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Aggregation of Alkyltrimethylammonium Surfactants in Aqueous Poly(styrenesulfonate) Solutions

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The aggregation of alkyltrimethylammonium surfactants $C_{12}TA^+$ and $C_{16}TA^+$ in dilute water solutions of sodium poly(styrenesulfonate) has been investigated. Aggregation numbers were estimated with the time-resolved fluorescence quenching technique. In the calculations, results from binding isotherms and solubility measurements were used. Binding isotherms for dodecyltrimethylammonium bromide to the polyelectrolyte were determined using a surfactant-selective electrode. The aggregation numbers were found to be independent of the concentration of surfactant and type of counterion, but to increase with increasing surfactant tail length. From the kinetics of the quenching of pyrene fluorescence with hydrophobic and hydrophilic quenchers, it was concluded that compact aggregates with net negative charge were formed, in which the polyelectrolyte is intimately associated with the surfactant. The aggregates are joined by surfactant-free parts of the polyelectrolyte chain, the lengths of which depend on the amount of bound surfactant. The quencher dimethylbenzophenone was found to migrate between the aggregates at the highest concentration of the long-tailed surfactant.

Introduction

The strong interaction between polyelectrolytes and ionic surfactants of opposite charge type has dramatic effects on solution properties and phase behavior.[1-3] At low additions of surfactant to a dilute polyelectrolyte solution a cooperative binding of the surfactant sets in above a critical aggregation concentration, cac, which is lower than the ordinary critical micellization concentration, cmc, of the pure surfactant. The binding has been characterized in a number of systems through measurements with surfactant-sensitive electrodes.[4,5] Most studies of binding and solution properties have been carried out in very dilute systems. Even in these, a precipitate is formed at surfactant concentrations close to charge neutralization. At higher polyelectrolyte concentrations a second, gel-like, liquid phase starts to form and can be separated already at surfactant concentrations much lower than those corresponding to charge neutralization. The phase behavior has been studied in detail recently, both experimentally and theoretically, for some surfactant–polyelectrolyte systems.[6] The interaction is dominated by strong electrostatic effects, and may therefore be tuned down by addition of salt. The cooperativity, however, which emanates from the hydrophobicity of the surfactant alkyl chains, and results in formation of micellar-like aggregates, persists also when the electrostatic effects have been weakened by salt,[5] or by using mixtures of ionic and nonionic surfactants.[7] As is well known, formation of micelles occurs also at concentrations well below the cmc

by anionic surfactants interacting with nonionic polymers like poly(ethylene oxide) (PEO) or poly(vinyl alcohol) (PVA).[8,9]

The aggregation behavior in nonionic polymers has been rather thoroughly studied, e.g., by small-angle neutron scattering (SANS)[8] and fluorescence quenching[10,11] methods. Small aggregates (aggregation number $\langle a \rangle \approx 20$) start to form at the cac, which is about 5 mM in the SDS–PEO system. Further addition of surfactant results in a growth of the bound aggregates, and at a second critical concentration the polymer becomes saturated with surfactant; formation of free micelles starts just after this point. The aggregates formed by SDS at the point of saturation are somewhat smaller than the free ones. Depending on its length, each polymer chain can be associated with many aggregates, and it appears as if the polymer wraps around the aggregates and shields the unfavorable contact between the hydrophobic core of the aggregates and the surrounding aqueous solution.[10]

Much less is known about the aggregates formed in contact with polyelectrolytes. Abuin and Scaiano[12] studied the effect of such aggregates on the photochemical behavior of several probes in aqueous poly(styrenesulfonate) (PSS)–dodecyltrimethylammonium bromide (DoTAB) solutions and found that several small ($\langle a \rangle$ = 7–10) clusters were formed with each polyelectrolyte chain, and that these had a negative surface charge. In contrast, Chu and Thomas[13] reported an aggregation number of 105 (which would be reduced to about 60 if corrected for the concentration of unaggregated surfactant) for decyltrimethylammonium bromide (DeTAB) in poly(methyl acrylate) at pH 8. These polyelectrolytes have high charge densities, and interact stronger with the surfactants.

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Hyaluronan, an anionic polysaccharide with alternating units of glucoronic acid (or its sodium salt) and N-acetyl-glucosamine, is a stiff polyelectrolyte with much lower charge density.[14] Even so it induces aggregate formation at concentrations of DeTAB at about half its cmc.[15] These aggregates, however, are rather unaffected by the presence of the polyelectrolyte, having almost the same aggregation number as free micelles under similar conditions with respect to salt concentration, both in dilute systems and in a concentrated gel phase.[15] Contrary to the PSS–DoTAB system,[12] the bromide counterions remain at a somewhat reduced concentration at the micelle interface.[15]

We have started a systematic investigation of the aggregation behavior of surfactants in polyelectrolytes, characterizing the aggregates with mainly fluorescence methods, in order to get a better understanding of the factors determining the size and structure of the aggregates. This paper deals with alkyltrimethylammonium surfactants interacting with poly(styrenesulfonate). The concentration of surfactant, the length of the alkyl chain, and the counterion have been varied.

Experimental Section

Chemicals. Poly(styrenesulfonate) (PSS) was prepared from polystyrene (Pressure Chemical Corp., molecular weights 37 000 and 860 000 g/mol) by the method of Vink,[16] yielding PSS with approximative molecular weights 67 000 and 1.5 × 10^6 g/mol, respectively. The charge density of PSS is high, one charge per 2.7 Å; i.e., 0.1% w/v PSS corresponds to 5 mM charged units.

The surfactants cetyltrimethylammonium bromide (CTAB) from Serva, cetyltrimethylammonium chloride[17] (CTAC), dodecyltrimethylammonium bromide (DoTAB) from Tokyo Casei Inc., and dodecyltrimethylammonium chloride (DoTAC) from Kodak were all used as supplied. Pyrene (Aldrich) and dimethylbenzophenone (DMBP) (Aldrich, 99%) were twice recrystallized from ethanol. Copper chloride (pa), potassium iodide (pa), and cetylpyridinium chloride (CPC), all from Merck, were used as supplied.

For the preparation of the surfactant ion selective electrode, poly(vinyl chloride) (PVC) (Aldrich), bis(2-ethylhexyl) phthalate (Aldrich), DoTAB (Sigma), CTAB (Serva), sodium dodecyl sulfate, specially pure, (BDH), and tetrahydrofuran (pa) (Merck) were used as supplied.

For the preparation of samples for fluorescence measurements, a certain amount of a stock solution of pyrene in ethanol was evaporated and redissolved in the aqueous surfactant solution, which was mixed with a polyelectrolyte solution to give the desired polyelectrolyte and surfactant concentrations. DMBP was similarly added from an ethanol stock solution, evaporated, and redissolved in a pyrene-containing surfactant–polyelectrolyte solution, to ensure the same pyrene concentration in the two solutions. When CPC was used as quencher, it was simply added from an aqueous stock solution. These new stock solutions were mixed to give the desired concentrations of surfactant, polyelectrolyte, and quencher. The pyrene concentration was kept low enough (<10^-5 M) to prevent excimer formation, and the DMBP or CPC concentrations, usually 3–4 for each surfactant–polyelectrolyte composition, were calculated to be less than or equal to one quencher per cluster. All solutions were allowed to stand for at least 1 day to ensure equilibrium conditions.

For the deoxygenation pure nitrogen was bubbled through the solutions for at least 30 min, prior to the fluorescence measurements.

Binding Isotherms. The free concentration of DoTAB in NaPSS solutions was determined with a surfactant-selective solid-state membrane electrode. The results were used to construct binding isotherms. The electrode membrane was prepared as
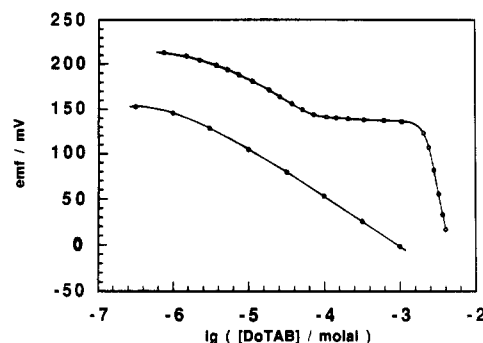
(14) Thalberg, K. Ph.D. Thesis, University of Lund, Lund, Sweden, 1990.

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Figure 1. Emf values in millivolts, given as a function of the logarithm of the DoTAB concentration, log ([DoTAB]/m), from measurements with the DoTAB-selective electrode, in 0.005 m solutions of PSS (as charge concentration), and in 0.01 m solutions of NaCl in distilled water. Open symbols correspond to PSS solutions.
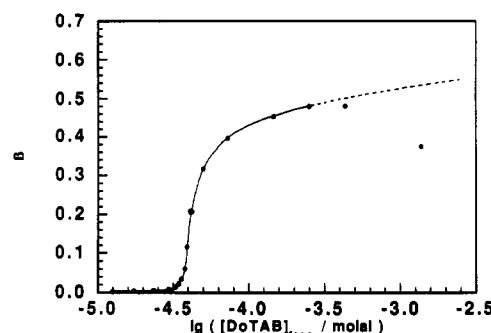

Figure 2. Binding isotherm for DoTAB to PSS. The degree of coverage, β, as defined in the text, is given as a function of the logarithm of the free DoTAB concentration, log ([DoTAB]$_{free}$/m), in solutions of 0.005 m PSS (as charge concentration). The broken line corresponds to the extrapolation described in the text.

described by Hayakawa and Kwak.[4] We used an experimental setup similar to that used by Satake and co-workers,[18] and measured the electromotive force, emf, with a Keithley 177 Microvolt DMM (internal resistance 10 MΩ), at 25 °C. For a check a few measurements were performed using two microvolt meters connected in series. Only a negligible difference in emf was observed, indicating that the internal resistance of the cell was far below 10 MΩ.

In principle, the emf will be the potential difference between a test solution and a reference solution, placed on each side of the membrane. The recorded curves for DoTAB in 5 × 10^-3 m PSS and 0.01 m sodium chloride solution are shown in Figure 1. It is evident from Figure 1 that the polyelectrolyte interacts with the membrane to change the membrane potential. The displacement of the curve in the presence of PSS from the calibration curve without PSS decreased with decreasing PSS concentration and increased added electrolyte, NaCl. To obtain a qualitatively useful binding isotherm (Figure 2), we simply subtracted each of the recorded PSS–DoTAB emf's by 64 mV, corresponding to the difference in emf between the curves with and without PSS, at DoTAB concentrations where no interaction between surfactant and polyion is expected; see Discussion. For DoTAB concentrations higher than 3 × 10^-3 m (log ([DoTAB]$_t$/m) = -2.52), the curve is extrapolated. It is probable that the interaction between PSS and the membrane is reduced at high surfactant concentrations.

Fluorescence Quenching. Time-resolved fluorescence decay data were collected with the single photon counting technique. The setup uses a mode-locked Nd-YAG laser (Spectra Physics Model 3800) to synchronously pump a cavity-dumped dye laser (Spectra Physics Model 375,344S) for the excitation, using DCM as dye, and a KDP crystal for frequency doubling. After frequency

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doubling, the excitation wavelength was 320 nm. The instrument response was less than 500 ps wide and could be treated as a δ-pulse in our experiments, thus allowing evaluation of data without deconvolution. The excitation rate was kept low enough, as compared to the cavity dumper frequency, to prevent pileup problems. The emission wavelength was selected with a double monochromator (Jobin Yvon Model H10), and the pyrene monomer emission was measured at 395 nm. The monochromator was connected to a photomultiplier (Hamamatsu Model R928). The start pulse was obtained from a diode monitoring part of the excitation beam. The emission photon pulses were discriminated in a constant fraction discriminator (Tennelec TC 455) and used as stop pulses in the time to amplitude converter, TAC (Tennelec TC 861A). The output from the TAC was connected via an ADC to a multichannel analyzer, MCA, based on an IBM PS/2. The software for the MCA was purchased from Nuclear Data. In a typical measurement, the number of channels was 512 or 1024 and the width of each channel 1.6 or 3.2 ns. All data analyses were performed on a Digital Equipment Vaxstation 2000 with programs developed from Löfroth's program,[19] according to a generalized model for fluorescence deactivation.[20] The zero time channel, ZTC, was always set to the channel of maximum excitation amplitude, according to the literature.[21]

Fluorescence steady-state spectra were recorded on a SPEX Fluorolog 1680 combined with a SPEX Spectroscopy Laboratory Coordinator DM1B.

Time-resolved fluorescence measurements were performed at 25 and 40 °C, while steady-state fluorescence measurements were performed at 25 °C only.

The method of time-resolved fluorescence quenching in microheterogeneous solutions is well described in the literature.[22] In a generalized version[20] of the equation proposed by Infelta et al.[23] and elaborated on by Tachiya[24]

$$F(t) = A_1 \exp[-A_2 t + A_3\{\exp(-A_4 t) - 1\}] \quad (1)$$

the parameters A_1–A_4 are given by

$$A_1 = F_0 \quad (2a)$$

$$A_2 = k_0 + k_q \langle x \rangle_s \quad (2b)$$

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

$$A_4 = k_q/(1 - \langle x \rangle s/\langle n \rangle) \quad (2d)$$

where F_0 is the fluorescence intensity at time $t = 0$, k_0 is the first-order decay constant, $k_0 = 1/\tau_0$, where τ_0 is the natural fluorescence lifetime, k_q is the first-order quenching rate for one quencher, $\langle x \rangle_s$ is the average number of quenchers in micelles with a surviving excited probe during the stationary part of the fluorescence decay, i.e., for the exponential tail, and $\langle n \rangle$ is the average number of quenchers in a micelle. From $\langle n \rangle$, the average aggregation number, $\langle a \rangle$, is easily obtained:

$$\langle a \rangle = \langle n \rangle S_m/Q_m \quad (3)$$

where S_m and Q_m are the concentrations of aggregated surfactant and quenchers in the micellar phase, respectively.

Due to polydispersity effects, the aggregation numbers calculated from eq 3 should be treated as quencher-averaged aggregation numbers, $\langle a \rangle_q$.[25] The weight-averaged aggregation number, $\langle a \rangle_w$, is related to $\langle a \rangle_q$ by[26]

$$\langle a \rangle_q = \langle a \rangle_w - 1/2\sigma^2 Q_m/S_m + 1/6\kappa[Q_m/S_m]^2 - \ldots \quad (4)$$

where σ^2 is the variance and κ the third cumulant, giving the skewness, of the size distribution of the system.

The natural lifetime, τ_0, was determined in separate experiments without quencher, and the difference between A_w and $1/\tau_0$ is a measure of how well the probe and quencher are stationary during the time window of the quenching experiments. If $\langle x \rangle_s$, depending on this difference, is close to zero, there is no exchange process at hand. The water solubility of DMBP may be significant in solutions with low surfactant concentration, as discussed below.

It should be noted here that the solutions in general were not deoxygenated, which means that the fluorescence was quenched by oxygen dissolved in the solutions. This only affects the decay constant k_0 and does not influence the use of eq 2. The use of eq 2 was further validated by the fact that the fluorescence decay curves from the samples without added quencher all gave straight lines in the logarithmic representation, showing that the presence of oxygen only caused an increase of k_0.

In order to handle an impurity in the preparation of PSS with low molecular weight, which perturbed the initial part of the decay by its fluorescence, a modified version of eq 1 was used, which contained terms representing the weighted contribution of the perturbation:

$$F(t) = A_1 \exp[-A_2 t + A_3\{\exp(-A_4 t) - 1\}] + F_{max}\sum \alpha_i \exp(-k_i t) \quad (5)$$

where the different k_i and α_i values were determined from solutions identical with the samples used for lifetime determinations, but without probe. The determination of the parameters for the perturbing fluorescence was done in two steps. In the first step, the different k_i values were determined with a simple multiexponential fit program, in which the slope at long times was assumed to give k_0. In general only one or two extra exponentials were needed to describe the initial, very short-lived, perturbation, for which the weight factors, α_i, were calculated as

$$\alpha_i = A_i/\sum A_i \quad (6)$$

where A_i is the amplitude for the different exponentials obtained from the fit.

Using eq 5 in the evaluations allowed computer calculations much closer to the ZTC with retention of acceptable statistics and more reliable estimates of the parameters given in eq 2.

Solubility Measurements. The distribution constant, as defined in eq 7, for DMBP between PSS-bound micelles and the aqueous phase, was estimated for DoTAB and CTAB at 25 °C by saturating the solutions with DMBP. We used the procedure

$$K_D = [\text{DMBP}]_{agg}/([\text{DMBP}]_f[\text{surf}]_{agg}) \quad (7)$$

described by Almgren and Alsins,[27] measuring the absorbance at 300 nm on a Varian Cary 2400 spectrophotometer. To calculate the concentrations of aggregated surfactant, [surf]$_{agg}$, in each sample, we used the binding isotherm for DoTAB, also in the case of CTAB. Figure 4 shows a plot of the concentration of DMBP in aggregates at saturtion, [DMBP]$_{agg}$, versus [surf]$_{agg}$. From the slope K_D was calculated, using for the concentration of DMBP in free solution, [DMBP]$_f$, the saturation concentration in water, experimentally found to be 7.82 × 10^{-5} M.

Results and Discussion

Pyrene lifetime and III/I ratios were determined for a number of systems with results as presented in Table I. These results confirm the findings of Abuin and Scaiano,[12] the only exception being that the lifetime of pyrene in aerated PSS is somewhat shorter in our study. The polarity sensed by pyrene, as measured by the III/I ratio,[28] is about the same in the normal micelles as in the PSS–surfactant aggregates, and much smaller than in

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Table I. Fluorescence Lifetimes and III/I Values from Steady-State Fluorescence Measurements at 25 °C with Pyrene as Probe (Lifetimes Were Largely Independent of Surfactant Concentration)

	τ_0/ns	III/I
DoTAB[a]	122	
PSS–DoTAB[b]	251	
DoTAC[a]	184	0.78
PSS–DoTAC[b]	255	0.81
CTAB[c]	120	
PSS–CTAB[b]	259, 358[e]	
CTAC[c]	177, 334[e]	
PSS–CTAC[b]	260, 365[e]	
H₂O	136, 185[e]	0.64
PSS[d]	158	0.61

[a] [surf] = 30×10^{-3} m. [b] [SS⁻] = 5×10^{-3} m; [surf] = 2.5×10^{-3} m. [c] [surf] = 50×10^{-3} m. [d] [SS⁻] = 5×10^{-3} m. [e] Deoxygenated solutions.

water or a PSS solution. The lifetime of pyrene fluorescence is mainly determined by the surface-bound bromide counterions in DoTAB and CTAB micellar solutions. The lifetimes obtained in the presence of the polyelectrolyte are independent of the counterion, however, indicating that the halide counterions are effectively expelled from the cluster surface, even at the highest concentrations of added surfactant. The lifetimes are much longer than those found in DoTAC or CTAC micelles, which means that pyrene in the surfactant–polyelectrolyte clusters is somewhat shielded from oxygen quenching. To verify that the polyelectrolyte exerts a shielding effect upon interaction with the aggregate, measurements were performed on deoxygenated samples, Table I. From these measurements, it is possible to calculate the second-order quenching constants k_{ox} for oxygen quenching and the pseudo-first-order constant k_{br} for bromide quenching, assuming that the estimated deactivation constant, k_{est}, is given by

$$k_{est} = k_0 + k_{ox}[O_2] + k_{br}\theta_{br} \qquad (8)$$

where θ_{br}, the bromide counterion degree of binding to the aggregate surface, is assumed to be 75% and [O₂], the oxygen concentration in air-saturated water, is 5.7×10^{-4} M.[29] The lifetimes for the long-chain surfactant, with and without PSS, given in Table I, give $k_{ox} = 4.7 \times 10^9$ M⁻¹ s⁻¹ in the PSS-free solutions, in excellent accordance with earlier findings.[10] The presence of PSS reduced the second-order constant by 60%, to 1.9×10^9 M⁻¹ s⁻¹, about $1^1/_2$ times more than what was found in the SDS–PEO system.[10] Consequently, the change of the lifetime on deoxygenation is smaller in the present systems than in the SDS–PEO system.

Turning to the quenching due to bromide counterions, the first-order constant is found to be 3.5×10^6 s⁻¹ for CTAB micelles, again in agreement with earlier findings.[15] It is also evident that in principle all bromide counterions are replaced by the PSS sulfonate groups, as the lifetimes in deoxygenated solutions are the same whether the counterion is bromide or chloride. The lifetimes for pyrene in pure CTAC micelles and PSS-bound CTAC aggregates, however, differ in the deoxygenated solutions. We attribute this to the benzene ring of PSS, which may cause a stabilizing effect on the pyrene excited state, as have been suggested by others for a similar system.[30]

In addition, the long lifetimes indicate that the impurity in PSS has no effect on pyrene in the micelles.

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Binding Isotherms. The free concentrations of surfactant in the PSS solutions were potentiometrically determined with a surfactant-selective electrode. As shown in Figure 1, a linear response is detected for DoTAB in a 10×10^{-3} m NaCl solution, as represented on a logarithmic scale, with deviations only at very low concentrations. At low DoTAB concentrations where no interaction with the polyion occurs, the response should ideally be the same whether polyion was present or not. This is not the case for PSS. The measured emf values are larger than what is possible to detect in PSS free systems of DoTAB, at comparable ionic strengths. A similar shift also occurs in surfactant-free PSS as compared to the response for an aqueous solution of NaCl at similar ionic strength. The emf shift increases with the PSS concentration, and is reduced on addition of salt (NaCl). One explanation could be that some of the PSS chains bind to the membrane surface, thereby reducing its potential, which allows more of the cationic surfactants in the reference solution to solubilize in the membrane. Hence, a larger emf is observed.

Under these circumstances a reliable quantitative use of the electrode seems impossible. Qualitatively, we can extract some results from the following assumptions: (1) There is no interaction of the surfactant with PSS at very low concentrations of DoTAB. (2) The emf shift, due to the polyion, is constant when the free concentration of DoTAB is low. These assumptions allow us to subtract the emf shift from the measured values. At high concentrations of free DoTAB this subtraction would result in a binding isotherm with negative slope, which is highly improbable. In this region, therefore, we extrapolated the curve, with careful use of binding isotherms from Hayakawa and Kwak.[4] When the free concentration of DoTAB starts to increase rapidly, at the point where the polyion is saturated with surfactant, bound PSS probably desorbs from the membrane.

The binding isotherm, calculated from the results in Figure 1, is shown in Figure 2. The degree of binding, β, is defined as $\beta = [\text{surf}]_b/[\text{SS}^-]$, where $[\text{surf}]_b$ is the concentration of surfactant bound to the polyion and $[\text{SS}^-]$ is the concentration of polyion monomers. Hayakawa and Kwak[4] have studied and thoroughly described the binding of DoTAB to PSS at low concentrations of the polyion, 5×10^{-4} m, in the presence of sodium chloride. The complication encountered in our determinations stem from the necessity to estimate the amount bound in salt-free systems at 5×10^{-3} m PSS.

It is evident from Figure 2 that for β values up to 0.45 there is still very little free surfactant in solution, although the binding is no longer cooperative. We note, in agreement with the results of Hayakawa and Kwak, that the binding is cooperative only at low β. At higher β than about 0.2 the binding becomes more and more noncooperative, probably due to neutralization of polyion charges when the chain wraps around the micelles.

The use of the DoTAB binding isotherm for CTAB can lead to an underestimation of β at low surfactant concentrations, since CTAB is expected to interact more strongly with PSS than DoTAB. Anyhow, even for DoTAB, the unbound part is very low for $\beta < 0.45$.

Aggregation Numbers and Number of Micelles per Chain. In the determination of the aggregation numbers from the time-resolved fluorescence quenching data, with DMBP as quencher, representative examples of which are shown in Figure 3, the correction for the impurity fluorescence seemed to work well. The primary results from fittings to the model given in eq 5 are values of $\langle n \rangle$,
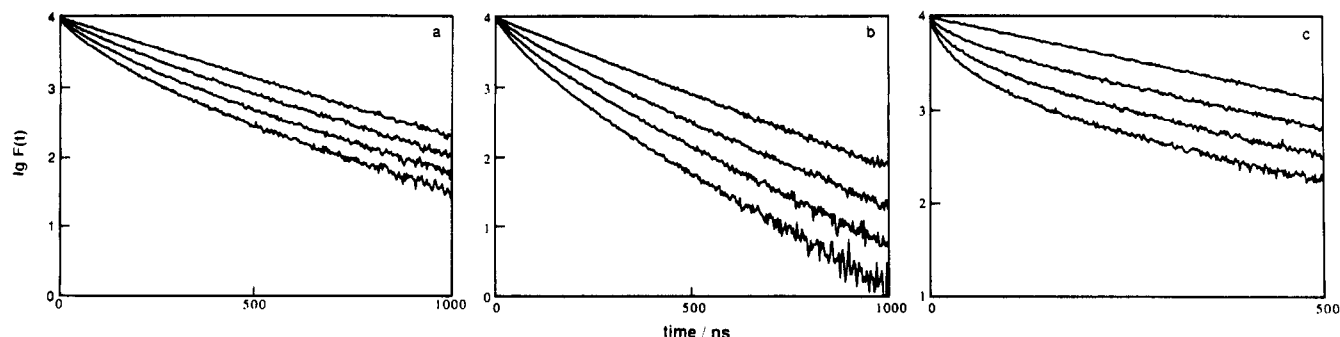
Figure 3. Fluorescence decays with time in nanoseconds on the horizontal axis and the logarithm of the fluorescence intensity on the vertical axis. The PSS concentration is 0.005 m (as charge concentration), and the quencher is DMBP in all examples. (a) 2.50 $\times 10^{-3}$ m CTAB ($\beta = 0.47$; β is defined in the text) at 25 °C with DMBP concentrations (10^{-3} m) from top to bottom: 0, 0.034, 0.076, and 0.10, long time scale. (b) 3.75 $\times 10^{-3}$ m CTAB ($\beta = 0.54$) at 40 °C with DMBP concentrations (10^{-3} m) from top to bottom: 0, 0.033, 0.064, and 0.10, long time scale. (c) 2.57 $\times 10^{-3}$ m DoTAB ($Q_c = 0.48$) at 25 °C with DMBP concentrations (10^{-3} m) from top to bottom: 0, 0.068, 0.13, and 0.20.
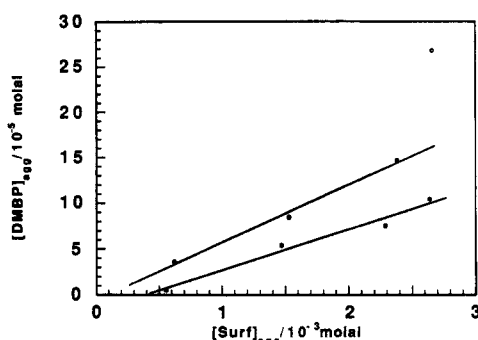

Figure 4. Solubility measurements. The concentration of DMBP in aggregates, [DMBP]$_{agg}$, is plotted against the concentration of aggregated surfactants, [surf]$_{agg}$, for DoTAB (●) and CTAB (O) in 0.005 m solutions of PSS. The concentration of DMBP in aggregates was estimated spectroscopically from saturated PSS–surfactant solutions of DMBP.

k_q, and $\langle x \rangle_s$. The latter two quantities report on the dynamics of the quenching process and will be discussed below. From $\langle n \rangle$ one obtains the concentration of aggregates in the solution, eq 3, or the mean number of clusters per polymer chain. In the calculation of the aggregation numbers, the amount of surfactant participating in the aggregation has to be known. In principle a significant part of the surfactants could be bound as monomers to the polyelectrolyte. Even though the binding isotherms indicate a cooperative process, it is not possible to conclude whether all the bound surfactant is aggregated or not. The III/I vibronic peak ratios from pyrene steady-state fluorescence spectra give information about the environmental polarity as sensed by probe,[28] and might thus be used to determine the cac of the system, and to further prove the cooperativity in the binding process, but do not give information on the amount or state of nonaggregated surfactants. All reported aggregation numbers in this work are estimated for solutions where the cooperative binding has started. We have considered all bound surfactant as aggregated.

Aggregation numbers for surfacant in PSS and water solutions, as calculated from eqs 3 and 4, are reported in Table II. Those calculated from eq 3 are quencher averaged, $\langle a \rangle_q$, and were all estimated at the same quencher to surfactant ratio. The aggregation numbers for DoTAB and DoTAC are in good agreement with values reported by De Schryver et al.,[31] whereas those for CTAB and CTAC are somewhat larger.

(31) (a) Roelants, E.; De Schryver, F. C. *Langmuir* **1987**, *3*, 209. (b) Reekmans, S.; Luo, H.; van der Auweraer, M.; De Schryver, F. C. *Langmuir* **1990**, *6*, 628.

Table II. Quencher-Averaged, $\langle a \rangle_q$, and Weight-Averaged, $\langle a \rangle_w$, Aggregation Numbers from Time-Resolved Fluorescence Quenching Measurements[a] Given Together with the Polydispersity Indices, $\sigma/\langle a \rangle_w$, for Various Solutions at 25 °C

	[surf][b]	[surf]$_b$[b]	β^c	$\langle a \rangle_q$	$\langle a \rangle_w$	$\sigma/\langle a \rangle_w$
PSS^d–DoTAB	1.27	1.22	0.25	37	41	0.27
	1.74	1.68	0.36	35		
	2.57	2.38	0.48	37	39	0.25
	2.85	2.49	0.50	38		
	3.25	2.60	0.52	41		
	3.61	2.67	0.53	43	52	0.53
DoTAB	50.0	35.0			65	0.62
PSS^d–DoTAC	2.50	2.35	0.47		37	0.22
DoTAC	50.0	29.0			57	0.78
PSS^d–CTAB	0.52	0.51	0.10	79		
	1.25	1.21	0.24	71	86	0.23
	1.90	1.86	0.37	66		
	2.50	2.34	0.47	59	64	0.27
	2.86	2.51	0.50	64		
	3.25	2.61	0.52	69	80	0.34
	3.75	2.69	0.54	63	76	0.42
CTAB	30.0	29.2			146	0.35
PSS^d–CTAC	2.50	2.35	0.47		53^e	0.25
CTAC	30.0	28.7			110	0.42

[a] With pyrene as probe and DMBP as quencher. [b] Total concentration of surfactant, [surf], and PSS-bound concentration of surfactant, [surf]$_b$, 10^{-3} m. [c] β = [surf]$_b$/[SS$^-$]. [d] [SS$^-$] = 5 $\times 10^{-3}$ m. [e] The corresponding value from short-time measurements on PSS–CTAB is $\langle a \rangle_w$ = 49.

When PSS is present the aggregation numbers are reduced to about half the values for free micelles. CTAB still forms larger aggregates than DoTAB. Thus, the surfactant chain length plays an important part even when aggregates are formed at the polyion. The counterion is of no importance for the aggregation numbers in PSS solutions, as illustrated by the values for DoTAC and CTAC, as expected due to the replacement of the normal counterions by the negatively charged polyion monomers.

A measurement on PSS–DoTAB, at 5 $\times 10^{-3}$ m PSS and 2.5 $\times 10^{-3}$ m DoTAB, using the cationic surfactant CPC as quencher, gave an aggregation number of 30. In this case, the final slope of the decay never reached single exponential behavior at 25 °C, because of the very low quenching rate within the aggregates. This results in an underestimation of the aggregation number.

For the PSS–DoTAB system there is no pronounced change in the aggregation number with the degree of coverage, β, and the apparent slight decrease for PSS–CTAB may be conicidental. Migration of the quencher at high β's, to be discussed later, and the fact that a separate binding isotherm for CTAB never was recorded, are contributing error factors. It is even possible that free

CTAB micelles are formed at the largest β, since its critical micelle concentration is about 0.85 mM. Anyway, all aggregation numbers, except for the one at the lowest β, lie between 59 and 71, almost twice the values for PSS–DoTAB.

Precise determinations of the polydispersity index require a long series of measurements with varying quencher concentrations. From the values of $\sigma/\langle a \rangle_w$ given in Table II, it may only be concluded that the size polydispersity of the bound aggregates is not larger than that of the free micelles. A small polydispersity is consistent with the concentration-independent size of the bound aggregates.

Abuin and Scaiano[12] estimated the aggregation number for PSS–DoTAB at 28 mM PSS and 14 mM DoTAB. From triplet quenching measurements, using Xanthone as probe and 1-methylanthracene as quencher, they reported an aggregation number on the order of 7–10. Although our study was performed at lower concentrations, their value seems very small. They used the relation $I = I_0 e^{-\langle n \rangle}$, proposed by Turro and Yekta,[32] where I_0 and I are the observed luminiscence intensities, without and with quencher present, respectively. $\langle n \rangle$ is the average number of quenchers in a micelle. As will be discussed below, we found that, for quenching of pyrene with DMBP or CPC, the pseudo-first-order quenching rate constant was quite small. Hence, the observed initial intensities from a quenched triplet decay, as used by Abuin and Scaiano, may have contributions from micelles with both probe and quencher. We have also found that DMBP shows a surprisingly poor solubility in the PSS–surfactant aggregates. Both aspects have to be considered in aggregation number determinations.

The overall picture will still be, as suggested by Abuin and Scaiano, an "aggregate of aggregates". The number of aggregates per polyion chain increases with increasing β, finally to level off at the highest β's, where a large cluster of aggregates is formed on each chain.

The distribution constant for DMBP between the hydrophobic subphase of the aggregates and the aqueous phase was estimated at 25 °C, in 5×10^{-3} m solutions of PSS. From Figure 4, the constants were calculated as 5.7×10^2 and 7.9×10^2 m^{-1} for PSS–DoTAB and PSS–CTAB, respectively. (In the CTAB case, one point was omitted. It corresponds to the highest CTAB concentration used, where we suspect coexistence of free and PSS-bound micelles.) Compared to the values for free surfactant micelles, for instance 5403 M^{-1} for CTAC and 2994 M^{-1} for SDS at 25 °C,[33] the solubility is very low when PSS is present. This could in part be a size effect, as the solubilization power in general decreases with the micelle size,[34] but it is probably also due to the fact that the polyion occupies the interfacial region of the aggregate where the solubilization mainly occurs. Ring-current effects in NMR chemical shift measurements[35] on PSS–DoTAB indicate that the first two methylene groups, next to the surfactant head, are positioned above the PSS phenyl groups. A typical aggregate can be visualized as having a surface made up from surfactant head groups surrounded by polyion charges in such a way that some of the phenyl groups are embedded in the interface. In normal cationic micelles, solubilized molecules like arenes are preferentially positioned at or near the interface.[34] Since these "sites"

to a large extent would be occupied by the phenyl groups of the polyion, the solubility is decreased, and the guest molecules would be more restricted to the inner parts of the aggregate core. The retreat from interfacial solubilization sites also explains the shielding against quenching by oxygen from the surrounding aqueous solution.

The fact that the difference in aggregation numbers between DoTAB and CTAB remains in the aggregates bound to the polyion suggests that the main driving force for the aggregation is the same as in the formation of micelles. Thalberg and Lindman, discussing the subject generally in a recent review,[36] suggested that the polyion has to adapt to the micelles, not the opposite. In the case of Hyaluronan, a stiff, hydrophilic polyion, the micelle formation can be envisioned as being induced by the concentration of the cationic surfactant molecules in the vicinity of the polyanion so that the local concentration exceeds the cmc, and normal micelles form. In the case of PSS, however, the polyion has a much more intimate influence due to interactions of the surfactant or surfactant aggregates with the hydrophobic backbone of PSS. The insertion of the polyion between the surfactant head groups at the interface must clearly hinder an extensive micellar growth.

The packing problems can be illustrated from a simple calculation based on the determined aggregation numbers. Using an average aggregation number of 38 for the DoTAB aggregates, and assuming that the surfactant tails are packed into a spherical hydrophobic core, a hydrophobic radius of 14.8 Å is found (assuming a volume contribution of 357 Å^3 per C$_{12}$ tail). The available interfacial area per surfactant head group is 72.4 Å^2, and the (equatorial) circumference is 93 Å. For CTAB aggregates with an aggregation number of 67, the hydrophobic radius would be 19.5 Å (volume per tail 469 Å^3), the area per head group 71.3 Å^2, and the circumference 123 Å. The fact that the available area per surfactant is similar in the two cases gives some credibility to the calculation, and the large value would allow polyion segments to be present at the surface. The circumference of the assumed spherical aggregates should be compared with the length of polyion required to neutralize the charges, about 103 Å for DoTAB and 181 Å for CTAB. This comparison suggests some packing problems, such that a length much longer than that corresponding to charge neutralization is required to comfortably wrap the polyion chain around the aggregate. The length of the remaining parts of the polyion, which link the successive aggregates, is then correspondingly reduced.

Quenching Constant and Interaggregate Migration of DMBP. The first-order quenching constant, k_q, and the values for $\langle x \rangle_s / \langle n \rangle$ are given in Table III. In spite of the low aggregation numbers, the quenching constants are much smaller in the PSS–surfactant aggregates than in the free micelles. The mobilities of the probe and quencher are thus strongly reduced, reflecting a less fluid environment in the bound aggregates than in free micelles. This is in accordance with the findings of Gao et al.[37] in a recent ^{13}C NMR relaxation study of the correlation time profile for the fast motion of the alkyl carbons of DeTAB. The correlation times were found to be much longer in PSS–DeTAB aggregates than in the free micelles. The effect on the quenching rate was even more pronounced with the cationic surfactant CPC as quencher, probably

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(33) Dr. Jan Alsins, private communication.
(34) Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 2021.
(35) Gao, Z.; Kwak, J. C. T.; Wasylishen, R. E. *J. Colloid Interface Sci.* **1988**, *126*, 1, 371.

(36) Lindman, B.; Thalberg, K. In *Polymer–Surfactant Interactions*; Goddard, E. D., Ananthapadmanabhan, K. P., Eds.; CRC Press: Boca Raton, FL, Chapter 6, in press.
(37) Gao, Z.; Wasylishen, R. E.; Kwak, J. C. T. *J. Phys. Chem.* **1990**, *94*, 773.

Table III. First-Order Quenching Rate Constants, k_q, and the Exchange Measure, $\langle x \rangle_s/\langle n \rangle$, from Time-Resolved Fluorescence Quenching Measurements (All Concentrations etc. as in Table II)
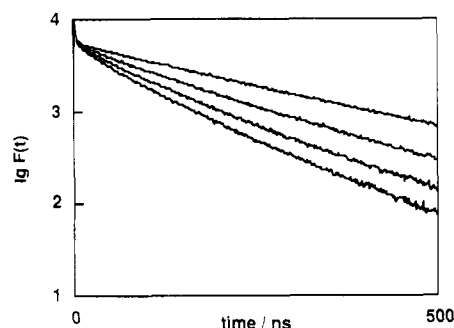
	β	$k_q/(10^7\ s^{-1})$	$\langle x \rangle_s/\langle n \rangle$
PSS–DoTAB	0.25	1.5	0.02
	0.36	1.4	~0
	0.48	1.5	0.02
	0.50	1.4	0.02
	0.52	1.4	0.03
	0.53	1.5	0.04
DoTAB		3.9	0.01
PSS–DoTAC		2.1	0.01
DoTAC		5.2	0.01
PSS–CTAB	0.10	0.9	0.03
	0.24	0.5	0.08
	0.37	0.6	0.07
	0.48	0.5	0.05
	0.50	0.5	0.04
	0.52	0.5	0.03
	0.54	0.5	0.23
CTAB		1.0	0.02
PSS–CTAC		1.0	0.10
CTAC		1.7	0.01

due to the fact that CPC also may be restricted in its motions by the electrostatic interaction with the polyion. For DMBP there is no change in quenching rates with β, as expected from the constant aggregation numbers.

The $\langle x \rangle_s/\langle n \rangle$ values in Table III report on the migration behavior of the quencher during the lifetime of the probe. (The probe pyrene is not expected to migrate.) In PSS–DoTAB systems no migration of DMBP was detected. Some migration seems to occur in the PSS–CTAB system even at low β values. At the highest β, migration, i.e., exchange of DMBP between aggregates, was obvious; see also Figure 3b. What we observe is probably interaggregate exchange of DMBP between aggregates bound to the same PSS chain. It is interesting that no such migration was observed in the PSS–DoTAB system. The reason for this difference is probably to be found in the different packing conditions for the small DoTAB aggregates compared to the much larger CTAB aggregates, as discussed above.

In systems where the first-order quenching rate is low, it is very important to make sure that the fluorescence decays show well-developed exponential tails. Thus, the choice of time scale for the experiments is decisive. For PSS–DoTAB and for the free micelle systems in this investigation, the time window 0–500 ns was enough. For PSS–CTAB it was not possible to conclude if migration was present or not after 500 ns. Extention of the time window to 0–1000 ns was necessary to observe single-exponential tails. With CPC as quencher in the PSS–surfactant solutions, increase of the temperature to 40 °C increased the quenching rate sufficiently to show that migration was insignificant. On the other hand, increasing the temperature in the PSS–CTAB system with DMBP as quencher made the migration more obvious.

Quenching by Ionic Quenchers. Several cations, e.g., Cu^{2+}, are known as good quenchers of pyrene fluorescence[38,39] in anionic micelles, and I^- strongly quenches pyrene in cationic micelles.[30] In the PSS–surfactant clusters pyrene was completely shielded against iodide quenching, whereas cupric ion was very effective as quencher. The decay curves and the Stern–Volmer plots, as illustrated in Figures 5 and 6, respectively, show great similarities between the quenching in PSS–DoTAB and

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(39) Almgren, M.; Linse, P.; van der Auweraer, M.; De Schryver, F. C.; Geladé, E.; Croonen, Y. *J. Phys. Chem.* **1984**, *88*, 289.

Figure 5. Fluorescence decay curve for CTAB–PSS (0.005 *m* as charge concentration) at $\beta = 0.47$ (β as defined in the text) at 25 °C and with Cu^{2+} as quencher. The quencher concentrations are from top to bottom ($10^{-3}\ m$): 0, 0.056, 0.094, and 0.15.
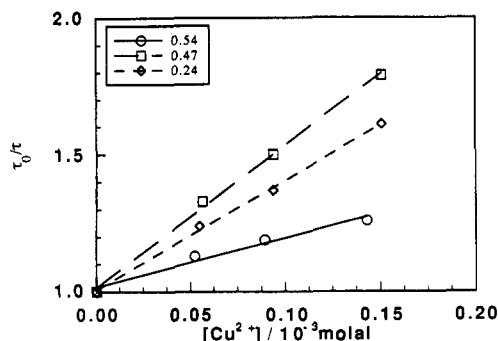
Figure 6. Stern–Volmer plots for CTAB–PSS (0.005 *m* as charge concentration) with Cu^{2+} as quencher at various β's (as defined in the text) and 25 °C. The inset legend shows the different β values.

that in PSS–CTAB. The cationic quencher is attracted to the "multicluster" with net negative charge formed by surfactant and polyelectrolyte. The quenching is strongest at the intermediate surfactant concentration. To understand this we have to consider the distribution of the quencher within the system. It is probably found close to the surfactant-free polyelectrolyte segments, with high charge density, that join the aggregates. These segments are longer and keep the divalent positive ions stronger at the lower surfactant concentration. When the surfactant concentration is increased, more of the polyion is involved in aggregates. The quenchers become more evenly distributed over the still highly negative charged multicluster. A the highest surfactant concentration, however, the free surfactant concentration is large, and the electrostatic effects are more shielded so that an appreciable fraction of the divalent quencher ions become free.

When Cu^{2+} is employed as quencher for pyrene in normal anionic micelles, an Infelta type of decay is obtained with a pronounced initial decay which stems from deactivation in micelles with "bound" quenchers, i.e. from those micelles which have a quencher ion close to the surface at the moment of excitation. No such initial stage can be seen in the decay curves for pyrene in the PSS–surfactant clusters; these decays are smoothly curved (in the logarithmic representation) over the whole time range, Figure 5. The absence of the fast initial stage is again likely a consequence of the fact that the quencher ion is more strongly attracted to the surfactant-free segments between the aggregates. As discussed above, the individual aggregates within the multicluster have presumably also a negative surface charge from an excess of PSS segments directly involved in the aggregates. Therefore, no large barriers for approach to the aggregate surface seem to exist. The nonexponential decay could be reminiscent of the fact that the divalent ion is free to diffuse in a restricted

volume, which is mainly extended in one dimension.[40] Measurements over longer time are required for quantitative evaluation of the decays.

Conclusions

The results from this study support the general picture proposed by Abuin and Scaiano. Several aggregates are formed at each polyelectrolyte chain and linked by polyelectrolyte segments. The surface charge of the cluster as a whole is determined by the polyelectrolyte. The aggregates, in view of aggregation numbers of surfactant in 5×10^{-3} m PSS solutions, are smaller than in the corresponding pure surfactant systems, but the size difference between DoTAB and CTAB is maintained. Interaction of surfactant with polyelectrolyte and formation of aggregates start at surfactant concentrations far below the cmc. The aggregation numbers do not change with increasing surfactant concentration; instead, more aggregates are formed at each polyelectrolyte chain. Only a restricted number of aggregates can be formed at each chain. The aggregates are more densely packed than normal micelles, due to inclusion of PSS segments. As a consequence, the solubility of aromatic compounds is comparatively poor. At high concentrations of CTAB, migration of DMBP between aggregates is observed during the lifetime of the probe, an indication of the fact that the aggregates are gathered together in clusters.

We conclude that the use of time-resolved fluorescence quenching gives valuable information about surfactant assemblies of this kind. It is very important, though, to estimate the distribution of quenchers and surfactants between the subphases in the system, and to use proper time scales in the measurements.

Registry No. DMBP, 54323-31-8; NaPSS, 9080-79-9; CTAB, 57-09-0; CTAC, 112-02-7; DoTAB, 1119-94-4; DoTAC, 112-00-5; CPC, 123-03-5; Cu, 7440-50-8; pyrene, 129-00-0.

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