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ORIGINAL CONTRIBUTION

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Interaction of cetyltrimethylammonium bromide and poly(2-(acrylamido)-2-methylpropanesulfonic acid) in aqueous solutions determined by excimer fluorescence

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Abstract The binding interaction of the cationic surfactant cetyltrimethylammonium bromide (CTAB) and anionic poly(2-(acrylamido)-2-methylpropanesulfonic acid) (PAMPS) in dilute aqueous solutions was studied using the excimer fluorescent emission of the cationic probe 1-pyrenemethylamine hydrochloride (PyMeA·HCl). In the absence of CTAB, the saturation binding of $PyMeAH^+$ on PAMPS is about 2.4 AMPS repeat units for one probe cation as determined by the relative emission intensity, I_E/I_M, of the excimer to monomer. With increasing CTAB concentration, I_E/I_M firstly increases, reaches a maximum, then decreases to zero. The I_E/I_M maximum indicates a critical aggregation concentration (cac) of 10^{-5} mol/l for CTAB in PAMPS solutions. The CTAB concentration at which I_E/I_M is zero is exactly equal to the PAMPS concentration, indicating that the probe cation is thoroughly excluded from the binding site of PAMPS by the CTAB cation and the equivalent stoichiometric aggregation is formed between CTAB and PAMPS. The blueshift of the excimer emission and the excitation spectra shows that the decrease of I_E/I_M with increasing CTAB concentration above the cac is caused mainly by the decrease of the static excimer.

Key words Polyelectrolyte · Surfactant · Cationic pyrene probe · Critical aggregation concentration · Excimer

Introduction

Recently, the binding process and the complex structure of surfactants with oppositely charged polyelectrolytes have being intensively studied owing to the fundamental and application interests [1, 2]. The surfactant concentration required for polyelectrolyte-bound surfactant to aggregate is referred to as the critical aggregation concentration (cac). The cac is always lower than the critical micelle concentration (cmc) for the same surfactant in polymer-free solutions. The effect of the ionic strength, the charge density of the polyelectrolyte, and the chemical nature of both surfactant and polymer on the binding equilibrium and cooperative parameters has been investigated [3, 4, 5].

Fluorescence techniques are powerful in determining the cac value and the aggregation number for polyelectrolyte–surfactant binding [6, 7, 8, 9, 10, 11, 12, 13]. The pyrene chromophore is frequently used for this purpose owing to its special photophysical properties and high efficiency of excimer formation [14, 15]. Chu and Thomas [7] reported the cac for decyltrimethylammonium bromide in dilute poly(methacrylic acid) solution estimated from the intensity ratio I_1/I_3 of the first emission peak to the third one of the pyrene probe and found micellelike aggregation consisting of about 100 surfactant molecules in one cluster. On the other hand, Chandar et al. [8] adopted the emission intensity ratio I_E/I_M of excimer to monomer of pyrene labeled on poly(acrylic acid) (PAA) to investigate the aggregation

of dodecyltrimethylammonium bromide (DTAB) as a function of pH. Oliveira et al. [16] showed from the fluorescence of the pyrene probe that the increase in the content of the hydrophobic moiety of ethyl methacrylate in an acrylic acid–ethyl methacrylate copolymer favored surfactant aggregation at low surfactant concentration. The pyrene group, however, does not only report the aggregation occurrence but also organizes hydrophobic aggregates for its high hydrophobicity. For example, pyrene labeled on PAA reported a lower cac than the free pyrene probe for binding [8].

The use of ionic derivatives of pyrene can overcome the defect mentioned previously. These ionic probes are dispersed in water individually as the result of electrostatic repulsion and hydrophilic interaction of the ionic groups. They can be used to detect the microenvironment surrounding oppositely charged polyelectrolytes by direct binding upon electrostatic attraction. The binding of ionic derivatives of pyrene to polyelectrolytes of the opposite charge has recently been demonstrated [17, 18, 19, 20, 21]. Caruso et al. [21] investigated the influence of polyelectrolyte charge density and polyelectrolyte flexibility on probe binding recently. Through the measurement of the emission ratio, I_E/I_M, of the probe excimer to monomer, the amount of probe electrostatically bound to the polyelectrolyte and hence the binding stoichiometry at saturation binding can be determined. On the basis of this principle, Caruso et al. [22] also investigated the electrostatic interaction in polyelectrolyte multilayer films by ionic derivatives of pyrene and obtained some results which were very different from the classical consideration that 1:1 stoichiometry of anionic and cationic groups should be maintained in the polyelectrolyte multilayers [23, 24]. In addition, the binding of other ionic probes, such as 6-carboxyfluorescein [22] and 2-(*p*-toluidino)-6-naphthalene sulfonate (TNS) on polyelectrolytes has been reported [25]. Dahlberg et al. [26] used the TNS binding result to research the flocculation reaction of cationic potato amylopectin and nanosized silica particles.

In this work, we firstly investigated the binding of a cationic pyrene probe, 1-pyrenemethylamine hydrochloride (PyMeA·HCl), on a strong polyelectrolyte, poly(2-(acrylamido)-2-methylpropanesulfonic acid) (PAMPS), then followed the interaction change and aggregation formation of a cationic surfactant, cetyltrimethylammonium bromide (CTAB), on PAMPS using this fluorescence probe.

Materials and methods

Materials and PAMPS sample

The ionic monomer 2-acrylamido-2-methylpropanesulfonic acid (AMPS, Fluka) and the cationic fluorescence probe PyMeA·HCl (Aldrich) were used without further purification. CTAB was recrystallized from methanol. The other reagents were all obtained from commercial sources and were purified according to standard procedures. Highly pure water was obtained by deionization and filtration with a Millipore purification apparatus.

AMPS was radically polymerized in water at 70 °C for 16 h under a nitrogen atmosphere with stirring, using 0.2 mol% ammonium persulfate as the initiator. The total monomer concentration was 0.46 mol/l. The product was dialyzed for 2 weeks against distilled water to thoroughly remove impurities. The dialyzed solution was condensed, freeze-dried and finally vacuum-dried at 60 °C to give sulfonate polyelectrolyte sample, PAMPS.

Fluorescence measurement

For measuring the fluorescence spectra of pyrene in polyelectrolyte–surfactant solutions, concentrated aqueous solutions of PAMPS, CTAB, and PyMeA·HCl were prepared, respectively. Then, desired amounts of each concentrated solution were added into a volumetric flask and diluted to the test concentration. The polyelectrolyte concentration is expressed by the molar concentration of the repeat unit AMPS.

Steady-state fluorescence spectra of the probe PyMeA·HCl were recorded with a Hitachi F-4500 fluorescence spectrometer. The excitation wavelength was 340 nm. The slit width for excitation and emission was 2.5 nm. All solutions were kept for more than 12 h to ensure the binding equilibrium. They were stirred for 1 min prior to recording the spectrum. All measurements were performed on air-equilibrated solutions at 25 °C. I_E/I_M is defined as the ratio of the intensity of the excimer emission (480–490 nm) to that of the monomer emission (395 nm).

Results and discussion

Binding of PyMeA·HCl onto PAMPS

In water, the probe molecule PyMeA·HCl ionizes into a cation probe $PyMeAH^+$ and Cl^-. $PyMeAH^+$ can bind on the anionic polyelectrolyte PAMPS by electrostatic attraction. In order to probe the aggregation of CTAB on PAMPS, we firstly studied the binding of the probe cation $PyMeAH^+$ on PAMPS. The emission spectra of PyMeA·HCl (5×10^{-6} mol/l) without PAMPS (curve A) and with PAMPS (curves B, C) in aqueous solution are shown in Fig. 1. PyMeA·HCl in water (curve A) exhibits the characteristic monomer emission with four peaks at 375, 380, 386, and 395 nm and a shoulder at 415 nm. Up to a PyMeA·HCl concentration of 1×10^{-4} mol/l there is no sign of excimer formation (It will be shown in Fig. 5) owing to the electrostatic repulsion between the probe cations. The presence of PAMPS (1×10^{-4} mol/l, curve B) causes a reduction in the monomer intensity and induces a typical pyrene excimer emission as the broad, structureless band centered around 490 nm. This is due to the binding of $PyMeAH^+$ on the polyelectrolyte, which results in an increase in the local concentration of the probe chromophore along the polymer chain and promotes the excimer formation and fluorescence quenching. At a high PAMPS concentration (2.5×10^{-3} mol/l, curve C), the probe cation can be

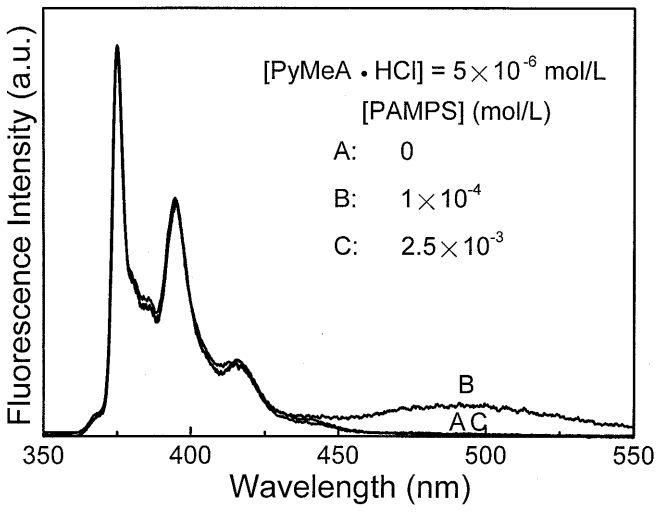

Fig. 1 Emission spectra of the cationic probe 1-pyrenemethylamine hydrochloride (*PyMeA·HCl*) (5×10^{-6} mol/l) in aqueous solutions without poly(2-(acrylamido)-2-methylpropanesulfonic acid) (*PAMPS*) (*A*) and with PAMPS (*B*, *C*) normalized at 375 nm

redistributed along the polymer chain owing to the increased number of available binding sites, sulfonate groups, in the polymer. This is evidenced by a decrease in the intensity of excimer emission.

The dependence of I_E/I_M on the PyMeA·HCl concentration at a given PAMPS concentration of 4.8×10^{-5} and 1×10^{-4} mol/l is shown in Fig. 2. Firstly, I_E/I_M increases with the increase in the probe concentration because more probe cations are provided for binding on PAMPS chains to form more excimers. At the maximum of I_E/I_M, the binding of PyMeA·HCl on PAMPS is saturated. Then, I_E/I_M decreases with a further increase in the probe concentration, since excess PyMeA·HCl is dissolved in water, leading to an increase in the emission intensity, I_M, of the monomer. The maximum value for the probe to be bound on a polyelectrolyte chain (i.e., saturation binding) can be estimated from the probe concentration corresponding to the I_E/I_M maximum. From Fig. 2, one can determine that the number of AMPS repeat units corresponding to the binding of one $PyMeAH^+$ probe cation is about 2.4 at the saturation binding on PAMPS. This fact indicates that the binding of the probe cation $PyMeAH^+$ does not neutralize all the charges of the PAMPS chains and cannot form 1:1 stoichiometric electrostatic aggregation with the PAMPS charges. According to the counterion condensation theory [27] the sulfonate groups on PAMPS should be condensed to about 63 mol% by counterions to form loose ion pairs. The previous fact indicates that the probe cation $PyMeAH^+$ only occupies about 42 mol% (1/2.4) of charged sites of the PAMPS chain, the remaining 21 mol% of charged sites which should be condensed have to be occupied by protons. The relative number of bound cations of the probe $PyMeAH^+$ and proton may be determined by the chain conformation and steric barrier.

Caruso et al. [21] investigated the saturation binding of poly(allylamine hydrochloride) and poly(diallyldimethylammonium chloride) and pointed out that there were approximately 5 allylamine hydrochloride or diallyldimethylammonium chloride units for each ionic probe, pyrenetetrasulfonic acid (with four sulfonate groups).

As expected, the addition of NaCl greatly reduces the excimer formation as shown in Fig. 3. I_E/I_M almost approaches zero at an NaCl concentration above 7.5×10^{-4} mol/l. In this system, there are three different

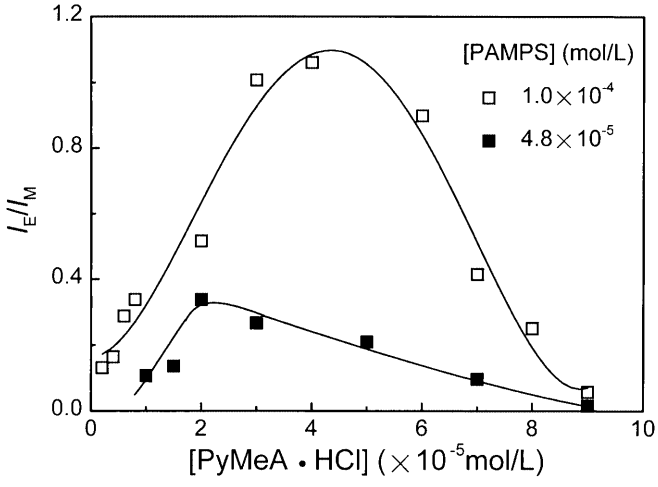

Fig. 2 Emission intensity ratio, I_E/I_M, of excimer to monomer as a function of PyMeA·HCl concentration in aqueous solution of PAMPS

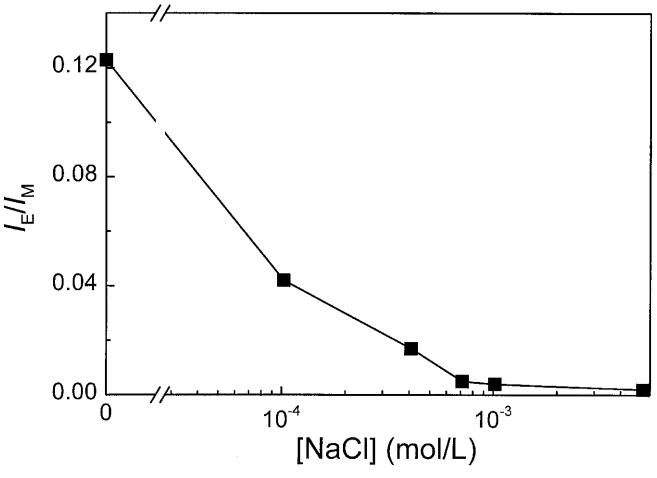

Fig. 3 I_E/I_M plotted against NaCl concentration for PyMeA·HCl in aqueous solution of PAMPS; $[PyMeA{\cdot}HCl] = 5 \times 10^{-6}$ mol/l, $[PAMPS] = 1 \times 10^{-4}$ mol/l

cations, H^+, Na^+, and $PyMeAH^+$. All of them can form loose ionic pairs with the sulfonate group on the PAMPS chain. The probability of binding $PyMeAH^+$ is decreased by adding salt with a concentration much higher than that of the probe. Another reason is the shielding effect of small molecular electrolytes, which weakens the electrostatic interaction. Dahlberg et al. [25] investigated the effect of ionic strength on the binding affinity of TNS and cationic potato amylopectin (CApS, with 4% of the monomers cationized) and found that salt could not separate completely the binding complex. They argued that the affinity for anionic TNS bound to CApS was a result of both electrostatic attraction and hydrogen bonding.

Aggregation of PAMPS and CTAB

The aggregate of the polyelectrolyte PAMPS and the surfactant CTAB with opposite charge can be formed by electrostatic and hydrophobic interactions. We used the ionic fluorescence probe PyMeA·HCl to investigate the aggregation. I_E/I_M for the ionic probe $PyMeAH^+$ in the presence of PAMPS is shown in Fig. 4 as a function of CTAB concentration. The data on the ordinate indicate the I_E/I_M value in PAMPS solutions without CTAB. With increasing CTAB concentration, the I_E/I_M value at a given PAMPS concentration firstly increases and reaches a maximum, then decreases. The interpretation of this behavior requires an understanding of the whole process for surfactant binding to the oppositely charged polyelectrolyte. Addition of the initial amounts of CTAB leads to coiling of the polyelectrolyte chains, which in turn enhances the excimer formation between bound probes. This coiling mainly results from the charge neutralization and the polymer becoming increasingly hydrophobic owing to surfactant binding. The I_E/I_M maximum corresponds the cac at which the CTAB begins to aggregate as proposed by Chandar et al. [8].

Because the pyrene probe used in this work is also a cationic species, addition of the cationic surfactant CTAB induces competitive binding of CTAB with the probe cation on the anionic sites of PAMPS. There should be an equilibrium in the bound composition of CTAB and PyMeA·HCl controlled by the free-energy change during the binding process. When the CTAB concentration is beyond its cac this binding equilibrium greatly shifts towards the formation of PAMPS and CTA^+ aggregation. Thus, the bound $PyMeAH^+$ is gradually replaced by CTA^+ from the binding site owing to the favorable binding free energy contributed from the electrostatic attraction between surfactant cation and polyanion as well as hydrophobic bonding among the alkyl tails of the surfactant. As a result, I_E/I_M decreases when the CTAB concentration is beyond the cac. Finally, the pyrene probe cation is almost completely removed from the polyanion and is dispersed in solution separately, which makes I_E/I_M approach zero at higher CTAB concentrations. Hayakawa et al. [28] also found that the bound probe cation proflavine was expelled from the anionic polymer pectate by the competitive binding of the cationic surfactant DTAB.

The presupposition for the previous discussion is that these ionic probes do not form excimers either in water by themselves or in the CTAB aggregate. Both curve A in Fig. 1 and curve C in Fig. 5 reflect no formation of probe aggregates in water without PAMPS even at

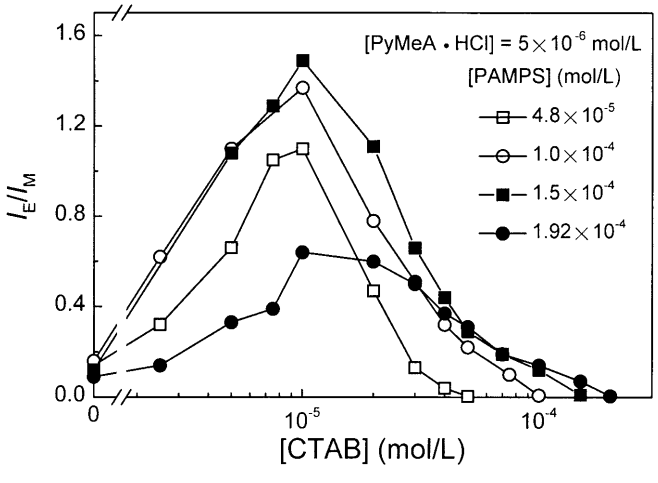

Fig. 4 I_E/I_M of the pyrene probe cation $PyMeAH^+$ as a function of cetyltrimethylammonium bromide (*CTAB*) concentration in aqueous PAMPS solutions at the concentrations indicated with [PyMeA·HCl] = 5×10^{-6} mol/l. The data on the ordinate were determined without CTAB

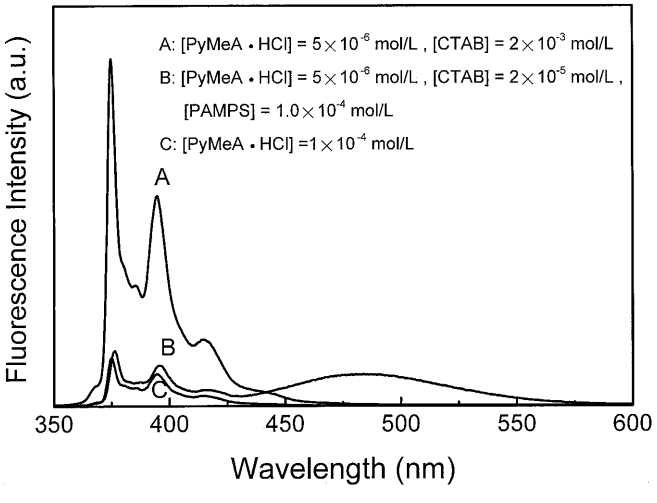

Fig. 5 Emission spectra of the cationic probe PyMeA·HCl in aqueous solutions. *A*: [PyMeA·HCl] = 5×10^{-6} mol/l and [CTAB] = 2×10^{-3} mol/l without PAMPS; *B*: [PyMeA·HCl] = 5×10^{-6} mol/l, [CTAB] = 2×10^{-5} mol/l, and [PAMPS] = 1×10^{-4} mol/l. *C*: [PyMeA·HCl] = 1×10^{-4} mol/l without CTAB and PAMPS

concentrations as high as 1×10^{-4} mol/l, which should be lower than the cmc of the ionic pyrene probe $PyMeAH^+$. By comparing curves A and B in Fig. 5 we find that without the existence of PAMPS the ionic probe $PyMeAH^+$ cannot form an excimer in the CTAB solutions even at concentrations higher than the cmc of the surfactant (curve A). These facts indicate that the excimer emission of the ionic probe $PyMeAH^+$ can be observed only when bound on PAMPS chains; therefore, I_E/I_M can be used to detect the competitive binding with CTAB on the PAMPS.

Chandar et al. [8] determined the cac of DTAB bound on PAA using the I_E/I_M maximum of pyrene labels. In that case, the pyrene aggregation at high DTAB concentration is solubilized in the relatively less polar microenvironment created by associated surfactants, resulting in a decrease in I_E/I_M. I_E/I_M, however, never goes down to zero even at a surfactant concentration 10 times as high as ours. The reason is that the pyrene label cannot be removed from the polyelectrolyte chains.

On the other hand, there are two kinds of the pyrene excimer, i.e., the static excimer and dynamic excimer. The former occurs if the pyrene groups are in juxtaposition owing to ground-state aggregation of pyrene groups. The latter is formed through the excitation of isolated pyrene groups and subsequent diffusional encounter with ground-state pyrene. According to Chandar et al. [8] these excimers can be distinguished by their emission wavelength. The static excimer of the ground-state pyrene dimers or aggregation emits at about 490 nm, while the emission maximum is blueshifted for the dynamic excimer. The emission wavelength, $\lambda_{excimer}$, of the excimer for all solutions in Fig. 4 is plotted against the CTAB concentration in Fig. 6. At very low CTAB concentrations, the excimer emission is centered on 488 nm, consistent with the existence of the static excimer. This excimer emission shifts to 481 nm as the CTAB concentration increased to 3×10^{-5} mol/l, showing the characteristics of a dynamic excimer. Thus, the decrease in I_E/I_M with increasing CTAB concentrations above the cac seems to be caused by a decrease in the number of static excimers. A similar finding was also reported by Winnik et al. [29].

The cac value for CTAB in dilute aqueous solutions of PAMPS was estimated from the maximum of I_E/I_M. For all PAMPS concentrations tested, the cac is the same at 1×10^{-5} mol/l, 2 orders of magnitude smaller than the cmc of about 1×10^{-3} mol/l for CTAB in water without polyelectrolyte. The cac should depend on the polyelectrolyte concentration because it alters the number of anionic binding sites and the distribution of the surfactant cation on the polymer chains. Hansson and Almgren [12] found that the cac for DTAB bound on PAA increased from 10^{-5} to 10^{-4} mol/l as the PAA concentration increased from 10^{-4} to 10^{-2} mol/l. However, the PAMPS concentration range in this work is too narrow to observe an obvious dependence of polyelectrolyte concentration. The PAMPS concentration is limited by the intensity requirement of excimer emission, I_E, and the precipitation of polyelectrolyte–surfactant complexes appearing at high CTAB concentrations. Benrraou et al. [9] have reported a similar observation for DTAB bound by completely ionized poly(maleic anhydride-*co*-methyl vinyl ether). When the polymer concentration was within $1–4 \times 10^{-4}$ mol/l, the cac was independent of the polymer concentration; however, the cac increased when the copolymer concentration was raised to 10^{-3} mol/l.

If we look at Fig. 4 carefully we can find that the CTAB concentration at which I_E/I_M equals zero,

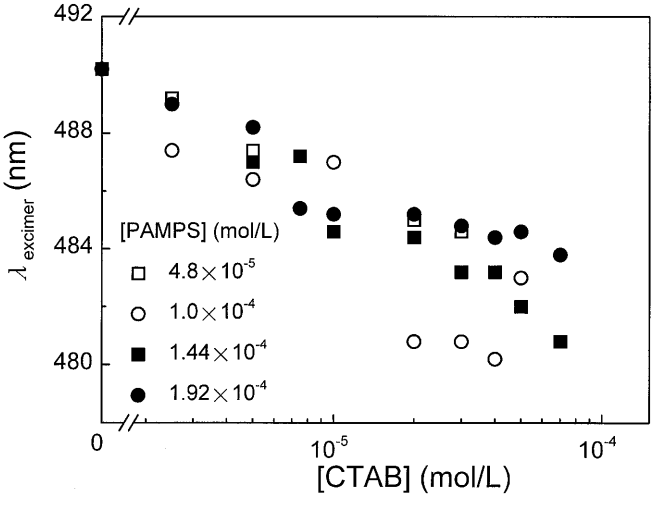

Fig. 6 Variation of the excimer emission wavelength, $\lambda_{excimer}$, with the CTAB concentration

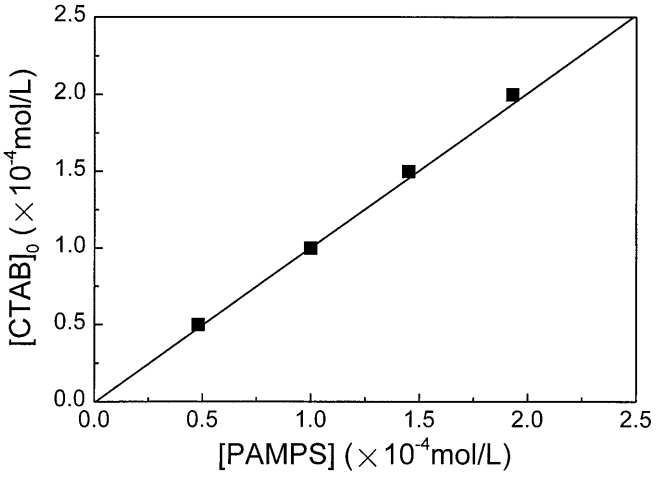

Fig. 7 CTAB concentration at which I_E/I_M is zero plotted against the PAMPS concentration

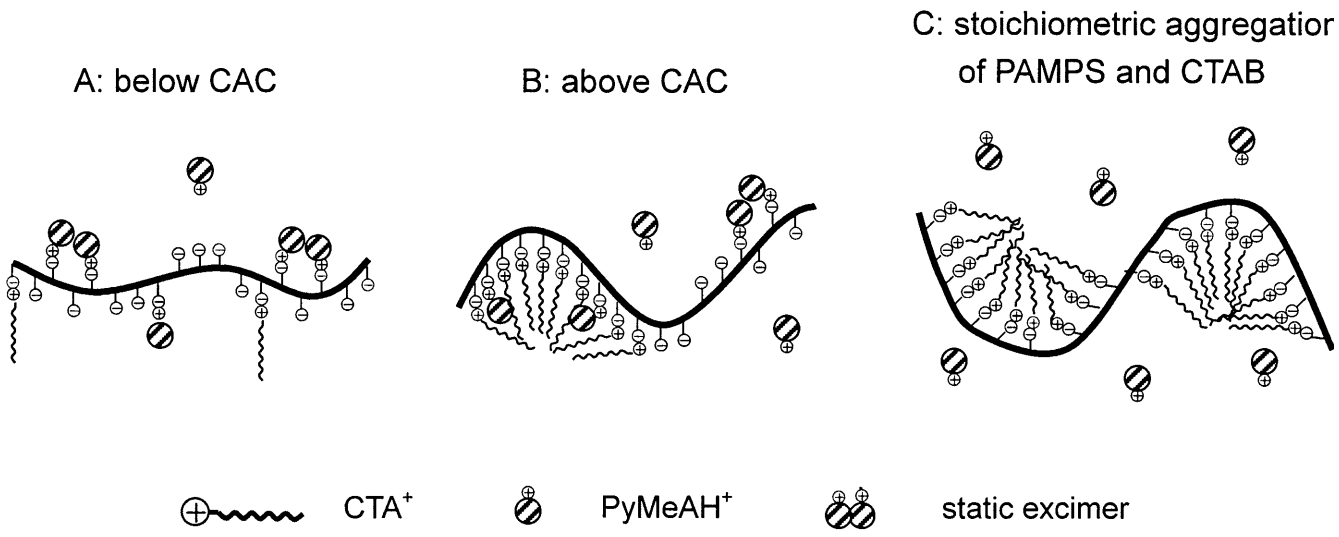

Fig. 8A–C Schematic representation for the aggregation of polyelectrolyte–surfactant. **A**: below the critical aggregation concentration (*cac*), **B**: above the cac, **C**: formation of stoichiometric aggregation; the proton and bromide anions are ignored for simplicity

$[CTAB]_0$, varies with the polyelectrolyte concentration, [PAMPS]. The relation between $[CTAB]_0$ and [PAMPS] is illustrated in Fig. 7. The result that $[CTAB]_0$ is equal to [PAMPS] within experimental precision is surprising. This finding means that the probe cations are thoroughly excluded from the binding sites of polyelectrolyte by the surfactant cations and the sulfonate groups of PAMPS are all occupied by CTAB cations. It is well known that the equivalent stoichiometry with respect to the charge is usually obtained in the solid complex of the polyelectrolyte and surfactant [2]. This fact indicates that the stoichiometric binding of oppositely charged surfactants occurs even in a polyelectrolyte solution much more dilute than that inducing precipitation. Besides the cooperative driving force, the smaller stereo barrier of the linear surfactant chain seems to be another reason for this.

By summarizing the results, we propose an aggregation model for the ionic surfactant binding on the oppositely charged polyelectrolyte in dilute solution as the schematic representation in Fig. 8. When the CTAB concentration is below the cac, all the cations condense randomly on the polyanion PAMPS to occupy about 63 mol% of the binding sites as required by the counterion condensation. Binding of CTAB and $PyMeAH^+$ makes the chain hydrophobic and coiling promotes the static excimer formation. Above the cac, the aggregates of CTAB exclude pyrene cations from the binding sites. A decrease in the extent of ground-state pyrene aggregate occurs with some solubilization of the pyrene probe within polymer-bound surfactant aggregates. At the final stage, all charged sites of the polyelectrolyte are bound with surfactants forming the polyelectrolyte–surfactant complex, which is soluble in less-polar solvents owing to the alkyl tail wrap. The probe cations are dissolved mainly in solvent again and the excimer formation is avoided by the electrostatic repulsion. With increasing CTAB concentration in PAMPS aqueous solution, the value of the relative emission intensity, I_1/I_3, for our cationic pyrene probe slightly decreases from 2.50 for [CTAB] = 0 to a minimum of 2.39 at the cac, then recovers to a value of 2.52 at $[CTAB]_0$, indicating that the probe $PyMeAH^+$ is primarily exposed to water again after the formation of the equivalent stoichiometric aggregation between PAMPS and CTA^+.

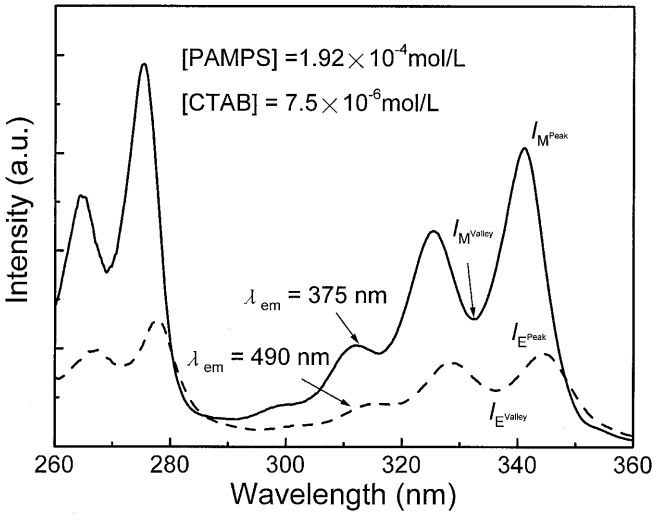

Fig. 9 Excitation spectra of PyMeA·HCl in aqueous solution with 7.5×10^{-6} mol/l CTAB (below the cac) and 1.92×10^{-4} mol/l PAMPS; the *solid line* indicates the monomer emission and the *dashed line* indicates the excimer emission

Table 1 Photophysical parameters of 1-pyrenemethylamine hydrochloride in aqueous solution of poly(2-(acrylamido)-2-methylpropanesulfonic acid) at 1.92×10^{-4} mol/l with cetyltrimethylammonium bromide (*CTAB*)

CTAB concentration (mol/l)	I_E/I_M	P_M	P_E	$\Delta\lambda$ (nm)
7.5×10^{-6} (below the critical aggregation concentration)	0.39	2.35	1.67	3.2
3×10^{-5} (above the critical aggregation concentration)	0.50	2.23	1.95	1.2

Excitation spectra of PyMeA·HCl

One can distinguish the static and dynamic excimers of the pyrene chromophore from their excitation spectra. The excitation spectra monitored at the monomer emission and at the excimer emission below the cac of CTAB in a PAMPS solution of 1.92×10^{-4} mol/l are displayed in Fig. 9; those above the cac have the same characteristics. From these excitation spectra the photophysical parameters of the peak-to-valley ratio P_M ($= {I_M}^{peak}/{I_M}^{valley}$) and P_E ($= {I_E}^{peak}/{I_E}^{valley}$) for the (0,0) transition observed at the monomer and excimer emission wavelength as well as the shift of the wavelength maximum of the (0,0) transition in the two excitation spectra $\Delta\lambda$ [$= \lambda_{max}$(excimer) $- \lambda_{max}$(monomer)] are evaluated and listed in Table 1. $P_E < P_M$ and $\Delta\lambda > 1$ at two CTAB concentrations, but the $\Delta\lambda$ value below the cac is higher than that above the cac. It is considered that P_E is always smaller than P_M and $\Delta\lambda$ is within 1–4 nm (redshift) when the pyrene preassociation takes place [15]. Therefore, the pyrene preassociation, i.e., the ground-state aggregate, exists in our PAMPS solutions with CTAB, in spite of being below or above the cac. The amount of pyrene preassociation above the CAC is decreased, resulting in a decrease in the amount of the static excimer.

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References

1. Wei Y-C, Hudson SM (1995) J Macromol Sci Rev Macromol Chem Phys C 35:15
2. Ober CK, Wegner G (1997) Adv Mater 9:7
3. Goddard ED (1993) In: Goodard ED, Ananthapadmanabban KP (eds) Interactions of surfactants with polymers and proteins. CRC, Boca Raton, Fla, p 171
4. Hayakawa K, Kwak J (1991) In: Rubingh D, Holland PM (eds) Cationic surfactant: physical chemistry. Dekker, New York, p 190
5. Lindman B, Thalberg K (1993) In: Goddard ED, Ananthapadmanabhan KP (eds) Interactions of surfactants with polymers and proteins. CRC, Boca Raton, Fla, p 203
6. Anthony O, Zana R (1996) Langmuir 12:1967
7. Chu D-Y, Thomas JK (1986) J Am Chem Soc 108:6270
8. Chandar P, Somasundaran P, Turro NJ (1988) Macromolecules 21:950
9. Benrraou M, Zana R, Varoqui R, Pefferkorn E (1992) J Phys Chem 96:1468
10. Almgren M, Hansson P, Mukhtar E, van Stam J (1992) Langmuir 8:2405
11. Hansson P, Almgren M (1994) Langmuir 10:2115
12. Hansson P, Almgren M (1995) J Phys Chem 99:16684
13. Hansson P, Almgren M (1995) J Phys Chem 99:16694
14. Morishima Y (1990) Prog Polym Sci 15:949
15. Winnik FM (1993) Chem Rev 93:587
16. Oliveira VAD, Tiera MJ, Neumann MG (1996) Langmuir 12:607
17. Herkstroeter WG, Martic PA, Hartman SE, Williams JLR, Farid S (1983) J Polym Sci Polym Chem Ed 21:2473
18. Tiera MJ, Neumann MG, Bertolitti SG, Previtali CM (1994) J Macromol Sci Pure Appl Chem A 31:439
19. Zimerman OE, Cosa JJ, Previtali CM (1994) J Macromol Sci Pure Appl Chem A 31:859
20. Hrdlovic P, Horinpva L, Chmela S (1995) Can J Chem 73:1948
21. Caruso F, Donath E, Mohwald H, Georgieva R (1998) Macromolecules 31:7365
22. Caruso F, Lichtenfeld H, Donath E, Mohwald H (1999) Macromolecules 32:2317
23. Decher G (1997) Science 277:1232
24. Laurent D, Schlenoff JB (1997) Langmuir 13:1552
25. Dahlberg A, Larsson A, Wall S, Akerman B (1999) Colloid Polym Sci 277:428
26. Dahlberg A, Larsson A, Akerman B, Wall S (1999) Colloid Polym Sci 277:436
27. Manning GS (1974) In: Selegny E, Mandel M, Strauss U (eds) Polyelectrolytes. Reidel, Dordrecht, The Netherlands, p 9
28. Hayakawa K, Satake I, Kwak JCT (1994) Colloid Polym Sci 272:876
29. Winnik FM, Winnik MA, Tazuke S (1987) J Phys Chem 91:492