ς is the volume fraction of the micellar solution occupied by bulk water, defined by eq 2

$$\varsigma = \frac{1\ \mathrm{L} - (V_M \times N_M)}{1\ \mathrm{L}} \quad (2)$$

The number of micelles, N_M, in 1 L of the solution was obtained from the relation $N_M = c_{Micelles} \times N_A$ (N_A − Avogadro number, $c_{Micelles}$ − concentration of micelles), whereas the average volume of a single micelle, V_M, was determined from the mean radius of a micelle, R_M. The quantity $V_M \times N_M$ is a measure of the total volume occupied by the micelles in 1 L of solution. The concentration of micelles was determined by using the well-known relation $c_{Micelles} = (c_S - \mathrm{cmc}) \times N^{-1}$. Table 1 presents literature values of *N* and R_M[4] and the values of ϵ_M, *S*, and ς obtained by us at three different surfactant concentrations.

TABLE 1: Mean Micellar Radius (R_M), Aggregation Number (*N*), Fraction of the Solution Occupied Exclusively by the Water Phase (ς), Molar Absorption Coefficient of the Maximum of the Long-Wavelength Absorption Band of 4-AP Dissolved Only in Micelles (ϵ_M), and Partition of 4-AP Molecules Solubilized in Micelles (*S*) and Dissolved in the Water Phase ($1 - S$) for Three SDS Concentrations (c_S)

					partition[f]	
c_S[a] [M]	R_M[b] [Å]	N[c]	ς[d]	ϵ_M[e] [$M^{-1} \times cm^{-1}$]	micelle S [1]	water $1 - S$ [1]
0.05	23	67	0.98	3740	0.63	0.37
0.15	24	78	0.93	3910	0.81	0.19
0.45	25	101	0.83	3970	0.91	0.09

[a] For SDS cmc = 0.008 M. [b] Determined from the data in ref 5. [c] Mean value from ref 4. [d] Determined from eq 2. [e] Determined from eq 3. [f] Determined from eqs 1 and 2. The molar absorption coefficient of the maximum of the long-wavelength absorption band of 4-AP in water is $\epsilon_w = 3710$.

The ς values given in Table 1 show that for high enough surfactant concentrations the volume occupied by all micelles is significant. The values of ϵ_M are the molar absorption coefficients of 4-AP solubilized in micelles without the contribution originating from 4-AP dissolved in the water phase. These values were obtained from eq 3 and using the law of absorption additivity and eq 1, which takes into account the fact that the experimental signal includes two contributions: one from the probe molecules solubilized in micelles and one from those dissolved in the water phase.

$$\epsilon_M = \frac{\epsilon_{M+SW} - (1 - S) \times \epsilon_W}{S} \quad (3)$$

The *S* and ϵ_M values given in Table 1 were determined assuming that irrespective of the surfactant concentration used (above cmc) *S* does not depend on the probe concentration.

3.2. Ratio of the Emission of 4-AP Dissolved in the Water Phase to the Total Emission Observed. In the emission measurements, one has to take into account the fact that part of the 4-AP molecules are dissolved in the water phase and part are solubilized in the micelles. The total fluorescence intensity of 4-AP for the whole SDS solution (I_{M+SW}^{em}) and that for 4-AP dissolved in the water phase (I_{SW}^{em}) in the same micellar solution are given by

$$I_{M+SW}^{em} = \phi_{M+SW} \times I_{Abs} \quad (4)$$

$$I_{SW}^{em} = \phi_W \times \frac{A_{SW}}{A_{SW} + A_M} \times I_{Abs} = \phi_W \times \frac{A_{SW}}{A_{M+SW}} \times I_{Abs} \quad (5)$$

where ϕ_{M+SW} is the fluorescence quantum yield of 4-AP dissolved in the micellar solution, ϕ_W is the 4-AP fluorescence quantum yield in water, A_{M+SW} is the total absorbance of the micellar solution, A_{SW} is the absorbance of 4-AP dissolved in water phase, A_M is the absorbance of 4-AP solubilized exclusively in the micelles, and I_{Abs} is the intensity of the light absorbed in the whole solution. By knowing the values of the molar absorption coefficient and using eq 1, we can present eq 5 as

$$I_{SW}^{em} = \phi_W \times (1 - S) \times \frac{\epsilon_{SW}}{\epsilon_{M+SW}} \times I_{Abs} \quad (6)$$

Dividing eq 6 by eq 4 on each side, we get the ratio (*f*) of the emission intensity originating from 4-AP present in the water

TABLE 2: Values of the Parameters Used in the Determination of the Ratio *f* of the Emission Intensity of 4-AP Present in the Water Phase to the Total Emission Intensity

c_S [M]	ϵ_{M+SW}[a] [M^{-1} cm^{-1}]	ϵ_W[b] [M^{-1} cm^{-1}]	ϕ_{M+SW}[b]	ϕ_W[b]	f[c]
0.05	3730_{max} 2790_{exc}	2560	0.060	0.022	0.124
0.15	3870_{max} 2900_{exc}		0.065		0.057
0.45	3950_{max} 3030_{exc}		0.100		0.017

[a] Given values correspond to excitation wavelengths λ_{exc}= 400 nm (exc) and to λ_{max}^{abs}(max). [b] Determined for the excitation wavelength. [c] Calculated from eq 7.

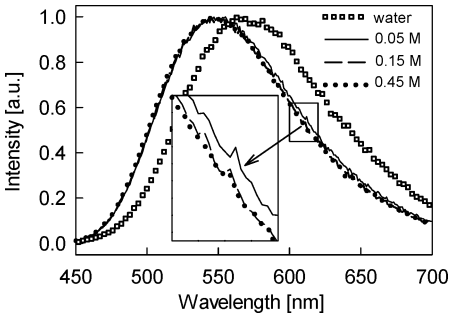

Figure 1. Steady-state FS_{M+SW} of 4-AP dissolved in aqueous solutions of SDS ($c_S \approx 0.05$, 0.15, and 0.45 M). For comparison, FS_W of 4-AP in water is shown. Spectra were normalized to the same intensity at the maximum, $\lambda_{exc} = 400$ nm.

phase to the total emission intensity originating from the whole solution:

$$f = \frac{I_{SW}^{em}}{I_{M+SW}^{em}} = \frac{\phi_W}{\phi_{M+SW}} \times (1 - S) \times \frac{\epsilon_W}{\epsilon_{M+SW}} \qquad (7)$$

In the above relation, both the fluorescence quantum yields and the molar absorption coefficients have to be determined for the same excitation wavelength. On the basis of the values of the fluorescence quantum yield and molar absorption coefficient determined in ref 10 and in this work, it was possible to determine *f* values for the three SDS concentrations used. The results are presented in Table 2.

As expected from the values of *S* (Table 1), the decrease in SDS concentration causes an increase in the contribution of the emission of 4-AP dissolved in the water phase in the total emission observed. It seems that a contribution of ~1.6% of the emission originating from 4-AP in the water phase is negligible for the SDS concentration of 0.45 M. However, one cannot omit the contribution of this emission for the smallest SDS concentration used in this work.

3.3. Steady-State Absorption, Emission, and Time-Resolved Emission Spectra. The experimentally measured AS for the SDS solution (AS_{M+SW}) and the AS_M of 4-AP solubilized in micelles were almost identical, which is a consequence of a profound similarity between AS_W and AS_{M+SW}. However, a difference was observed between the FS measured for the whole SDS solution (FS_{M+SW}) and the FS determined exclusively for 4-AP solubilized inside micelles (FS_M). Figure 1 presents the experimentally determined FS_{M+SW} for the three surfactant concentrations used in this work. The long-wavelength part of FS_{M+SW}, for the concentration of 0.05 M SDS, is clearly bathochromically shifted relative to the FS_{M+SW} for the other two surfactant concentrations. Taking into account the greatest

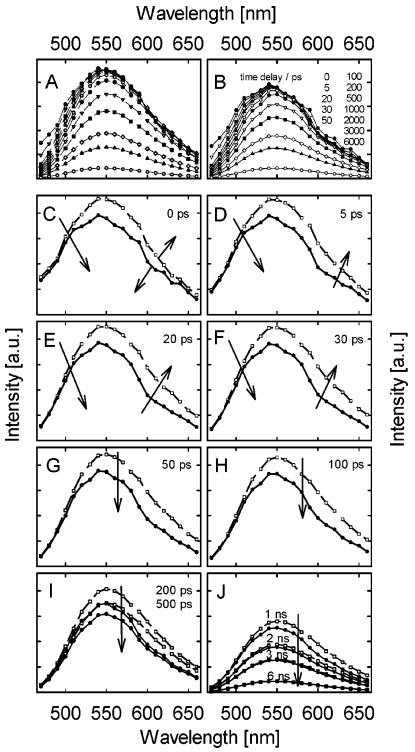

Figure 2. TRES of 4-AP in M-SDS ($c_S \approx 0.05$ M) before, $TRES_{M+SW}$ (A), and after subtraction, $TRES_M$ (B), of the emission originating from 4-AP in the water phase for different time delays. Panels C−J present a comparison of $TRES_{M+SW}$ (dashed lines, empty squares) and $TRES_M$ (solid lines, filled circles) for different time delays. The arrows indicate the directions of change in the spectra. For the sake of clarity, the experimental points for the same time delay are connected by lines.

bathochromic shift of FS_W of 4-AP in water and Bales et al.[5] observations, this bathochromic shift could be explained as being due to an increase in the water concentration inside the micelles in parallel to a decrease in the SDS concentration. The subtraction of the emission spectrum FS_{SW} originating from the fraction of the molecules dissolved in the water phase from the FS_{M+SW} gave the emission spectrum FS_M of 4-AP solubilized exclusively in micelles. The FS_M's were identical for three used surfactant concentrations and were the same (within experimental error) as the FS_{M+SW} for $c_S \approx 0.45$ M. The maxima in these spectra were at $\lambda_{max}^{em} = 545$ nm. The fwhm (full width at half-maximum) of FS_{M+SW} was equal to 3910, 3860, and 3850 cm^{-1} for $c_S \approx 0.05$, 0.15, and 0.45 M, respectively, and to about 3840 cm^{-1} for the subsequent FS_M irrespective of the surfactant concentration. In the determination of FS_M, the *f* values given in Table 2 were used.

Therefore, the differences in the shape of the FS_{M+SW} of 4-AP for the three surfactant concentrations used were not caused by the differences in hydration of the micelles for these surfactant concentrations, but they were a result of a different contribution of the emission originating from 4-AP dissolved in the water phase. Similar to the situation for AS_M, no influence of the surfactant concentration on the shape and position of FS_M was observed. Such an influence was, however, observed in the 4-AP TRES. The TRES were obtained using the method proposed by Fleming and Maroncelli.[21] For initial time delays, $TRES_{M+SW}$ and $TRES_M$ were different for each SDS concentration used. ($TRES_M$ were obtained after the subtraction of the emission of 4-AP dissolved in the water phase taking into account the *f* values given in Table 2, using $TRES_{SW}$ of 4-AP dissolved in bulk water, $TRES_M = TRES_{M+SW} - TRES_{SW}$.) Figure 2 presents a comparison of the $TRES_{M+SW}$ of 4-AP dissolved in

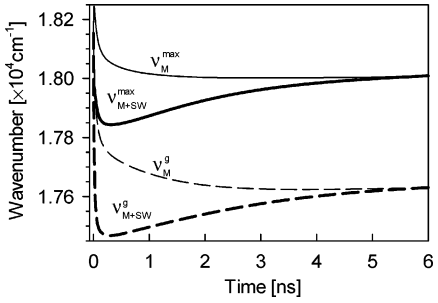

Figure 3. Time dependencies of the maximum frequency ν_x^{max} (solid lines) and gravity frequency ν_x^g (dashed lines) before (ν_{M+SW}^{max}, ν_{M+SW}^g) and after (ν_M^{max}, ν_M^g) subtraction of the emission originating from 4-AP dissolved in the water phase for the lowest SDS concentration ($c_S \approx$ 0.05 M) used.

SDS solutions and the $TRES_M$ of 4-AP solubilized only in micelles for the lowest concentration of SDS used in this work. Similar to the situation for the steady-state emission spectra, the differences were especially observed in the long-wavelength spectral range, where the emission originating from 4-AP dissolved in the water phase is the greatest. After about 3 ns, the $TRES_M$ and $TRES_{M+SW}$ are almost identical, which is a result of the lifetime of 4-AP in water of about 1 ns. The arrows on the C−J panels of Figure 2 indicate the directions of change in the spectrum at selected time delays. In the long-wavelength range, the intensity of $TRES_M$ decreases up to about 5 ps after excitation, and then it increases similarly to that observed in $TRES_{M+SW}$. In both cases in the short-wavelength range, the intensity decreases for each time delay. For the two remaining surfactant concentrations (0.15 and 0.45 M), the differences between $TRES_{M+SW}$ and $TRES_M$ are less significant, which is in agreement with the steady-state results.

To make an additional comparison of $TRES_{M+SW}$ and $TRES_M$, after the conversion of TRES to wavenumbers requiring multiplication by λ^2, the spectra were approximated by log-normal functions.[22] Figure 3 presents time dependencies of the maximum frequency (ν_x^{max}) and gravity frequency (ν_x^g) of the log-normal functions fitted to subsequent $TRES_x$ of 4-AP in 0.05 M SDS solution before ($x \equiv$ M+SW) and after ($x \equiv$ M) the subtraction of the emission originating from 4-AP dissolved in the water phase.

The values of ν_{M+SW}^{max} and ν_{M+SW}^g obtained for the lowest SDS (0.05 M) concentration change in a way that is difficult to explain. Initially they decrease, in agreement with the results presented in ref 10; however, after ~250 ps, they start to increase. Solvation as well as the establishment of a new equilibrium between two emissive 4-AP species cannot be responsible for such time dependencies of ν_{M+SW}^{max} and ν_{M+SW}^g.[10] The time dependencies of ν_M^{max} and ν_M^g, corrected for the emission of 4-AP present in water phase, are completely different. The values of ν_M^{max} and ν_M^g monotonically decrease in time. In view of these results, the time dependencies of ν_{M+SW}^{max} and ν_{M+SW}^g, which are difficult to explain, are a result of not taking into account the emission originating from 4-AP dissolved in the water phase. After a sufficiently long time, the values ν_{M+SW}^x and ν_M^x are similar both for the maximum frequency ($x \equiv$ max) and the gravity frequency ($x \equiv$ g).

The subtraction of the emission of 4-AP dissolved in the water phase for the other two SDS concentrations (0.15 and 0.45 M) did not produce such spectacular results. For 4-AP dissolved in the most concentrated solution, the correction practically did not change the shape and the position of TRES for subsequent time delays. This could be expected by taking into account small

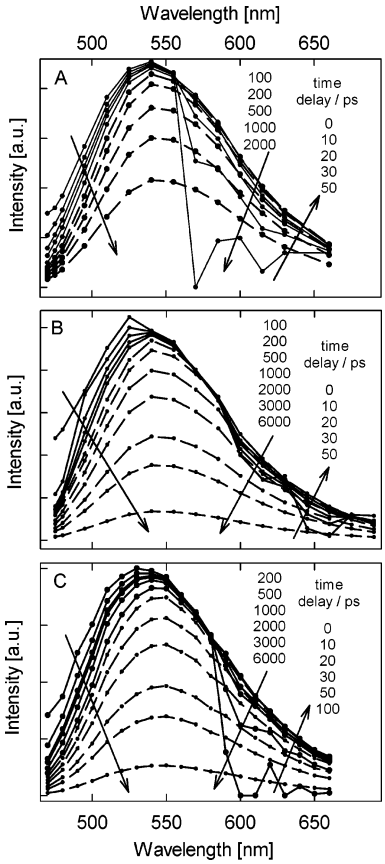

Figure 4. $TRES_M$ of 4-AP obtained after subtraction of the emission originating from 4-AP dissolved in the water phase surrounding the micelles: (A) 0.15 M SDS (2.44 ps/channel), (B) 0.15 M SDS (12.2 ps/channel), (C) 0.45 M SDS (6.1 ps/channel). Points correspond to experimental results. For the sake of clarity, the experimental points for the same time delays are connected by lines.

f values given in Table 2. For the 0.15 M SDS concentration, although about 19% of the probe molecules were dissolved in the water phase and the emission of 4-AP dissolved in the water phase was about 5% of the total observed emission, the corrected $TRES_M$ were very similar to the uncorrected $TRES_{M+SW}$. Figure 4 presents the time delay values at which the initial increase in the intensity in the long-wavelength range of the $TRES_M$ followed by a decrease in the signal over the whole spectral range is observed. The experimental points in Figure 4, for short time delays at which an increase in the intensity in long-wavelength range is observed, are connected by a solid line. For longer time delays, at which a decrease in the intensity over the whole spectral range is observed, the experimental points are connected by a dashed line.

Although there are no significant differences between $TRES_{M+SW}$ and $TRES_M$, the times of individual processes responsible for the shape and position changes in the TRES of 4-AP in 0.15 M SDS solution were, after the application of the correction, somewhat different from those given in ref 10 (see below). Further analysis and discussion will refer exclusively to the results obtained after the subtraction of the emission of 4-AP dissolved in the water phase.

A comparison of the $TRES_M$ presented in Figures 2B and 4 indicates that the $TRES_M$ of 4-AP in M-SDS depend on the surfactant concentration, although FS_M for these concentrations are very similar. Differences are clearly visible when comparing the $TRES_M$ obtained for the lowest and highest SDS concentrations used in this work (0.05 and 0.45 M). They are best pronounced in the long-wavelength part of the TRES for the

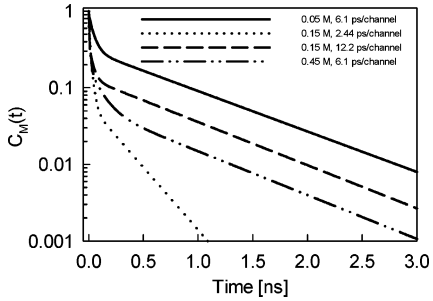

Figure 5. $C_M(t)$ for 4-AP for the three surfactant concentrations used (0.05 M, 6.1 ps/channel; 0.15 M, 2.44 ps/channel; 0.15 M, 12.2 ps/channel; and 0.45 M, 6.1 ps/channel) obtained using the gravity frequency ν^g_M.

initial time-delay values. The shape of the long-wavelength part of $TRES_M$ of 4-AP in 0.05 M SDS solution does not change in time as significantly as for the remaining surfactant concentrations. For $c_S \approx 0.15$ M on the long-wavelength side of the $TRES_M$, a strong increase in the fluorescence is observed (Figure 4A). Because of the time in which these changes take place, this region is less visible in the $TRES_M$ for the same surfactant concentration but is obtained at a lower time resolution (Figure 4B). The results for the lowest and highest SDS concentrations used were obtained for the same time resolution, which facilitates their comparison. The increase in the intensity in the long-wavelength range of TRES is a result of the process of a new concentration equilibrium establishment between 4-AP in the S_1-ICT state and in S_1-exc. A comparison of the $TRES_M$ shape changes for the three surfactant concentrations used in this work indicates that the process of S_1-exc formation is slowest for the highest surfactant concentration and fastest for the lowest surfactant concentration.

Similar to the situation for the lowest SDS concentration, the $TRES_M$ obtained for the two higher surfactant concentrations were approximated by log-normal functions. The correlation function $C_M(t) = (\nu^g_M(t) - \nu^g_M(\infty)) \times (\nu^g_M(0) - \nu^g_M(\infty))^{-1}$ obtained for ν^g_M values for the three SDS concentration used was determined (Figure 5).[23] For the smallest surfactant concentration, the time dependence of ν^g_M is given in Figure 3.

Correlation function $C_M(t)$ was approximated by a multiexponential decay function. Its decay time (τ_{Si}) and amplitude (b_i) values are given in Table 3. The same Table presents the mean relaxation time of 4-AP solvation, $\langle\tau\rangle = \sum_i \tau_{Si} \times b_i$. Also, the absolute shifts of $\Delta\nu^g_M$ ($\Delta\nu^g_M = \nu^g_M(\infty) - \nu^g_M(0)$) are given. As follows from the data given in Table 3 and $C_M(t)$ presented in Figure 5, the character of $TRES_M$ changes of 4-AP in 0.05 M SDS solution is significantly different from that of the other surfactant concentration. First, $\Delta\nu^g_M$ for $c_S \approx 0.05$ M is definitely the smallest. It is the highest in the most concentrated SDS solution, whereas in 0.15 M SDS solution it takes different values depending on the time per channel used. For a time resolution of 2.44 ps/channel, the value of $\Delta\nu^g_M$ is similar to that obtained in 0.45 M SDS solution, and for the lower time resolution, it is clearly smaller, although still nearly twice as high as for 0.05 M SDS.

The increase in the surfactant concentration leads to an increase in the difference between $\nu^g_M(0)$ and $\nu^g_M(\infty)$. However, it does not mean that the environment of the excited 4-AP in micelles formed in the solution of the highest surfactant concentration is the most polar! If this had been the case, then 4-AP FS_M in this solution should have been the most bathochromically shifted among the three measured FS_M, whereas no differences in the position of these spectra are observed. The increase in $\Delta\nu^g_M$ is then a result of a hypsochromic shift of the $TRES_M$ at $t = 0$ ps (see the value of $\nu^g_M(0)$ given in Table 3) occurring together with the SDS concentration increase, relative to a similar position of the $TRES_M$ at $t \rightarrow \infty$ ps for all surfactant concentrations used (see the value of $\nu^g_M(\infty)$ given in Table 3). Thus, the highest surfactant concentration leads to the lowest mean polarity of the environment of the probe in the micelle at the moment of excitation (and before it). The values of $\nu^g_M(\infty)$ given in Table 3 are very similar to $\nu^g_M = 17\,650$ cm^{-1} obtained for FS_M, and they are 600 cm^{-1} higher than $\nu^g_W = 17\,020$ cm^{-1} obtained for FS_W. Very similar values of ν^g_M obtained for the $TRES_M$ at $t \rightarrow \infty$ and for the FS_M show that the solvation processes are much faster than the mean fluorescence lifetime of the probe used. A comparison of ν^g_M values obtained for the $TRES_M$ at $t \rightarrow \infty$ and for the FS_W leads to the conclusion that the environment of the excited probe in the micellar phase is less polar than in water. The polarity of M-SDS is connected to the degree of hydration of these micelles, so the $\Delta\nu^g_M$ values obtained are an independent confirmation of the results reported by Bales et al.[5] of the dependence of the micelles' degree of hydration on the surfactant concentration. One should also regard the influence of the time per channel value used (at the same full width at half-maximum of IRF) on $\Delta\nu^g_M$ values. The application of the highest time resolution allows a more precise determination of the shape and position of $TRES_M$ at $t = 0$ ps. However, as already mentioned, the position of the $TRES_M$ at $t \rightarrow \infty$ is the same, irrespective of the surfactant concentration and time resolution applied. Finally, the time per channel as well as the surfactant concentration used determine the value of $\Delta\nu^g_M$. Taking this into account, it can be assumed that the real value of the absolute 4-AP TRES spectral shift is clearly higher in 0.45 M solution than in 0.15 M, whereas in 0.15 M solution it is clearly higher than in 0.05 M solution.

An analysis of $\langle\tau\rangle$ values given in Table 3 could suggest that the increase in SDS concentration also leads to a reduction in the mean relaxation time of 4-AP solvation, parallel to a simultaneous increase in $\Delta\nu^g_M$. Such an assumption is not justifiable. As shown in Figures 2 and 4, the shape of 4-AP $TRES_M$ in 0.15 and 0.45 M SDS solution undergoes abrupt initial changes in the long-wavelength region, whereas in 0.05 M SDS solution such changes are not visible. As a result, in

TABLE 3: Values of the Parameters (τ_{Si}, b_i) of the Multiexponential Function Fitted to $C_M(t)$ and $\Delta\nu^g_M$, $\nu^g_M(\infty)$, and $\nu^g_M(0)$ Values for 4-AP at SDS Concentrations of 0.05, 0.15, and 0.45 M

c_S [M]	τ_{S1} [ps]	b_1	τ_{S2} [ps]	b_2	τ_{S3} [ps]	b_3	$\langle\tau\rangle$ [ps]	$\Delta\nu^g_M$[cm^{-1}]	$\nu^g_M(0)$ [cm^{-1}]	$\nu^g_M(\infty)$ [cm^{-1}]
0.05 (6.1 ps/ch)	2	0.09	45	0.60	823	0.31	282	570	18 190	17 620
0.15 (2.44 ps/ch)	3	0.51	24	0.43	266	0.06	28	1640	19 250	17 610
0.15 (12.2 ps/ch)	18	0.71	136	0.11	903	0.18	190	940	18 560	17 620
0.45 (6.1 ps/ch)	10	0.81	103	0.13	759	0.06	67	1740	19 350	17 610

more concentrated solutions the greatest and the quickest ν_M^g changes occur in the initial few dozen picoseconds, which is evidenced by the amplitudes of the fastest $C_M(t)$ components given in Table 3 and by the $C_M(t)$ time dependencies presented in Figure 5. The contributions of these fast components increase with decreasing contribution of the long-time components, thus the value of $\langle\tau\rangle$ is the lowest for the highest SDS concentration (0.45 M) and the highest for the lowest SDS concentration (0.05 M). The great effect of the initial abrupt changes in the $TRES_M$ shape on the $\langle\tau\rangle$ values and generally on the $C_M(t)$ is evidenced by a comparison of the $C_M(t)$ and $\langle\tau\rangle$ values for $c_S \approx 0.15$ M obtained for two different time per channel values: 2.44 and 12.2 ps/channel. The initial $TRES_M$ changes for 2.44 ps/channel (Figure 4A) lead to the fastest $C_M(t)$ decay from among the correlation functions determined for three surfactant concentrations. Such changes do not appear in the $TRES_M$ of 4-AP for the same SDS concentration but are measured at a lower time resolution. As a result, the initial $C_M(t)$ changes are slower, leading to higher $\langle\tau\rangle$ values. For 4-AP dissolved in micelles, the quantity $\langle\tau\rangle$ can serve only as an indicator of the degree of the TRES shape changes at the initial time.

Similarly to the situation for $\langle\tau\rangle$ values, time τ_{Si} and amplitude b_i values of the multiexponential decay function, fitted to $C_M(t)$ (Table 3), give information about the dynamics of the $TRES_M$ shape changes. As we have shown in ref 10, the long-time components of these functions (see τ_{S3} in Table 3) can be used to estimate the time of nonspecific solvation. However, such an analysis must be carried out by taking into account the TRANES shape and position changes.

Isoemissive points appeared both in the experimental $TRANES_M$ (obtained by $TRES_M$ normalization) and in those determined from the log-normal functions fitted to the experimental $TRES_M$ obtained for $c_S \approx 0.15$ and 0.45 M, similar to the situation reported in ref 10. However, in the $TRANES_M$ obtained for $c_S \approx 0.05$ M the isoemissive point did not appear. The $TRANES_M$ determined for the three surfactant concentrations used are presented in Figure 6.

The time of appearance and presence of isoemissive points in individual $TRANES_M$ was determined on the basis of the time dependence of the normalized emission intensity for the wavenumber at which the isoemissive point appeared.[24] In the spectra shown in Figure 6B (0.15 M SDS, 2.44 ps/channel), a distinct isoemissive point appears in the time period from $t \approx$ 10 to 50 ps (i.e., at the same time as it occurred in the $TRANES_{M+SW}$ not corrected for the emission of 4-AP dissolved in the water phase[10]). Because of the low time resolution used (12.2 ps/channel), a reliable determination of the isoemissive point time appearance in $TRANES_M$ shown in Figure 6C was impossible. However, it was possible for the $TRANES_M$ obtained for $c_S \approx 0.45$ M SDS, in which the isoemissive point appeared in the time period from $t \approx 50$ to 100 ps.[25] The times of appearance and presence of the isoemissive points in the $TRANES_M$ are much shorter than the longest components (see value of τ_{S3}) of $C_M(t)$ given in Table 3, which means that similar to the earlier studies of 4-AP in M-SDS[10] the processes of S_1-exc formation and 4-AP nonspecific solvation can be separated.

4. Discussion

The results presented provide unambiguous evidence of the influence of the SDS concentration on the solvation process of 4-AP dissolved in an aqueous solution of this surfactant. The absence of such an influence on the AS of the probe is not surprising when taking into account small differences in the shape and position of these spectra of 4-AP dissolved in different

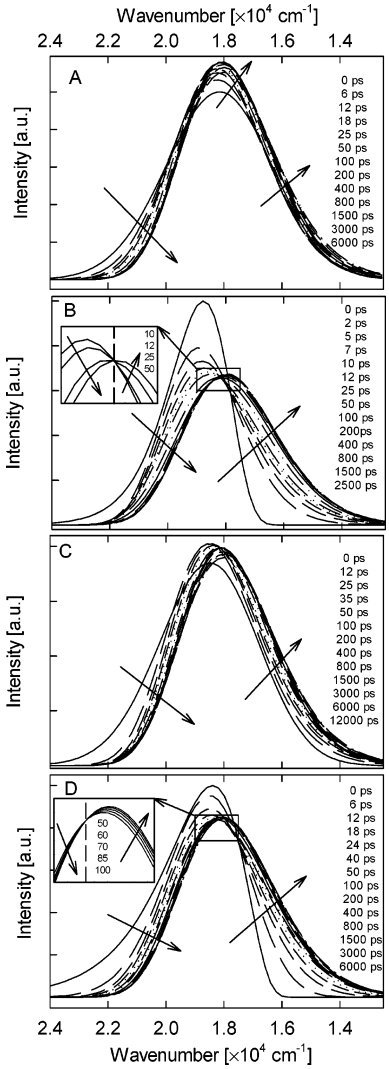

Figure 6. $TRANES_M$ of 4-AP determined on the basis of the area-normalized log-normal functions fitted to $TRES_M$: (A) 0.05 M SDS, 6.1 ps/channel, (B) 0.15 M SDS, 2.44 ps/channel, (C) 0.15 M SDS, 12.2 ps/channel, (D) 0.45 M SDS, 6.1 ps/channel. Insets: $TRANES_M$ for selected time delays for which isoemissive points are visible.

solvents and different micellar solutions. Also, the FS_M for different surfactant concentrations are identical, although when the emission originating from the probe dissolved in the water phase is not subtracted there are small differences between the FS_{M+SW} obtained for the smallest surfactant concentration and the FS_{M+SW} obtained for the other two surfactant concentrations.

Irrespective of the character of the initial course of the 4-AP solvation in the SDS solutions studied, its course some time after the excitation must be similar for each surfactant concentration. Such a conclusion is based on very similar positions of $TRES_M$ at $t \rightarrow \infty$ for the three SDS concentrations used and clearly different positions of $TRES_M$ at $t = 0$ ps. Moreover, the presence of the isoemissive point in $TRANES_M$ (Figure 6) indicates the presence of two emissive species: 4-AP in the S_1-ICT state and S_1-exc. As a result of excitation, the concentration of S_1-exc, emitting in a more long-wavelength region than 4-AP in the S_1-ICT state, increases. The abrupt changes in the shape of $TRES_M$ in the initial period of the observed 4-AP solvation are related to the concentration changes of these species.[10] The S_1-exc formation process by 4-AP in the S_1-ICT state and the water molecule occurs in the time in which the isoemissive point in $TRANES_M$ is observed. For the SDS solution of the lowest concentration (0.05 M), no

isoemissive point was observed. The absence of the isoemissive point in TRANES of 4-AP for the lowest SDS concentration was not a result of similar times of S_1-exc formation and nonspecific solvation of both emitting species. The longest time component of the multiexponential decay (τ_{S3}), fitted to the correlation function of spectral relaxation, $C(t)$, for the lowest SDS concentration and the τ_Γ time in which 90% of the changes in the half-width (Γ) of log-normal functions, fitted to TRES, are significantly different ($\tau_\Gamma \approx 30$ ps, whereas τ_{S3} is much longer; see Table 3). The changes in Γ correspond to those in the shape of TRES, which can be related to the process of reaching a new concentration equilibrium between 4-AP in the S_1-ICT state and S_1-exc. Also, when the isoemissive points were observed in TRANES (i.e., for 4-AP dissolved in 0.15 M SDS), τ_{S3} and τ_Γ were significantly different.[10] The τ_{S3} was much longer than the τ_Γ time, in which the most significant changes in Γ occurred. This meant that the S_1-exc formation process occurred in a much shorter time than the nonspecific solvation, to which both the exciplex and noncomplexed 4-AP in the S_1-ICT state were subjected. The processes responsible initially for the changes in the shape and position and later mainly only for the changes in the position of $TRES_M$ are then well separated in time, similar to the results presented in ref 10 for 4-AP dissolved in M-SDS. This indicates that most probably the process of a new concentration equilibrium establishment between 4-AP in the S_1-ICT state and S_1-exc, in micelles formed in the 0.05 M surfactant solution, occurs too rapidly to permit the observation of the isoemissive point at the time resolution used. This conclusion is supported by the shape of the $TRES_M$ of 4-AP in 0.05 M SDS solution (Figure 2B), in which no significant changes in the long-wavelength region are observed. Moreover, the smallest $\Delta\nu_M^g$ value from among the observed ones (Table 3) indicates the most bathochromic shift of the $TRES_M$ at $t = 0$ ps for this surfactant concentration. This is equivalent to a significantly higher mean polarity of the environment of nonexcited 4-AP in micelles formed in 0.05 M surfactant solutions than for the other two surfactant concentrations. The polarity change in the M-SDS Stern layer, in which 4-AP molecules are present, can be related to the change in the number of SDS and water molecules, which is a result of changes in the surfactant concentration. Because the aggregation number decreases with decreasing surfactant concentration,[3,4] only an increase in the water molecule concentration in the vicinity of 4-AP in the micelle can be the reason for the observed increase in the mean polarity of the 4-AP environment before excitation. Increasing surfactant concentration is accompanied by abrupt changes in the shape of the $TRES_M$ in the long-wavelength region. This region is as very visible in the $TRES_M$ of 4-AP in 0.45 M SDS as in 0.15 M. Taking into account the times of the isoemissive points' appearance in $TRANES_M$ (from $t \approx 10$ to 50 ps for $c_S \approx 0.15$ M and from $t \approx 50$ to 100 ps for $c_S \approx 0.45$ M), it is reasonable to conclude that the decrease in the water concentration in M-SDS, which is a consequence of the surfactant concentration increase, causes an increase in the time of S_1-exc formation.

There are four possible reasons for the increase in this time. (i) The time for reaching a new concentration equilibrium of both emissive species depends on their initial concentrations. In micelles formed in 0.05 M SDS solution, the initial concentration of complexes 4-AP···H_2O in the ground state is higher than in micelles formed in solutions of higher surfactant concentration (because of a lower concentration of water in the vicinity of the probe in more concentrated SDS solutions). Assuming that the excited complex 4-AP···H_2O has the same photophysical properties as the exciplex S_1-exc, then because of an already lower initial number of noncomplexed 4-AP molecules the new concentration equilibrium between the emissive species after excitation will be established in a shorter time in a solution of a lower surfactant concentration. (ii) The decrease in the water concentration in micelles together with an increase in the surfactant concentration leads to an increase in the mean distance between 4-AP and water molecules. The formation of a hydrogen bond between the probe and water molecules requires their approach to each other and appropriate arrangement. The time needed for these molecules to meet is, in an obvious way, related to the distance separating them. The increase in this distance must affect the time to reach a new concentration equilibrium between the emissive species. (iii) The increase in the surfactant concentration leads to a decrease in the free space between SDS molecules, accessible to both water and 4-AP molecules. This process occurs because a higher aggregation number of the micelles needs a greater packing of the surfactant molecules co-creating the micelle.[5] The mean volume occupied by a single surfactant molecule for $c_S \approx 0.45$ M is about 650 Å^3; for $c_S \approx 0.15$ M, about 740 Å^3; and for $c_S \approx 0.05$ M, about 760 Å^3.[26] This means that the average viscosity of the 4-AP environment increases with increasing c_S, leading to a decrease in the diffusion coefficient of both 4-AP and water molecules. As a consequence, the time needed for the water and probe molecules to meet increases. Also, the time needed for their rotation necessary to assume the positions for the creation of S_1-exc increases. (iv) The restriction of possible translational and rotational motions of the water molecules, studied by the molecular dynamics simulation by Berkowitz et al.,[27] seems to be the principal reason for the solvation retardation of 4-AP in M-SDS. Such a restriction is due to hydrogen bond formation between the O−H group of the water molecules present in the Stern layer and the lone electron pairs of the SDS oxygen atom.[28] Therefore, it is in the influence of the SDS concentration on the probability of forming such hydrogen bonds that one should see the main source of the differences in the S_1-exc formation time. A higher SDS concentration leads to a lower water concentration. Therefore, the probability that a selected water molecule forms one or two hydrogen bonds with SDS molecules increases. As a consequence, this leads to a slowing down of the S_1-exc formation because this process needs such water−SDS hydrogen bonds to break before the same water molecule can form a new hydrogen bond with 4-AP.

The values of decay times of the long-time components of the correlation function $C_M(t)$ (Table 3) give some information about the nonspecific solvation relaxation time of 4-AP in M-SDS. The τ_{S3} values were used in our earlier paper[10] to determine the rate of nonspecific solvation. The τ_{S3} values given in Table 3 for $c_S \approx 0.15$ M, for two different time per channel values applied, and the $C_M(t)$ time dependencies presented in Figure 5 reveal their dependence on the time resolution used. This is incomprehensible because the applied time resolution should not influence the $TRES_M$ determined at high time delays. However, the energy of stabilization, ΔE_3, related to this long-time component of the nonspecific solvation is relatively small. Taking into account the amplitudes (b_i) of the long-time components of the correlation function $C_M(t)$, we find that this energy equals ($\Delta E_3 = b_3 \times \Delta\nu_M^g$) ~180 cm^{-1} ($c_S \approx 0.05$ M), ~100 cm^{-1} ($c_S \approx 0.15$ M, 2.44 ps/channel), ~170 cm^{-1} ($c_S \approx 0.15$ M, 12.2 ps/channel), and ~100 cm^{-1} ($c_S \approx 0.45$ M). Therefore, taking into account the absolute values of this energy and the experimental errors, it is not surprising that τ_{S3} can be

charged with high uncertainty. However, the τ_{S3} values given in Table 3 for $c_S \approx 0.15$ M obtained at 2.44 and 12.2 ps/channel are significantly different, even more than when the emission originating from 4-AP dissolved in the water phase is not taken into account (Table 3 in ref 10). An additional uncertainty can also be introduced by the procedure of the subtraction of the emission originating from 4-AP present in the the water phase. It seems that for $c_S \approx 0.15$ M the τ_{S3} value should be intermediate between the values for two extreme surfactant concentrations used. Taking this into account, it was assumed that the proper τ_{S3} values were about 800−900 ps for all M-SDS systems studied. The choice made exclusively on the basis of the τ_{S3} values obtained for $c_S \approx 0.05$ and 0.45 M can hardly be justified in the light of the earlier described reasons for the differences in the time of the presence of the isoemissive points in the TRANES of 4-AP. If the increase in the SDS concentration had led to a decrease in the number of water molecules in the micellar system and to an increase in the viscosity of the micellar environment and in the number of water molecules hydrogen bonded to SDS molecules, then the 4-AP solvation for the lowest SDS concentration would have occurred faster than in solutions of higher surfactant concentrations. The values given in Table 3 show that this is not the case. The contributions of individual processes responsible for the change in the shape and position of 4-AP TRES are different for individual SDS concentrations, and this can influence the precision of the determination of the longest $C_M(t)$ time component. Taking into account the scatter of the τ_{S3} values related to different time resolutions applied, it is reasonable to suppose that although the 4-AP solvation relaxation for $c_S \approx 0.15$ M is probably better described by $C_M(t)$ obtained for the lowest time resolution, the τ_{S3} values for all surfactant concentrations are charged with great errors. This error is significant enough to make it difficult to draw any conclusions about the differences in the relaxation time of the nonspecific solvation of 4-AP dissolved in micelles formed for different surfactant concentrations. Our results can, however, be compared to those recently published by Shirota et al.[29] These authors studied the dependence of solvation dynamics on the SDS concentration for two coumarins (C102 and C153). They did not observe any significant differences in the solvation dynamics when changing the SDS concentration. However, they observed a dependence on SDS concentration of the position of the coumarins' TRES maximum at $t = 0$ ps. This dependence was similar to the one reported by us in this paper (i.e., a higher SDS concentration led to a hipsochromic shift of the TRES at time delay 0 ps). Similar to our τ_{S3} values, Shirota et al. obtained dynamic solvation parameters not significantly dependent on the surfactant concentration. However, again similar to the case of ΔE_3 values reported by us, the total observed spectral shift (stabilization energy) connected to the $C(t)$ components reported by Shirota et al.[29] was very small. The total spectral shift of the TRES maximum position reported in ref 29 does not exceed 50 cm^{-1}, which is more than 1 order of magnitude less than the smaller $\Delta\nu_M^g$ given in Table 3 for 4-AP. Because the TRES directly recorded by means of a streak camera are not deconvoluted with the instrument response function, a significant part of the TRES changes for coumarins might not have been observed by Shirota et al. Therefore, it cannot be excluded that the TRES obtained for coumarins with a higher time resolution could reveal a dependence on SDS concentration similar to the one we observed for 4-AP. Additionally, one cannot exclude that the differences in the results obtained by us for 4-AP and by Shirota et al.[29] for coumarins followed from differences in the properties of the probes used.

5. Conclusions

The results presented have shown that a study of micelles by optical emission spectroscopy requires taking into account the fact that part of the observed emission can originate from the probe molecules dissolved in the water phase surrounding the micelles. Depending on the surfactant concentration applied, this contribution can have a different influence on FS_{M+SW} and $TRES_{M+SW}$. A decrease in the surfactant concentration is accompanied by an increase in the emission fraction originating from the probe molecules dissolved in the water phase. The time dependencies of (ν_{M+SW}^{max}, ν_{M+SW}^{g}) determined from the total signal of the micellar solution have been compared with the corresponding (ν_M^{max}, ν_M^g) values determined for the probe present in the micellar phase at the lowest SDS concentration. It has shown clearly that the emission originating from 4-AP dissolved in the water phase surrounding the micelles must be taken into account. The elimination of the emission of the probe present in the water phase allowed a determination of the differences in $TRES_M$ of 4-AP solubilized in the micelles formed for different SDS concentrations. The increase in the surfactant concentration leads to an increase in the time of significant shape changes in the $TRES_M$. The time of appearance of the isoemissive point allows an estimation of the time of S_1-exc formation. This time increases with increasing SDS concentration, which is related to decreasing water molecule concentration and increasing mean viscosity in the micelle region in which 4-AP is present. This result is in agreement with the observations of Bales et al.,[5] indicating the dependence of the micelles degree of hydration on the surfactant concentration.

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Appendix: Nomenclature and Abbreviations

4-AP = 4-aminophthalimide
A = absorbance
AS = absorption spectra
AS_x = AS of 4-AP dissolved in an x environment[30]
A_x = absorbance of 4-AP dissolved in an x environment[30]
b_i = ith amplitude of the multiexponential function fitted to $C(t)$
$C(t)$ = solvation correlation function
$C_M(t)$ = $C(t)$ − solvation correlation function of 4-AP in micellar environment
cmc = critical micellar concentration
$c_{Micelles}$ = micelle concentration
c_S = SDS concentration
c_x = 4-AP concentration in an x environment[30]
exc = exciplex formed by 4-AP in the S_1-ICT state and water
f = ratio of the emission intensity originating from 4-AP present in the water phase to the total emission intensity originating from the whole micellar solution
$f(D, n)$ = Lippert−Mataga polarity function
FS = fluorescence spectrum
FS_x = FS of 4-AP dissolved in an x environment[30]
H = polarity index introduced by Mukerjee et al.[7]

I_x^{em} = total emission intensity of 4-AP dissolved in an *x* environment[30]

I_{abs} = intensity of absorbed light

ICT = internal charge-transfer electronic state

k_{in} = rate coefficient for the entry of excited-state naphthalene from the water phase into the micelles

k_{out} = rate coefficient for the departure of excited-state naphthalene from the micelles to the water phase

LE = locally excited electronic state

M-SDS = micelles formed in SDS in aqueous solution

N = micelle aggregation number

N_A = Avogadro's number

N_M = number of micelles inside the micellar solution

R_M = micelle radius

S = ratio of the number of 4-AP molecules solubilized only inside micelles to the number of 4-AP molecules dissolved in the whole micellar solution

SDS = sodium dodecyl sulfate

TRANES = time-resolved area-normalized emission spectra

$TRANES_x$ = TRANES of 4-AP dissolved in an *x* environment[30]

TRES = time-resolved emission spectra

$TRES_x$ = TRES of 4-AP dissolved in an *x* environment[30]

V_M = micelle volume

$\Delta\nu_M^g$ = total spectral shift of 4-AP TRES in a micellar environment

ν_x^g = gravity frequency of the spectrum

ν_x^{max} = maximum frequency of the spectrum

λ_{max}^{em} = maximum of the fluorescence spectrum

λ_{max}^{abs} = maximum of the long-wavelength band of the absorption spectrum

ς = volume fraction of the micellar solution occupied by bulk water

ϵ_x = molar absorption coefficient of 4-AP dissolved in an *x* environment[30]

ϕ_x = fluorescence quantum yield of 4-AP dissolved in an *x* environment[30]

λ_{exc} = excitation wavelength

τ = lifetime

τ_{Si} = *i*th decay time of the multiexponential function fitted to $C(t)$

References and Notes

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