Micellar Properties of Aqueous Solutions of Hexadecyltrimethylammonium Salts in the Presence of Nonionic Polymer

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ABSTRACT: Aqueous solutions of cetyltrimethylammonium surfactant molecules (CTAX; $X^- = Cl^-$, ClO_3^-, NO_3^-) in the presence of nonionic polymer (poly(propylene oxide), MW = 1000; poly(vinyl alcohol)–poly(vinyl acetate), MW = 110 000) were investigated by means of photophysical techniques. The observed reduction of the critical aggregate concentration for the different surfactants and the decrease of the aggregation number in the presence of polymer were indicative for micelle–polymer associations. Conductivity measurements provided information on the role counterions play in the interaction between a cationic micelle and a neutral polymer chain. The change in micellar size, in micropolarity, and in aggregation behavior upon addition of polymer was studied by dynamic and static fluorescence quenching. The results suggest that the polymer strands are wrapped around the aggregates with their hydrophobic segments penetrating into the Stern layer where water molecules are replaced. From the polymer point of view, turbidity measurements indicated an increase of the clouding point temperature upon addition of surfactant, and viscosity data revealed an uncoiling of the polymer chain in a micellar solution. The global compartmental analysis of multiple fluorescence decays of naphthalene in aqueous hexadecyltrimethylammonium chloride solutions provided data on the partitioning of this fluorophore in a micellar solution in the absence and presence of polymer. Steady-state fluorescence measurements provided the complementary data required for the analysis, showing that micelle–polymer association leads to an improved solubilization capacity. The process of probe migration appeared to be enhanced in micelle–polymer complexes, probably due to the higher local concentration of the micelles along the polymer strands in comparison to the micellar concentration in the bulk.

1. Introduction

The recognition of the possible interaction between nonionic, water-soluble polymers and surfactants occurred much later than the notion of aggregation of surfactants. Over the years several models were proposed to describe such micelle–polymer "complexes", but none could fully explain all the experimental observations until Cabane proposed a micelle–polymer model that is now quite generally accepted.[1] The main driving force for micelle–polymer interaction is believed to be the reduction of the interfacial area between the hydrophobic polymer segments and the solvent water by association of these segments with the exposed hydrophobic parts of aggregating surfactants.[2] Here the hydrophobicity of the polymer chain plays a major role, although also steric requirements at the micellar surface and the perturbation of the hydration sheath by the surfactant head groups and counterions may influence the free energy of transfer of the polymer from the aqueous to the micellar phase. Since the hydrophobic polymer strands are believed to replace water molecules structured around the micellar head groups,[3] stabilization of the micelle upon binding to a polymer strand results from a reduction of the interfacial tension between the hydrophobic core and water. Furthermore, specific interactions such as hydrogen binding between the polymer and the head groups may play a role.[4]

The work of Saito and others[3] indicates that anionic micelles show a greater affinity for nonionic polymers in comparison to cationic surfactants. A definite explanation for this experimental observation has not been proposed. This contribution shows that under appropriate conditions considerable interaction between cationic micelles and nonionic polymer can be observed.

An important property of micellar systems is their ability to solubilize a variety of substances ranging from hydrocarbons to inorganic ions. Physical models describing solubilization processes in a micellar environment consider the solubilization site to depend on the relative hydrophobic or lyophilic nature of the substrate. Strong evidence has been presented that solubilization of relatively hydrophobic molecules or ions in the micelle–water interface is an entropically favored process with the release of bound or interfacial water molecules as a chief driving force.[5] In this paper results treating the influence of polymer addition on the solubilization capacity of cationic surfactants are presented. The fluorophore naphthalene was chosen as substrate since its solubility behavior in aqueous micellar systems permits study of the gradual change of its partitioning within the surfactant concentration range of interest. The recently developed global compartmental analysis of fluorescence decays[6,7] provided the parameters needed to estimate the partitioning of the substrate.

Kinetic expressions for fluorescence quenching in micellar systems and the use of the global iterative nonlinear least-squares method to analyze multiple decay curves, where the model is a nonexponential decay function corresponding to a Poisson distribution of decay times as found for the fluorescence quenching in micelle systems, were discussed extensively in preceding papers.[8] Immobile quenchers were used to simplify the micellar kinetics. Consequently, the following equation for intramicellar fluorescence quenching[8] could be applied to analyze the fluorescence decays of the excited solubilized pyrene

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derivatives:

$$I(t) = A_1 \exp[-A_2 t - A_3(1 - \exp(-A_4 t))] \quad (1)$$

where $A_1 = I(0)$, assuming δ-pulse excitation at $t = 0$, $A_2 = k_0$, the monomolecular decay constant of the excited probe, $A_3 = [Q]/[M]$, with [M] the quencher concentration and [M] the micellar concentration, and $A_4 = k_q$, the first-order intramicellar quenching rate constant for a micelle with one quencher and one probe (s^{-1}).

Previous papers[9,10] pointed out that the fitting of synthetic decay data, simulating the probe migration process, by an Infelta–Tachiya type equation usually yields statistically acceptable parameters. Based on Almgren's approach[9] approximate analytical expressions for the A_i parameters were derived.[10] In this paper the applicability of the approximate solution is supported by experimental data obtained in micelle–polymer systems.

2. Experimental Section

2.1. Experimental Methods. Fluorescence decay curves were obtained by making use of a mode-locked argon ion laser (Spectra-Physics) pumping synchronously a cavity-dumped DCM (4-(dicyanomethylene)-2-methyl-6-(*p*-(dimethylamino)styryl)-4*H*-pyran) dye laser (excitation wavelength after frequency-doubling: 325 nm) or R6G (rhodamine 6G) dye laser (excitation wavelength after frequency-doubling: 295 nm) with single-photon-timing detection. All fluorescence decay curves were observed under magic angle (54.44°), contained 10^4 peak counts, and were collected in 1/2K data points of the multichannel analyzer. Additional details concerning the picosecond time-resolved fluorometer and the optical and electronic components were described previously.[11]

The fluorescence characteristics of the different probes were determined by means of fully-corrected steady-state spectra recorded on an SLM 8000 spectrofluorometer. All samples used for fluorescence measurements were degassed by repeated freeze–pump–thaw cycles.

Absorption measurements were performed on a Perkin-Elmer Lambda 6 UV–vis spectrophotometer, ^{13}C NMR spectra were recorded on a Bruker WM 250 spectrometer with TMS as an external reference, the equivalent conductivity was measured by a Taccussel CD6N conductivity device, and the kinematic viscosity of the surfactant solutions was determined by a capillary Ostwald microviscometer fabricated for foamy solutions.

The reference convolution method used in the analysis of the fluorescence decays has been discussed extensively in a previous paper.[12] Estimates of the fitting variables are computed by a global iteratively reweighted reconvolution program based on the Marquardt algorithm for nonlinear least squares.[12]

2.2. Chemicals. Fluorescence Probes. 1-Methylpyrene (1-MePy) was purified by column chromatography on silica gel with dichloromethane–*n*-hexane as eluent. Pyrene (Py, Aldrich) was purified by repeated recrystallization from ethanol and subsequent sublimation. Naphthalene (Naph, Fluka) was recrystallized twice from ethanol and sublimed. After these purification procedures, solutions of excited 1-MePy or Py in methanol and a solution of Naph in water at room temperature showed a monoexponential fluorescence decay with decay times of 190, 350, and 35 ns, respectively. Sodium 1-pyrenesulfonate (PSA) was purchased from Molecular Probes. The purity was checked by thin-layer chromatography on silica gel with methanol and by measuring the lifetime in different solvents.[27] A monoexponential decay was obtained in all cases.

Detergents. Hexadecyltrimethylammonium chloride (CTAC, Kodak) contained fluorescent impurities and was purified by Soxhlet extraction with diethyl ether followed by recrystallization from a 1/1 (v/v) acetone–diethyl ether mixture. $CTANO_3$ was prepared by titration of CTAOH with HNO_3, whereas $CTAClO_3$ was prepared by counterion exchange from a dilute aqueous solution of CTAC (<0.001 M) in the presence of $NaClO_3$ in excess.[32] After lyophilization, the product was dissolved in methanol–acetone mixtures to remove the salt in excess. The final products were purified by recrystallization from acetone in the presence of carbon black. No fluorescent impurities could be detected from the blank CTAX solutions under the experimental conditions. 1-MePy solubilized in aqueous solutions of these surfactants at room temperature showed a monoexponential decay (190 ns). Tetradecylpyridinium chloride (TPyCl) was recrystallized from methanol. Hexadecylpyridinium chloride (HPyCl) did not show any fluorescent impurities and was used as received.

Table I
^{13}C Spectral Shifts (ppm) of CTAC in the Absence and Presence of PPO (298 K)[a]

^{13}C nuclei	CTAC	CTAC + PPO
C'_1	52.603	52.5452
additional line		48.562
C_1	66.211	66.241
additional line		65.877
C_2	25.739	25.871
additional line		23.437
C_3	29.101	28.954

[a] The C atoms of the CTAC chain are labeled starting from the C closest to the ammonium head group as C1. C′ represents the C atoms of the methyl groups on N^+.

Polymers. Poly(propylene oxide) (PPO, weight-average MW = 1000, Janssen) and poly(vinyl alcohol)–poly(vinyl acetate) (PVOH-Ac, weight-average MW = 110 000, Aldrich, 88% hydrolyzed) were used as received since no fluorescent impurities were detected for the blanks under the experimental conditions described in this paper.

Water was deionized by means of a Millipore Milli-Q water purification system.

3. Results

3.1. Experimental Evidence for and Characterization of Polymer–Micelle Association. 3.1.a. ^{13}C Chemical Shifts. NMR techniques have been extensively used to study amphiphile conformations and micellar dynamics.[1,13,14] Used in the study of micelle–polymer interactions, this technique provides information on the shift of various atoms of both the surfactant and polymer molecules. Table I lists some values for the ^{13}C spectral lines of the carbon atoms of the CTAC molecules. The solutions are composed of 0.02 M CTAC and 0.02 M + 0.5 g/dL PPO in D_2O. At these concentrations the mixed solution contains micelle–polymer complexes and some surfactants in excess forming regular "free" micelles in the bulk (vide infra). Upon addition of PPO additional spectral lines appear for both the ^{13}C nuclei of the polymer and the nuclei that constitute the hydrated parts of the surfactant molecules. The origin of these changes in chemical shift can be interpreted either by the "medium effects", i.e., direct effects of the environment, or by "conformational effects", i.e., a change of the conformation of the alkyl chain.[1,14] Nevertheless, it is beyond the scope of this study to unravel the details of these effects, since for the intended purpose only the relative positions of the nuclei of the CTAX and PPO molecules are of interest. Variations of the chemical shifts reflect changes in the local environment of the observed nuclei and thus provide information on the number and location of the nuclei perturbed by the association.[13]

3.1.b. Determination of the Critical Aggregation Concentrations by Means of Conductivity Measurements. In this paragraph critical micellar concentration (cmc) values and dissociation constants (α), obtained by means of conductivity measurements, are listed for CTAX systems in the absence and presence of polymers. The enhanced counterion binding arising the very moment that micellization takes place results in a clear break in a conductivity versus concentration plot, indicative of the cmc, as shown in Figure 1.

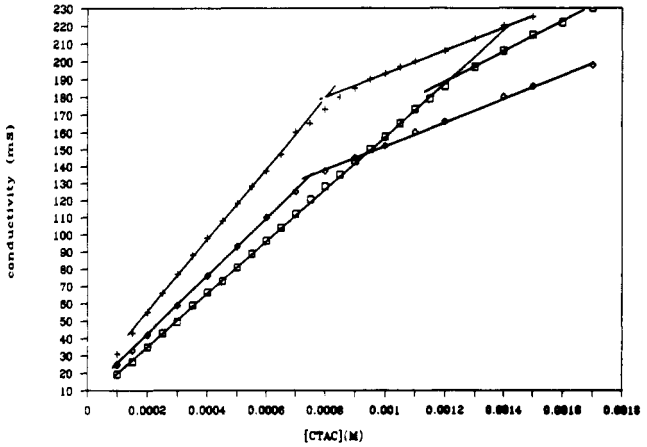

Figure 1. Plot of conductivity versus CTAX concentration for solutions of CTAC (□), $CTANO_3$ (+), or $CTAClO_3$ (◇).

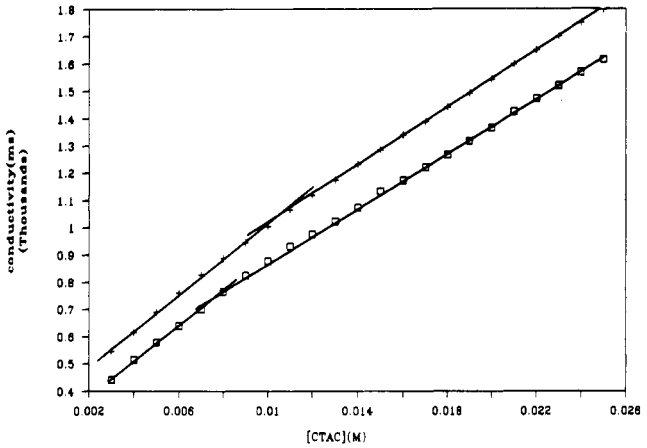

Figure 2. Plot of conductivity versus CTAC concentration for a 6 g/L PVOH-Ac (□) and 10 g/L PVOH-Ac (+) solution.

Table II
Determination of Critical Micellar Concentrations and Dissociation Constants by Means of Conductivity Measurements ($\times 10^{-4}$ M)

cmc	CTAC	12	CTAC + PVOH-Ac	8
	$CTANO_3$	8 ± 1	$CTANO_3$ + PVOH-Ac	8 ± 1
	$CTAClO_3$	7	$CTAClO_3$ + PVOH-Ac	5
α	CTAC	0.53	CTAC + PVOH-Ac	0.69
	$CTANO_3$	0.33 ± 0.04	$CTANO_3$ + PVOH-Ac	0.58 ± 0.04
	$CTAClO_3$	0.34	$CTAClO_3$ + PVOH-Ac	0.59

The presence of associating polymer, however, weakens the counterion binding since the penetrating polymer segments partly take over the screening role of the counterions, as shown by the α values in Table II. From a low micelle to polymer ratio and a low counterion binding (cmc) the system proceeds to a situation where the polymer chains are becoming saturated with larger micelles requiring an increased counterion binding. A nonlinear part after the first inflection point in the conductivity curve reflects this tendency. Figure 2 shows the appearance of a second inflection in the conductivity curve, indicative of the formation of free micelles that are characterized by a stronger counterion binding. As can be deduced from Figure 2 the second inflection point depends on the polymer concentration (and on the molecular weight!), contrary to the first inflection point, which relates to the cmc value. Viscosity data will reveal that at the CTAC concentration corresponding to the second inflection point the polymer chains are not yet saturated (vide infra).

Table II lists the cmc and α values for systems composed of CTAC, $CTANO_3$, or $CTAClO_3$ to which a given concentration of PVOH-Ac (1 g/dL) was added. All

Table III
Mean Aggregation Numbers for CTAC Micelles and Micelle–Polymer Complexes Obtained by Simultaneous Analysis of Four Decay Curves at 22 °C ([PVOH-Ac] = 10 g/L = [PPO])

concn (M)	CTAC	CTAC + PPO	CTAC + PVOH-Ac
0.007	69	21	28
0.010	72± 5	24± 2	31± 2
0.020	81	27	42
0.040	90	32	

experiments were carried out at 25 °C. The cmc values were determined by the intersection of the tangents to the conductivity curves. The dissociation constant α was derived from the ratio of the slope in the micellar region to the slope in the premicellar region.[18] Both the successive reduction of the cmc values for the CTAC, $CTANO_3$, and $CTAClO_3$ solutions and the decreasing α values, indicative of a stronger binding of the counterions to the head groups, prove the influence counterions exert on the aggregation behavior. The association with PVOH-Ac seems to level out the difference in counterion binding.

3.1.c Determination of the Micellar Aggregation Numbers by Means of Time-Resolved Fluorescence Spectroscopy. A study of the fluorescence decay of excited probe molecules solubilized in the micellar Stern layer is a method to gather information on the micellar size and shape. The analysis of these fluorescence decays by the appropriate kinetic model for intramicellar fluorescence quenching allows one to recover decay parameters from which aggregation numbers can be calculated.[8]

The fluorescence decays of 1-MePy (10^{-5} M), solubilized in aqueous CTAC micellar systems and quenched by the immobile quencher HPyCl, are described by eq 1. Several fluorescence decays with different quencher concentrations (eight quencher concentrations varying from 0.4 to 2.3 quenchers per micelle for CTAC systems and three quencher concentrations varying from 1 to 2 quenchers per micelle for CTAC/PVOH-Ac systems) were analyzed simultaneously, and the decay parameters k_0 and k_q were linked over the different decay curves. The standard errors on the aggregation number are estimated to be ±5 for the CTAC aggregates and ±2 for CTAC–PVOH-Ac complexes (Table III).

This marked decrease of the aggregation numbers for CTAC upon interaction with PPO or PVOH-Ac is comparable with the reduction of the aggregation numbers of SDS micellar systems in the presence of PEO or PPO.[17] The aggregation number in a 0.020 M SDS solution approximates 53,[17] whereas the aggregation numbers in SDS(0.020 M)/PEO(0.5 g/dL) and in SDS(0.020 M)/PPO-(0.5 g/dL) solutions are estimated to be 34 and 29, respectively.

3.1.d. Micelle–Polymer Complexes as Polyelectrolytes: Viscosity Measurements and Clouding Point Determination. Micelle–polymer complexes show some features, such as their size and shape dependence on the ionic strength, which allow one to state that their electrochemical behavior is similar to that of polyelectrolytes. A study of the viscosity behavior of such solutions confirms this point. Figure 3 shows an increase of the reduced viscosity of PVOH-Ac upon addition of surfactant to the system because the electrostatic repulsion between the cationic micelles bound to the polymer causes the coils to expand. The viscosity of the solution increases until the polymer chains are fully saturated, and any further addition of detergent only induces the further formation of nonbound micelles. The slight decrease of

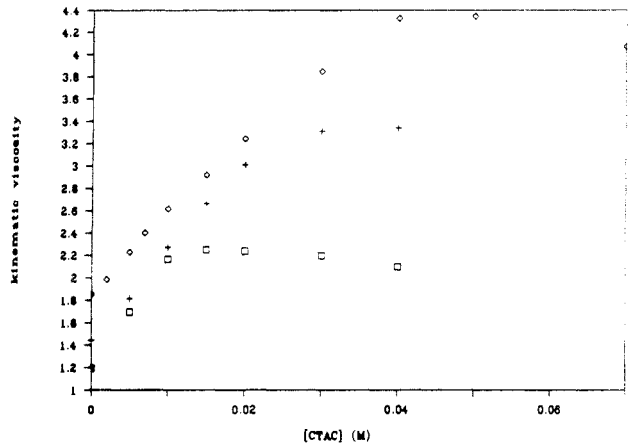

Figure 3. Relative viscosity versus CTAC concentration for solutions of 2 g/L PVOH-Ac (□), 4 g/L PVOH-Ac (+), and 6 g/L PVOH-Ac (◇).

Table IV
Clouding Points (°C) of PPO (10 g/L) in the Presence of Various Cetyltrimethylammonium Salts (0.01 M)

PPO	32	$CTANO_3$ + PPO	41
$CTAClO_3$ + PPO	38	CTAC + PPO	42

the viscosity after the saturation concentration has been observed in other systems[16,21] and was interpreted in terms of a contraction of the extended coils because of a decrease of the electrostatic repulsion between charged particles due to the higher ionic strength of the solution. Figure 3 shows that an increase of the polymer concentration increases proportionally the saturation concentration of the CTAC/PVOH-Ac systems.

The clouding point for a CTAC/PPO system was determined to obtain an idea of the overall shape of the polymer. The hydrophobic attraction in water is a consequence of the ordered water structure in the hydrophobic regions of the polymer. Upon addition of water structure breaking agents, the hydrophobic interactions are weakened and the expansion of the polymer chain is restored,[22] giving rise to the so-called salting-in effect, which manifests itself by an increase of the clouding point. At higher temperatures a breakdown of the hydration layer facilitates interpolymer interaction,[23] and a microphase separation into a polymer-rich and a water-rich phase takes place. Especially for a hydrophobic polymer such as PPO the unfavorable entropy associated with the hydrophobic hydration and the cooperativity of interpolymer London dispersion forces may drive the system toward microphase separation. For aqueous PVOH-Ac solutions no clouding point was detected within the temperature range that micelles are normally observed. The clouding behavior of PPO in the presence of CTAX is presented in Table IV.

3.2. Solubilization Capacity of Micelle–Polymer Complexes. This section attempts to evaluate how the interaction with polymer may affect the solubilization capacity of a micelle. In view of the information on micellar size and micellar concentration obtained for CTAC/PVOH-Ac solutions, the solubilization behavior of this system was studied using naphthalene as a fluorophore. Its solubility behavior in aqueous medium ($[Naph]_{aq,max} = 2.2 \times 10^{-4}$ M) and micellar medium (in CTAB (0.02 M) $[Naph]_{mic,max} = 1.11$ M)[24] allows us to study the gradual change of its partition within the surfactant concentration of interest (0.004–0.020 M). The recently developed global compartmental analysis of fluorescence decay curves allows the analysis of the kinetics of excited-state processes[6,7] and the determination of the concentration and equilibrium constants in a biocompartmental system, based on Scheme I.

Scheme I

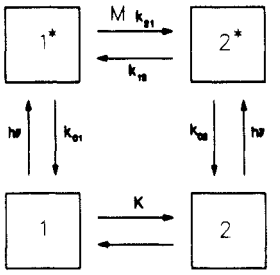

Table V
I_1/I_3 Values for Pyrene (10^{-5} M) in the Respective Aqueous Solutions

system	I_1/I_3	system	I_1/I_3
H_2O	1.93	CTAC (0.010 M)	1.45
PVOH-Ac (10 g/L)	1.92	CTAC (0.010 M) + PVOH-Ac (10 g/L)	1.39

In this scheme "M" represents a micelle, "1" is the fluorophore in the ground state in the water phase, and "2" represents the same fluorphore solubilized in the micelle "M". An asterisk indicates the excited state of the respective species. These excited states can depopulate via several pathways: fluorescence (k_F), internal conversion (k_{ic}), and intersystem crossing (k_{isc}). The deactivation rate constants for the excited species 1* and 2* are represented by k_{01} ($k_{F1} + k_{ic1} + k_{isc1}$) and k_{02} ($k_{F2} + k_{ic2} + k_{isc2}$), respectively. k_{21} is the exchange constant for the fluorophore from the aqueous to the micellar phase and is dependent on [M], whereas k_{12} is the exchange constant for the probe leaving the micelle. An extensive description of the theoretical background of two-state excited-state processes is reported elsewhere.[6]

Absorption, steady-state, and time-resolved fluorescence measurements were performed to obtain the input data required for the compartmental analysis. These complementary experiments confirm the applicability of the two-state excited-state model to the system studied.

3.2.a. Polarity Measurements. Within the scope of this specific study it is important to know whether PVOH-Ac itself interacts with naphthalene or not. If so, the picture of a biocompartmental system may be no longer appropriate to describe the system. Polarity measurements may provide information on the microenvironment of a fluorophore if there are any polarity-sensitive spectral changes. Pyrene is often used for this purpose.[25,26] The 0–0 band of pyrene (I_1) is due to a symmetric vibronic transition and is forbidden in apolar solvents. Nevertheless, solvent–solute interactions may enhance the intensity of these so-called forbidden transitions. Dipole–dipole coupling, π-orbital interactions between solute and solvent, and bulk dielectric properties of the solvent all cause perturbations of the solute vibronic bands.[25] The ratio I_1/I_3 refers to the intensity ratio of the (0,0) band (373 nm) to the (0,2) band (384 nm) in the emission spectrum of pyrene. A relative decrease of the 0–0 intensity and hence the I_1/I_3 ratio is indicative of a decrease of the polarity, or for the more hydrophobic character of the environment where the probe is located. A possible close positioning of the pyrene molecules to PVOH-Ac chains can thus be traced. Table V lists the observed I_1/I_3 values.

3.2.b. Steady-State and Dynamic Fluorescence Experiments. Fluorescence measurements are an excellent method to determine the partition of fluorescent solubilisates between the aqueous and the micellar phases,

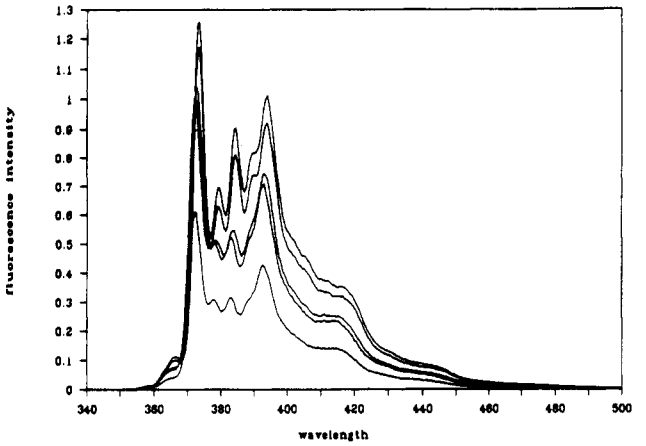

Figure 4. Fluorescence emission spectra of Naph ($<1.3 \times 10^{-4}$ M) at various CTAC concentrations ([CTAC] = 0.002–0.040 M) (25 °C).

Table VI
Absolute Quantum Yields for Naphthalene in Various CTAC and CTAC/PVOH-Ac(6 g/L) Systems

	quantum yield			quantum yield	
CTAC (M)	CTAC	CTAC/PVOH-Ac	CTAC (M)	CTAC	CTAC/PVOH-Ac
0.000	0.060	0.059	0.006	0.085	0.096
0.002	0.073	0.083	0.010	0.088	0.097
0.004	0.083	0.092	0.020	0.090	0.096

since the rate constants for deactivation of the excited probe depend on its microenvironment. The fluorescence of Naph ($<1.3 \times 10^{-4}$ M) in the presence of PVOH-Ac (6 g/L) and CTAC at concentrations varying between 0 and 0.020 M were investigated and no excimer emission was observed (Table VI). For the single-photon-timing experiments, the frequency-doubled rhodamine 6G was used as excitation source. Values for the extinction coefficients of Naph in aqueous and micellar medium were determined as 2500 ± 100 and 2750 ± 70 (285 nm), respectively. Upon addition of polymer the values for the extinction coefficients remained unchanged within the experimental error. Absolute quantum yields were determined for various CTAC and CTAC/PVOH-Ac solutions to assess the concentration where only very little Naph remains in the aqueous phase and to calculate k_{F1} and k_{F2} values (eq 4). The respective emission spectra are represented in Figure 4.

Global compartmental analysis of an ensemble of fluorescence decay curves, obtained in both CTAC and CTAC + PVOH-Ac solutions, provided values for the k_{01}, k_{02}, k_{12}, and k_{21} rate constants of Scheme I. Two more fitting parameters included in the analysis are c_i and b_i.

$$c_1 = k_{F1}\int \rho_1(\lambda_{em})\, d(\lambda_{em}) \tag{2}$$

with ρ the spectral emission density at wavelength λ_{em}.

Since the spectral emission density at λ_{em} = 323 nm turned out to be equal for all of the steady-state fluorescence spectra at the various surfactant concentrations, $\tilde{c}_1$ ($=c_1/(c_1 + c_2)$) could be written as

$$\tilde{c}_1 = k_{F1}/(k_{F1} + k_{F2}) \tag{3}$$

Knowing the quantum yield values for Naph in H_2O and in micellar medium (Table VI), one can calculate k_{F1} and k_{F2} using eq 4.

$$\Phi_1 = k_{F1}/k_{01} \tag{4}$$

Since at higher surfactant concentrations (>0.020 M) the experimental decay curves of 1-MePy could be fitted to a monoexponential decay law, one might assume that in these solutions almost all of the probes are solubilized in the micellar medium. Values for k_{02}(CTAC) and k_{02}(CTAC/PVOH-Ac) were determined in this way and equaled (1.16 ± 0.02) × 10^7 and (1.15 ± 0.02) × 10^7 s^{-1}, respectively. An aqueous solution of Naph provided a value for $k_{01}(H_2O)$ equal to (2.765 ± 0.02) × 10^7 s^{-1}. $\tilde{c}_{1CTAC}$ and $\tilde{c}_{1CTAC/PVOH-Ac}$ were calculated to be 0.59 ± 0.01. Furthermore

$$b_1 = [1^*]_{t=0} \tag{5}$$

and

$$\frac{[1^*]_{t=0}}{[2^*]_{t=0}} = \frac{\epsilon_1[1]}{\epsilon_2[2]} = \frac{b_1}{b_2} \tag{6}$$

Hence

$$\tilde{b}_1 = \frac{\epsilon_1[1]}{\epsilon_1[1] + \epsilon_2[2]} \tag{7}$$

where [1] = the concentration of Naph in the aqueous phase and [2] = the concentration of Naph in the micellar phase.

The model parameters were obtained by global compartmental analysis of seven decay curves. Statistically acceptable fits were obtained. Except for the local fitting parameter $\tilde{b}_{1i}$ (i = CTAC or CTAC/PVOH-Ac), all parameters were linked within the same experimental series. Parameter $\tilde{c}_{1i}$ and k_{01} were kept fixed at their calculated values. Compartmental analysis provided $\tilde{b}_{1i}$ values, which allowed the calculation of the Naph concentration in the aqueous and micellar phase.[26] Values for k_{02} were found to equal the value obtained previously ((1.15 ± 0.02) × 10^7 s^{-1}). K, the equilibrium constant in the ground state, can be calculated as follows:

$$K = \frac{[M_{Naph}]}{[Naph][M]} = \frac{[2]}{[1][M]} \tag{8}$$

Equation 7 can be written as

$$\tilde{b}_1 = \frac{\epsilon_1}{\epsilon_1 + \epsilon_2 K[M]} \tag{9}$$

Since the total concentration of naphthalene, C_{tot}, and the total absorbance at 285 nm, S, are known, the following expression can be derived:

$$g = \frac{C_{tot}}{S} = \frac{[1] + [2]}{\epsilon_1[1] + \epsilon_2[2]} \tag{10}$$

or

$$g = \frac{1 + K[M]}{\epsilon_1 + \epsilon_2 K[M]} \tag{11}$$

Hence

$$\tilde{b}_1 = \frac{g\epsilon_1}{1 + K[M]} \tag{12}$$

and

$$K = \frac{g\epsilon_1 - \tilde{b}_1}{\tilde{b}_1[M]} \tag{13}$$

Values for K are listed in Table VII. A K value equal to 10 400 was obtained in a 0.020 M CTAC/PVOH-Ac solution. Conductivity measurements (Table II) showed that at this detergent concentration both micelle–polymer

Table VII
K Values for Naphthalene (1.337×10^{-4} M) in CTAC and CTAC/PVOH-Ac(6 g/L) Systems (K Values Obtained Based on Equation 13)

	CTAC		CTAC + PVOH-Ac	
[CTAC] (M)	$[Naph]_{aq}$ (M)	K (M^{-1})	$[Naph]_{aq}$ (M)	K (M^{-1})
0.004	4.4×10^{-5}	10600	3.0×10^{-5}	15500
0.006	3.8×10^{-5}	10200	2.1×10^{-5}	19700
0.010	3.1×10^{-5}	10600	1.4×10^{-5}	17200
0.020	1.5×10^{-5}	10800	[a]	
		ave 10500		ave 17500

[a] See text immediately following eq 13.

complexes and free micelles are present. The intermediate value of K confirms this observation.

3.3. The Probe Migration Process in Micelle–Polymer Systems. The analysis of the fluorescence quenching process in a micellar system may provide information on the structural properties of a micelle and can in such a way clarify the influence of additives. With this objective in mind one may appeal to immobile probes and quenchers to simplify the analysis. As the kinetic parameters are correlated to the dynamics of the probe–quencher–micelle system, one may also investigate whether exchange processes may be favored upon perturbation of the Stern layer.

A previous paper[10] treated the kinetic aspects of probe migration among micelles occupied by Poisson-distributed quenchers. An exact and general solution for the kinetic analysis of the fluorescence decays of the excited probes was derived and expressed as a series of generalized convolution products with application to any kinetic system that can be described by a probe (singlet, triplet, or radicals) migrating among micelles occupied by a quencher or scavenger.

Almgrem pointed out[9] that even in the presence of quencher exchange or probe migration the fluorescence decay might still be described to a good approximation by the Infelta–Tachiya equation, but with a more generalized interpretation of the parameters. The following relations for the decay parameters of eq 14 were derived.

$$I(t) = A_1 \exp[-A_2 t - A_3(1 - \exp(-A_4 t))] \quad (14)$$

$$A_2 = k_q \langle x \rangle_s + k_0 \quad (15)$$

$$A_3 = n(1 - \langle x \rangle_s / n)^2 \quad (16)$$

$$A_4 = k_q (1 - \langle x \rangle_s / n)^{-1} \quad (17)$$

where $\langle x \rangle_s$ is the asymptotic value of the average number of quenchers in the subset of micelles that still contain one excited probe as obtained by an iterative calculus over the stationary distribution.[9] k_0 and k_q are the monomolecular decay rate constant of the excited probe and the first-order intramicellar quenching rate constant for a micelle with one quencher and one probe, respectively, whereas n equals [Q]/[M]. Recently, an expression was derived leading to an approximated evaluation of $\langle x \rangle_s$.[10]

$$\langle x \rangle_s \approx k\{1 - \exp[-nk_1(k_q + k)^{-1}]\}/k_q \quad (18)$$

with $k = k_p$[M]. k_p is the second-order rate constant for the probe migration process. Equation 21 allows the determination of all the decay parameters of eqs 18–20 based on Almgren's expressions:

$$A_2 = k_0 + k\{1 - \exp[-nk_q(k_q + k)^{-1}]\} \quad (19)$$

Table VIII
Rate Constants, Decay Times, and Associated Parameters for the Fluorescence Quenching of Pyrenesulfonic Acid ([PSA] = 10^{-5} M) by HPyCl ([HPyCl] = 1.2×10^{-4} to 3.0×10^{-4} M) in CTAC and CTAC/PVOH-Ac Solutions[a]

	[CTAC] (M)			
	0.007 [PVOH-Ac] = 5 g/L	0.007 [PVOH-Ac] = 10 g/L	0.010 [PVOH-Ac] = 0	0.010 [PVOH-Ac] = 10 g/L
τ_0 (ns)	126	126	120	126
k_q (10^6 s^{-1})	22.6	13.1	13.3	21.7
k (10^6 s^{-1})	8	3.8	1.5	6

[a] Equations 19–21 were used to fit the data.

$$A_3 = n\{1 - k(1 - \exp[-nk_q(k_q + k)^{-1}])/k_q n\}^2 \quad (20)$$

$$A_4 = k_q\{1 - k(1 - \exp[-nk_q(k_q + k)^{-1}])/k_q n\}^{-1} \quad (21)$$

In the present contribution global analysis is applied to a series of single-photon-timing data obtained in a system composed of CTAC/PVOH-Ac/PSA/HPyCl. The probe concentration was 10^{-5} M in these experiments, whereas the mean occupation number for the quenchers in a micelle varied between 1 and 2. Table VIII summarizes the experimentally determined rate constants k_q and k and values for τ_0. The model parameters k_0, k_q, k, and M were linked within the same experimental series and were obtained by simultaneous analysis for four decay curves including the monoexponential decay of a sample identical to the other three but without added quencher. For every CTAC concentration samples with and without added polymer were prepared, and the quencher concentration was adjusted to obtain the same occupation number for the two systems.

The fitting to eqs 19–21 of the fluorescence decay curves recorded using 0.010 and 0.020 M CTAC micellar solutions without added polymer provides statistically acceptable fits, although the low values for k compared to k_q indicate that here the probe migration process can be neglected.

4. Discussion

The addition of nonionic polymer to a surfactant solution induces the formation of aggregates that are characterized by their specific critical aggregation concentrations and aggregation numbers, suggesting more than a simple adsorption of individual surfactant molecules along polymer strands.

An indirect clue to the occurrence of micelles associated with the polymer is given by conductivity measurements. They indicate that the binding of the surfactants to nonionic polymer strands occurs only above a critical concentration of surfactant, which in addition is lower than the cmc value obtained in surfactant solutions without added polymer (Table II). The existence of a critical binding concentration implies that a cooperative process is taking place and cluster formation must be involved.

The chemical shifts of the polymer and surfactant ^{13}C NMR lines provide information on the environment of the nuclei. The experimental results suggest that the micellar concept does not alter upon addition of polymer. The additional NMR signals in the spectra arise from a modification of the distribution of electrical charges around the polar head groups and/or of the average conformation of the first segments of the CTAC molecules. This may be interpreted by a replacement of water molecules by some monomers of the polymer interacting with the detergent/water interface. The observed shifts indicate a perturbation of only the hydrated methylene units and the methyl groups of the polar heads, without experi-

mentally observed penetration of the polymer into the hydrophobic core.

Further evidence for the release of H_2O molecules around the polar head groups of the surfactant upon interaction of the polymer with the micellar surface is given by polarity measurements providing I_1/I_3 values for pyrene in CTAC/PVOH-Ac solutions (Table V). The observed reduced intensity of the forbidden (0,0) vibronic band is indicative of the reduced polar environment of pyrene in the Stern layer. Micelle–polymer complexes obviously provide a less polar environment for solubilisates. This observation may also explain the increase of K values reported in Table VII; a more hydrophobic environment will enhance the solubilization of hydrophobic molecules such as naphthalene. At equal CTAC concentrations a smaller naphthalene fraction will remain in the aqueous phase upon addition of PVOH-Ac to the system. Naphthalene molecules do not interact with PVOH-Ac, as can be deduced from the data listed in Table V. Therefore, the addition of PVOH-Ac to an aqueous solution of Py does not alter the I_1/I_3 values, indicative of the microenvironment of the probe.

In Nagarajan's approach to polymer–micelle complexes the penetration of polymer segments is shown to produce two opposite effects:[29] on the one hand, the area of the hydrocarbon core exposed to water is reduced (lower cmc values, Table II), while on the other hand, the micellar surface area that is excluded for the head groups increases. The resulting increase of the repulsion between the head groups gives rise to the dramatic decrease of the aggregation numbers as observed in the CTAC/PVOH-Ac and CTAC/PPO systems (Tables III).

These two major observations, the decrease of the critical aggregate concentration (Table II) and the lower aggregation numbers (Table III), allow one to state that in the micelle–polymer associations studied in this paper the hydrocarbon core of the complexed aggregate remains unperturbed. Penetration of the polymer into the core would induce an expansion of the micellar interior, as is the case for solubilized alkanes and long-chain alcohols. A previous study[30] demonstrated that the addition of long-chain alcohols (heptanol through decanol) to SDS and DTAC solutions led to a change of the chemical shifts of the ^{13}C nuclei of the surfactant up to C_7. The micellar core, swollen by the incorporation of these hydrocarbon chains, gave rise to a larger micellar surface area, promoting the absorption of more detergent molecules. A drastic increase of the aggregation numbers was observed in these systems. The addition of water-soluble 1-butanol led to a change of the chemical shift of the ^{13}C nuclei of the alkyl chain of SDS up to C_4, and conductivity and time-resolved fluorescence quenching measurements for this system indicated a lowering of the cmc value and a reduction of the aggregation numbers. In the studied CTAC/PVOH-Ac system a decrease of the cmc value (Table II) and the aggregation number (Table III) is observed. These results suggest that only the polar head group region of the micellar surface is affected upon interaction with the polymer segments.

The reduction of the critical micellar concentrations, which can be taken as an indicator of micellar stabilization, fails to be the ultimate criterion to reveal whether polymer–micelle interaction occurs or not, as suggested by other authors:[16] the addition of PPO to CTAX systems hardly affects the cmc value, although the aggregation numbers obtained in this system, presented in Table III, are indicative of strong interactions. It is, however, decisive in one sense: if a reduction of the cmc is observed, it definitely points to association. The addition of PVOH-Ac to CTAX solutions clearly stabilizes the aggregates.

It should be noticed that upon addition of PPO the α values in the various systems are higher (Table II) and the N_{agg} lower (Table III) than in the presence of PVOH-Ac. These two observations are consistent because a stronger binding of the counterions will improve the shielding of the electrostatic repulsion between the head groups. The lower counterion binding observed in CTAX/PPO and CTAX/PVOH-Ac complexes suggests that polymer segments take over the stabilizing effect of the counterions or that they compete with the counterions in shielding the head groups. In accordance with this statement it has been shown that the addition of inorganic salt to complexed micelles has a reduced additional stabilizing effect.[17,31]

Conductivity measurements in CTAC/PVOH-Ac(0.6 g/dL) systems show a second inflection point at 0.009 M CTAC, indicative of the formation of free micelles, whereas viscosity measurements demonstrate that only at 0.040 M CTAC the curve flattens out, indicative of a saturation of the polymer chain with micelles. Both conductivity and viscosity measurements provide "saturation" points that increase proportionally with the polymer concentration. The formation of free micelles in solution seems to occur at surfactant concentrations well below the saturation concentration of the polymer chain.

In solution of 1.0 g/dL of PVOH-Ac (88% hydrolyzed, MW = 110 000), the polymer chain and the polymer unit concentrations are about 1×10^{-4} and 2.2×10^{-1} M, respectively, for 1 polymer chain is calculated to be composed on average of 2200 units, of which 260 are acetate units. The CTAC concentration at the second inflection in the conductivity curve is approximately 1.5×10^{-2} M in the studied system, corresponding to a micellar concentration of 4×10^{-4} M. Consequently, one may estimate that there are at this concentration on the average 4 micelles associated with 1 polymer chain, or 65 acetate units for 1 micelle, or 2 acetate units for 1 detergent molecule. Further addition of detergent molecules induces the formation of "free" micelles in the solution. As viscosity data clearly indicate, the second inflection point at 1.5×10^{-3} M is not indicative of a saturation of the polymer chain, which in fact occurs at a total detergent concentration (micelle–polymer complexes + free micelles) of approximately 0.040 M.

The results presented in Tables II and III indicate that the choice of the counterion (Cl^-, Br^-, ClO_3^-, or NO_3^-) does not play a major role if one attempts to improve micelle–polymer association: the reduction of the cmc values for the different counterions in PVOH-Ac systems is proportional to the reduction of the cmc values in pure surfactant systems. The degree of interaction in these systems seems to be mainly determined by the polymers, penetrating with their hydrophobic segments into the Stern layer where they compete for space with the counterions. Furthermore, in pure micellar systems the choice of the counterion and the detergent concentrations are known to affect largely the aggregation number,[8,33] whereas in the polymer solutions the addition of surfactant seems to increase the number of aggregates rather than their size. Further indication for the hydrophobic polymer segments taking over the stabilizing role of the counterions is given by data on CTAB–NaSal (Sal = salicylate) or CTATs (tosylate) systems[32] in the presence of PVME (poly(vinylmethyl ether)), in which the formation of rodlike micelles does not occur until the saturation concentration of PVME is reached.

The midpoint of the clouding behavior of PPO (32 °C) is raised upon addition of surfactant, just as the viscosity of the solution, because of the electrostatic repulsion between the cationic micelles along the various polymer strands that causes the PPO coils to expand. Although the difference in clouding point for the three counterions is small, one can relate the observed tendency with the values shown in Table II. Lower α values imply stronger counterion binding ($ClO_3^- > NO_3^- > Cl^-$) and consequently a better shielding of the charges on the micelle–polymer complexes, inducing contraction of the extended coils.

A previous study concerning migration of PSA in aqueous CTAC solutions[27] pointed out that only at surfactant concentrations higher than 0.025 M ([M] > 0.00035 M) probe migration has to be taken into account ($k > 10^6\ s^{-1}$). Values of the probe migration constant k are known to depend on the micellar concentration.[27] Consequently, one might expect that the association of several micelles with one polymer chain could affect the migration process because of their vicinity on the chain. The results presented in Tables VI and VII confirm this assumption: the addition of PVOH-Ac to CTAC solutions enhances the migration of PSA. Is this to be explained by structural changes of the micellar surface imposed by the polymer or by their near positioning on one chain? Polarity and solubilization experiments already pointed out the more hydrophobic character of the Stern layer in such micelle–polymer complexes. The results presented in Table VIII point out the major role played by the local concentration of micelles associated to the polymer chain: an increase of the polymer concentration (0.5 → 1.0 g/dL, 0.007 M) induces a redistribution of the micelles among a larger number of chains, and one observes a decrease of the k value ($8.0 \times 10^6 \rightarrow 3.8 \times 10^6\ s^{-1}$). An increase of the surfactant concentration (0.007 → 0.010 M) at a fixed polymer concentration (1.0 g/dL) increases the number of micelles per chain, and the k values increase ($3.8 \times 10^6 \rightarrow 6.0 \times 10^6\ s^{-1}$). The lower k_q value ($1.31 \times 10^7\ s^{-1}$) suggests that an increase of the polymer concentration at fixed surfactant concentration provokes a more restricted mobility on the micellar surface, indicative of a more perturbed environment. k_q values for the fluorescence quenching of 1-MePy by HPyCl in CTAC and CTAC/PVOH-Ac systems are calculated as 14×10^6 and $8 \times 10^6\ s^{-1}$, respectively, although the aggregation numbers decrease from approximately 80 to 30. One might suggest a more restricted mobility of the probe/quencher pair on the perturbed micellar surface or state that not only the outer part of the micelle but an extended micelle–polymer complex has to be considered as diffusion space.

5. Conclusions

The results presented in this paper give further evidence for the topology of a micelle–polymer complex where a polymer chain is wrapped around several aggregates and only disturbs the hydrophobic outer part of the micelles by means of its penetrating segments. The presence of these segments induces the release of H_2O molecules and causes a reduced counterion binding. Consequently, micelle–polymer complexes provide a more hydrophobic environment for solubilisates and are characterized by a lower micellar aggregation number. Due to the presence of associated charged particles the polymer coil expands, and its topology stimulates the migration process among neighboring micelles.

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