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ORIGINAL CONTRIBUTION

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Binding on strong polyelectrolytes of mixed ionic and nonionic surfactants below their critical micelle concentration observed by fluorescence

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Abstract The binding of mixed surfactants of cationic cetyltrimethylammonium bromide (CTAB) and nonionic octaethylene glycol monododecyl ether ($C_{12}E_8$) on anionic polyelectrolyte poly[2-acrylamido-2-methylpropanesulfonic acid (PAMPS)] and fluorophore-labeled copolymers containing about 40 mol% of AMPS was investigated at different mole fractions, Y, of CTAB in the surfactant mixture. The excimer emission of the cationic probe 1-pyrenemethylamine hydrochloride (PyMeA·HCl), nonradiative energy transfer (NRET) between pyrene and naphthalene labels and I_1/I_3 of the pyrene label were determined by varying the total surfactant concentration, c_{Surf}. The I_E/I_M value of PyMeA·HCl firstly increases and then decreases to 0 with c_{Surf}, showing a maximum on every curve. The critical aggregation concentration of the mixed surfactants determined from the I_E/I_M maximum decreased from 5×10^{-5} to 1×10^{-5} mol/l as Y increased from 0.1 to 0.50, and then leveled off as Y increased up to unity. And at least 5×10^{-6} mol/l CTAB was required for the mixed surfactants to bind on the PAMPS cooperatively. Equimolar binding of CTAB on AMPS was formed at $I_E/I_M=0$ when $Y \geq 0.25$, while at $Y=0.1$ some CTAB molecules in the mixed micelle were directed to the water phase without binding with AMPS. Both the intramolecular and the intermolecular NRET increased and then decreased with c_{Surf}, having a maximum on each curve corresponding to the equimolar binding of CTAB and AMPS so long as $Y>0$, indicating the coiling of the chain and interchain aggregation upon bound surfactants. The $I_{\mathrm{Py}}/I_{\mathrm{Np}}$ value at the maximum decreased with decreasing Y because more nonionic surfactant $C_{12}E_8$ participated into the polyelectrolyte-mixed surfactant complexes together with bound CTAB.

Keywords Polyelectrolyte · Mixed surfactants · Binding · Cationic pyrene probe · Fluorescence nonradiative energy transfer

Introduction

The interaction between polymers and surfactants has attracted intense attention owing to its intrinsic scientific interest, its potential for exploitation in industrial processes, and its parallel with biological structural motifs [1, 2, 3]. The effects of ionic strength, charge density of the polyelectrolyte, and the chemical nature of both the surfactants and the polymers on the binding equilibrium and the cooperative parameter have been investigated [4, 5, 6, 7]. A systematic study of different combinations of macromolecules has shown the following trends [8]. The binding between nonionic polymers and surfactants is weak and depends on the polymer type; however, when the polymer carries charges on its chain to become a polyelectrolyte, the binding with oppositely charged surfactants is greatly enhanced by the contribution of electrostatic and hydrophobic interactions. The critical aggregation concentration (cac) is usually 2 orders of magnitude smaller than the critical micelle concentration (cmc) of the same surfactant in aqueous solutions without polyelectrolyte. Above the cmc, the Coulombic attraction between the surfactant micelle and the polyelectrolyte is so strong that rapid and irreversible precipitation takes place during the phase separation.

An innovative scheme of reducing the charge density of the micellar surface by mixing ionic surfactants with nonionic surfactants was introduced by Dubin and coworkers [9, 10, 11], which attenuates the Coulombic attraction to a level where polyelectrolytes and oppositely charged surfactant micelles can form a soluble complex. The premise for the formation of the complex of the polyelectrolyte–surfactant mixed micelle is that the surface charge density of the mixed micelle should exceed a certain value, which can be adjusted experimentally by varying the mole fraction, Y, of the ionic surfactant in the ionic–nonionic surfactant mixture. Mizusaki and coworkers [12, 13, 14, 15, 16] studied binding of micelles of *n*-dodecyl hexaethylene glycol monoether ($C_{12}E_6$) and *n*-hexadecyltrimethylammonium chloride (CTAC) mixtures on fluorophore-labeled poly(sodium 2-acrylamido-2-methylpropanesulfonate) (PAMPS) and its hydrophobic modifiers using steady-state and time-resolved fluorescence quenching with the quencher incorporated in the micelle and fluorescence nonradiative energy transfer (NRET). They found that the critical Y value, Y_c, corresponding to the onset of complex formation was about 0.05, above which the polyelectrolyte and the micelles of mixed surfactants formed the complex [12, 13]. If the polyelectrolyte is greatly hydrophobically modified by dodecyl- or cholesteryl-containing side chains, the formation of the polymer–mixed micelle complex appears to be mainly governed by hydrophobic interaction [14, 15, 16].

Fluorescence techniques are powerful in investigating polyelectrolyte–surfactant binding [5, 6, 7]. The pyrene chromophore is frequently used for this purpose owing to its special photophysical properties and high efficiency of excimer formation. Chu and Thomas [17] estimated the cac for decyltrimethylammonium bromide in dilute poly(methacrylic acid) solution from the intensity ratio I_1/I_3 of the first to the third emission peaks of the pyrene probe and found micellelike aggregates consisting of about 100 surfactant molecules in one cluster. Chandar et al. [18] 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. Almgren and coworkers [19, 20] studied the interaction of alkyltrimethylammonium bromide or alkyltrimethylammonium chloride with poly(styrenesulfate) and sodium polyacrylate by time-resolved fluorescence quenching of pyrene and reported that the aggregation number increased with the increase in the surfactant tail carbon number, *n*. Saito [21, 22] pointed out no obvious binding for nonionic surfactants on water-soluble polymers. Vasilescu et al. [23] observed from time-resolved fluorescence quenching of a pyrene probe for nonionic poly(oxyethylenic) (PEO) surfactants with PAA that the aggregation number of the clusters was smaller than that of the free micelles, but the difference was very small. However, the pyrene group does not only report the aggregation occurrence but also organizes hydrophobic aggregates because of its high hydrophobicity. For example, the pyrene labeled on PAA had a lower cac for DTAB than the free pyrene probe [18]. Use of ionic derivatives of pyrene can overcome this defect owing to the electrostatic repulsion between the ionic headgroups. They can be used to detect the microenvironment surrounding oppositely charged polyelectrolytes by direct binding upon the electrostatic attraction. Caruso and coworkers recently investigated using ionic derivatives of pyrene the influence of polyelectrolyte charge density and chain flexibility on the probe binding [24] and the electrostatic interaction in polyelectrolyte multilayer films [25].

Fluorescence NRET has been widely used to study the binding and hydrophobic association in polyelectrolyte–surfactant aqueous solutions. Schild and Tirrell [26] found by NRET the weak binding between a neutral polymer and an ionic surfactant derivative of pyrene in aqueous solutions. Itaya et al. [27] determined the cac of sodium 1-octanesulfonate bound on poly(allylammonium) chloride by NRET from 2-naphthalenesulfonate ion to 1-pyrenesulfonate ion. Hayakawa et al. [28] investigated the solubility of dyes in surfactant micelles bound on polyelectrolytes by NRET. Hashidzume et al. [15] used NRET of naphthalene and pyrene doubly labeled polyelectrolytes with hydrophobic modification to probe the chain conformation change upon binding with mixed micelles of neutral and ionic surfactants.

Recently, we observed the fluorescence of dansyl-labeled polyelectrolytes in the presence of cetyltrimethylammonium bromide (CTAB) and dodecyltrim- ethylammonium chloride in dilute aqueous solution as well as in the solid [29]. It is interesting that the polyelectrolyte with higher charge density forms the less-polar polyelectrolyte–surfactant complex in dilute aqueous solution, which can be reserved into the solid state. We used the excimer emission of a cationic pyrene probe, 1-pyrenemethylamine hydrochloride (PyMeA·HCl), to follow the binding of CTAB on PAMPS and found the formation of equimolar aggregates in dilute solutions without precipitation [30, 31, 32]. We found the occurrence of intermolecular aggregation of surfactant-bound polyelectrolytes induced by the hydrophobic association of the alkyl tails in the surfactant and the effects of the surfactant structure on this aggregation by excimer emission of the cationic pyrene probe and intermolecular NRET of the labeled polyelectrolytes [32, 33].

Up to now, not enough attention has been paid to the binding of mixed ionic and nonionic surfactant mixtures without independent micelles dispersed in the solution. This requires that the surfactant concentration range below the cmc and above the cac and the cmc for the nonionic surfactant usually be close to the cac for the ionic one. In this work, we chose the cationic surfactant CTAB, and the nonionic surfactant octaethylene glycol monododecyl ether ($C_{12}E_8$) to bind on PAMPS and its copolymers in dilute solutions to reveal the formation of micellelike aggregations of mixed surfactants with strong polyelectrolytes.

Materials and methods

Materials and polyelectrolyte samples

Cationic fluorescence probe PyMeA·HCl (Aldrich) was used as received. Fluorophore label monomers *N*-(1-naphthylmethyl)methacrylamide (NpMAm) and *N*-(1-pyrenylmethyl)methacrylamide (PyMAm) were synthesized in our laboratory following the procedure of Refs. [34, 35] and were confirmed with ^1H NMR spectra. Anionic monomer AMPS (Fluka) was used without further purification. *N*, *N*-Dimethylacrylamide (DMAA, Kohjin, Japan) was distilled before use. Cationic surfactant CTAB (Fluka) was recrystalized from ethanol. Nonionic surfactant $C_{12}E_8$ (Fluka) was used as received. Other reagents and solvents were all purchased from commercial sources and purified according to standard procedures. Highly pure water was obtained by deionization and filtration with a Millipore purification apparatus.

Three fluorophore-labeled copolymers of AMPS and DMAA, referred to as ADN50 (with naphthalene), ADP50 (with pyrene), and ADNP50 (with naphthalene and pyrene), respectively, were polymerized in dimethylformamide solution initiated by 2,2′-azobis(isobutyronitrile) [33]. The total monomer concentration was 0.5 mol/l with 1 mol% of NpMAm or/and PyMAm. The solution was degassed three times with nitrogen bubbling and sealed in a polymerization bottle, which was maintained at 60 °C for 12 h. The mixture was poured into a large excess of ether to precipitate the copolymer. The copolymers were purified by precipitation from methanol into ether three times. Finally, the aqueous polymer solution was dialyzed against pure water for 1 week and lyophilized. The composition of the copolymers was estimated from the C, N, and H content determined by elemental analysis with a Heraeus CHN-O apparatus. The fluorophore content in the sample was verified by UV absorbance. Gel permeation chromatography (GPC) measurements were carried out with a Waters GPC instrument at 40 °C using 0.1 mol/l Na_2SO_4 aqueous solution as the elutant and narrowly distributed PEO as the standard. The results are listed in Table 1.

PAMPS was synthesized according to the method described previously [30]. The molecular weight, M_w, of PAMPS determined by GPC was 1.9×10^6.

Measurements

For measuring the fluorescence spectrum of the cationic probe PyMeA·HCl, naphthalene, and/or the pyrene-labeled polyelectrolytes in aqueous solutions with surfactants, concentrated solutions of polymers, PyMeA·HCl, CTAB, $C_{12}E_8$, and a mixture of CTAB and $C_{12}E_8$ were prepared, respectively. Then, desired amounts of concentrated solutions were mixed in a volumetric flask and diluted to test concentrations. The PAMPS concentration in this work is expressed by the molar concentration of the repeat unit AMPS, and the concentration of the labeled copolymers is expressed by weight concentration (grams per liter). The mole fraction of CTAB in the mixed surfactants solution, *Y*, is defined as $Y = \{[CTAB]/([CTAB]+[C_{12}E_8])\}$.

Steady-state fluorescence spectra were recorded with a Hitachi F-4500 fluorescence spectrometer. All solutions were kept for more than 12 h to ensure the binding equilibrium was attained, and then stirred prior to measurement. All measurements were performed on air-equilibrated solutions at 25 °C. The excitation wavelength was 290 or 340 nm as indicated. I_E/I_M is defined as the emission intensity ratio of excimer (480–490 nm) to monomer (395 nm) of the pyrene residue. The NRET efficiency was characterized by the emission intensity ratio I_{Py}/I_{Np} of the pyrene label at 396 nm to the naphthalene label at 338 nm. I_1/I_3 is the emission intensity ratio for the first peak (375 nm) to the third peak (386 nm) of pyrene.

Results and discussion

Observation with excimer emission of cationic probe PyMeA·HCl

In water, PyMeA·HCl dissociates into the cation probe $PyMeAH^+$ and Cl^-. $PyMeAH^+$ can bind on the anionic polyelectrolyte PAMPS by electrostatic attraction. We have observed the fluorescence spectrum of PyMeA·HCl with and without binding on PAMPS [30, 31, 32, 36]. For an aqueous solution of PyMeA·HCl at a concentration below 1×10^{-4} mol/l, there is no excimer owing to the electrostatic repulsion between the probe cations. The addition of PAMPS causes a reduction in the monomer emission and induces the typical pyrene

Table 1 Composition and molecular weight of fluorophore-labeled polyelectrolyte samples

Sample	$M_w/10^4$	F_{AMPS}/mol%	NpMAm/mol%	PyMAm/mol%
ADN50	6.0	40.1	1	0
ADP50	4.7	37.1	0	1
ADNP50	7.0	39.6	1	1

excimer emission because of an increase in the local pyrene concentration along the polymer chain due to the binding of PyMeAH$^+$ on PAMPS, promoting the excimer formation. We have also observed the fluorescence spectrum of PyMeA·HCl in the presence of CTAB or $C_{12}E_8$ [30, 32]. No excimer is formed even when the CTAB concentration is beyond its cmc of 1×10^{-3} mol/l, but the excimer emission appears with the reduction of monomer emission intensity when the $C_{12}E_8$ concentration is above its cmc of 8×10^{-5} mol/l [23]. These facts indicate that the excimer of the ionic probe PyMeAH$^+$ can be formed either bound on PAMPS chains or encapsulated in the $C_{12}E_8$ micelle. Therefore, we can use the I_E/I_M of PyMeA·HCl to monitor the competitive binding of PyMeAH$^+$ with cationic surfactants on PAMPS and to detect the formation of $C_{12}E_8$ micelles. With this method, we have found the formation of the equimolar aggregate between the AMPS unit and CTAB in dilute aqueous solutions below the cmc of CTAB without precipitation [30] and the promoting effect of PAMPS on the micelle formation of $C_{12}E_8$ [32].

With the knowledge of excimer formation of PyMeA·HCl, we followed the binding of surfactant mixtures of cationic CTAB and nonionic $C_{12}E_8$ on PAMPS with the CTAB mole fraction, Y, from 0.1 to 0.75. The total surfactant concentration, c_{Surf}, dependence of I_E/I_M for the PyMeAH$^+$ probe at $Y = 0.1$, 0.25, 0.5, and 0.75 in the presence of PAMPS is depicted in Fig. 1a–d. All the curves in this figure are quite similar to those for CTAB in PAMPS solutions [30]. With increasing c_{Surf}, the I_E/I_M at a given PAMPS concentration increases firstly and then decreases, showing a maximum on each curve. Binding of the cationic surfactant on PAMPS will neutralize its charges and enhance the chain hydrophobicity, leading to a more coiled polyelectrolyte chain. This in turn enhances the excimer formation between bound probes and increases I_E/I_M. Because both the pyrene probe and CTAB are cationic species, their binding on anionic PAMPS is competitive. When the surfactant concentration is high enough, the binding will occur in a cooperative manner owing to both the electrostatic attraction between the surfactant headgroup and the charge site of the polyanion and the hydrophobic aggregation among alkyl tails of the surfactants. Therefore, the binding of surfactants becomes dominant and the bound probe PyMeAH$^+$ is gradually excluded from the charge site of PAMPS, resulting in the decrease in I_E/I_M.

As suggested by Chandar et al. [18], the surfactant concentration corresponding to the I_E/I_M maximum in Fig. 1 can be considered as the cac, where the micelle like surfactant aggregation begins to take place. The

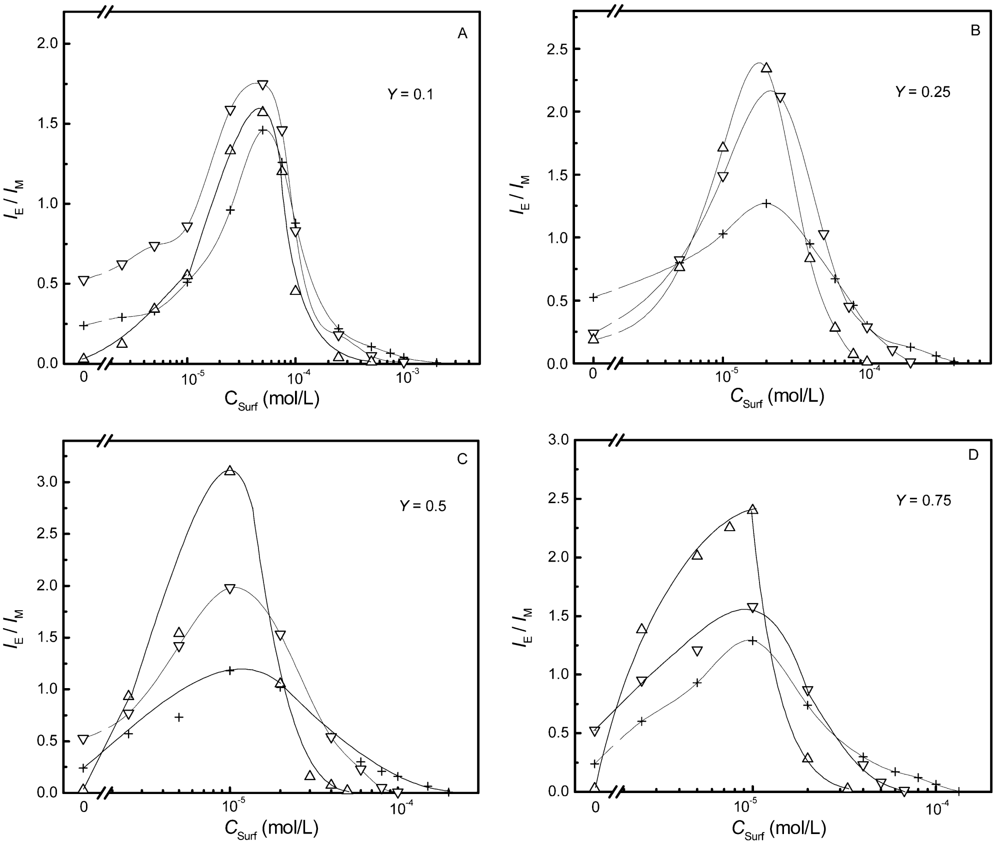


Fig. 1a–d I_E/I_M of the pyrene probe cation PyMeAH$^+$ as a function of total surfactant concentration, c_{Surf}, with indicated cetyltrimethylammonium bromide (*CTAB*) mole fraction, Y, in aqueous poly[(2-acrylamido-2-methylpropanesulfonic acid) (*PAMPS*) solutions of the indicated concentrations with [PyMeA·HCl] = 3×10^{-6} mol/l. The PAMPS concentrations (mol/l) were 2.5×10^{-5} (*up triangles*), 5.0×10^{-5} (*down triangles*), and 1.0×10^{-4} (*crosses*)

Y-dependence of the cac so determined for CTAB and $C_{12}E_8$ surfactant mixtures is depicted in Fig. 2a and Y-dependence of the CTAB concentration at the cac, $[\mathrm{CTAB}]_{\mathrm{cac}}$, is depicted in Fig. 2b. The cac decreases from 5×10^{-5} to 1×10^{-5} mol/l with increasing Y from 0.1 to 0.5 and then becomes constant at 1×10^{-5} mol/l for $Y > 0.5$. The cac in PAMPS solution for $C_{12}E_8$ and CTAB is 8×10^{-5} and 1×10^{-5} mol/l, respectively [30, 32]. The observed change in the cac with Y indicates that the addition of CTAB decreases the cac for $C_{12}E_8$ and that mixing of CTAB with $C_{12}E_8$ reduces the charge density requirement from $Y = 1$ to 0.5 for the appearance of the cac at $c_{\mathrm{Surf}} = 1\times10^{-5}$ mol/l. Dubin and Oteri [9] also pointed out that the cmc of mixtures of anionic and nonionic surfactants displayed a broad minimum with surfactant composition and did not exceed the cmc of the pure nonionic component. This may be due to the enthalpy decrease for the neutralization of opposite charges on the surfactant and PAMPS compensating the entropy loss during the cooperative binding.

$[\mathrm{CTAB}]_{\mathrm{cac}}$ estimated form the cac and Y plotted in Fig. 2b is constant at 5×10^{-6} mol/l when $Y \leq 0.5$ and then increases to 1×10^{-5} mol/l with increasing Y from 0.5 to 1. This fact suggests that at least 5×10^{-6} mol/l CTAB is required for the mixed surfactants to bind on the PAMPS cooperatively to form micellelike aggregates, which is just the half of the cac for CTAB in PAMPS aqueous solutions. There should be a critical value, Y_c, of Y at each c_{Surf} below which no cooperative binding occurs [9, 12, 13]. The micelle like aggregates may have a composition different from that of the CTAB and $C_{12}E_8$ mixture in the solution. However, the proportion of $[\mathrm{CTAB}]_{\mathrm{cac}}$ to Y in Fig. 2b when $Y > 0.50$ means that the composition of the aggregates would be the same as that in the solution.

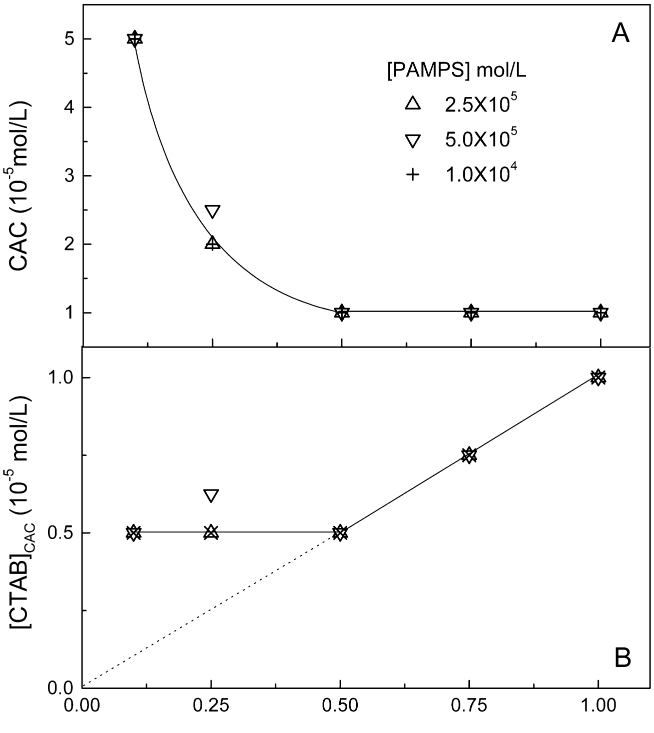


Fig. 2 The dependence of **a** the critical aggregation concentration (cac) and **b** the CTAB concentration of the mixed surfactants at the cacs, $[\mathrm{CTAB}]_{\mathrm{cac}}$, calculated from the CTAB mole fraction, Y, on Y

No PAMPS concentration effect on the cac can be recognized from Fig. 2 for the mixed surfactant of CTAB and $C_{12}E_8$ at the same Y. Benrraou et al. [37] have reported the phenomenon of DTAB binding on ionized poly(maleic anhydride-*co*-methyl vinyl ether). When the polymer concentration was within $1–4\times10^{-4}$ 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. The PAMPS concentration range in the present work is too narrow as it is limited by the proper excimer emission intensity I_E and the precipitation of the polyelectrolyte–surfactant complex appearing at high concentration.

As found from our previous work [30], binding of CTAB will finally exclude the bound cationic probe completely and lead to $I_E/I_M = 0$, where the CTAB concentration $[\mathrm{CTAB}]_0$ just equals the concentration of PAMPS repeat units. This fact manifests the formation of equimolar binding of CTAB–AMPS without precipitation at a surfactant concentration slightly higher than its cac. Now, we discuss again $[\mathrm{CTAB}]_0$ and $[C_{12}E_8]_0$ at $I_E/I_M = 0$ in the mixed surfactant. The $[\mathrm{CTAB}]_0$ and $[C_{12}E_8]_0$ so obtained are plotted against Y in Fig. 3a and b, respectively. It is interesting that $[\mathrm{CTAB}]_0$ is also equal to the AMPS unit concentration for the mixed surfactants so long as $Y \geq 0.25$, where the probe cation is thoroughly excluded from the binding site by the cationic surfactant and the sulfonate groups of PAMPS are all occupied by CTAB cations. For $Y = 0.1$, a $[\mathrm{CTAB}]_0$ higher than the PAMPS concentration is required to make $I_E/I_M = 0$. In this case, some ionic headgroups of CTAB do not bind on the sulfonate groups of the polyelectrolyte but are aligned to the water phase as assembled in the micelle like aggregation.

As seen from Fig. 3b, $[C_{12}E_8]_0$ is higher than its cma when $Y \leq 0.50$. This means that the nonionic surfactant $C_{12}E_8$ has formed micelles together with the ionic surfactant CTAB. At $Y = 0.1$, some CTAB cations in the mixture micelle bind on PAMPS and some point to water, leading to $[\mathrm{CTAB}]_0$ higher than the PAMPS concentration, while for the case of $Y \geq 0.25$, all CTAB cations in the mixture micelles bind on the charged sites of PAMPS.

According to the results at $I_E/I_M = 0$, we suggest a tentative model for the binding of the surfactant

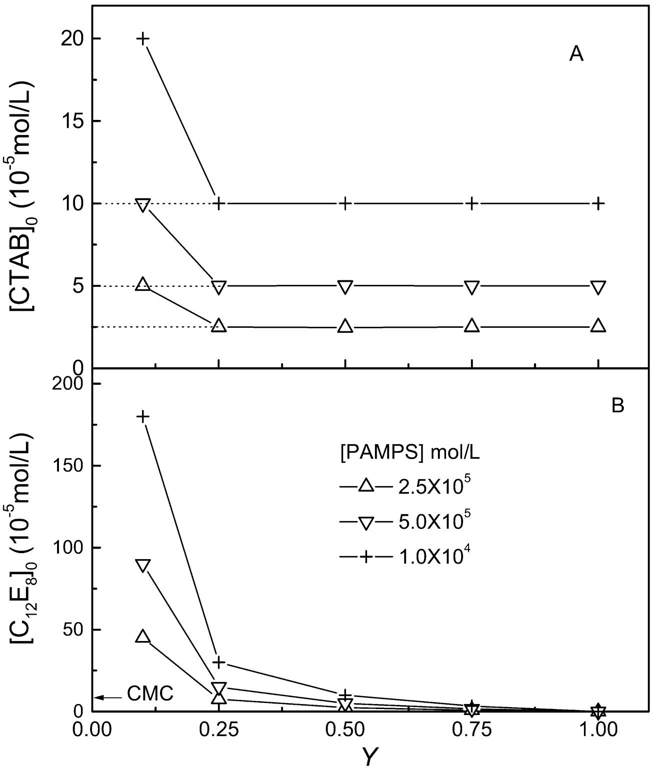


Fig. 3 a CTAB concentration, $[CTAB]_0$, and **b** octaethylene glycol monododecyl ether (*C_{12} E_8*) concentration, $[C_{12}E_8]_0$, at which I_E/I_M is zero against *Y*

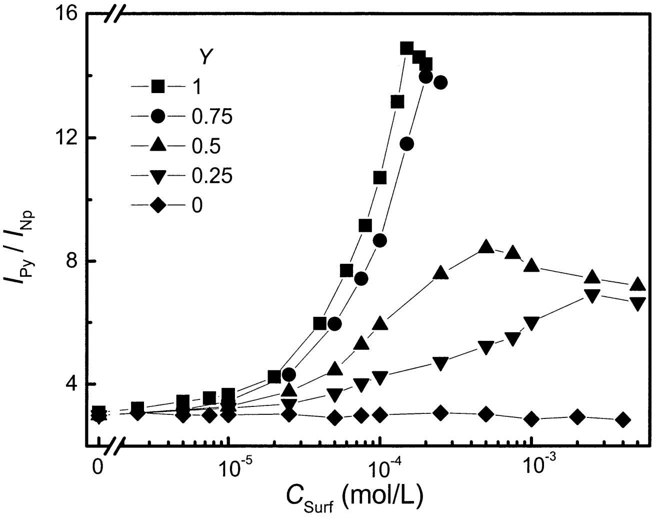
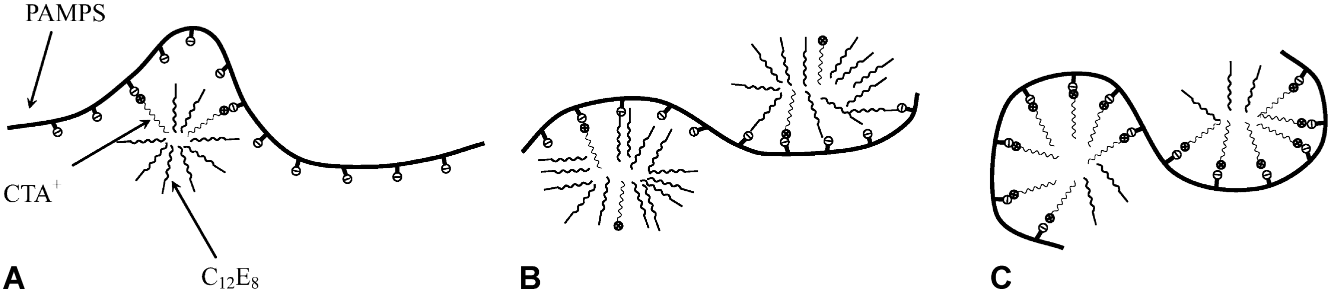


Fig. 5 I_{Py}/I_{Np} due to nonradiative energy transfer (*NRET*) as a function of total surfactant concentration, c_{Surf}, in aqueous solution of doubly labeled ADNP50 at 1.45×10^{-4} mol 2-acrylamido-2-methylpropanesulfonic acid (*AMPS*)/l

mixtures on the oppositely charged polyelectrolyte in dilute solution to form micelle like aggregations as in the schematic representation in Fig. 4. CTAB binds on PAMPS by electrostatic attraction and $C_{12}E_8$ aligns with the bound CTAB owing to hydrophobic interaction between the alkyl tails to form the polyelectrolyte–mixed surfactant aggregation (Fig. 4a). When $Y \leq 0.1$, not all of the CTAB in the micelle like aggregations binds on the AMPS site of PAMPS because the lower charge density of the aggregate cannot restrict the strong polyelectrolyte chain on it (Fig. 4b). In contrast, all CTAB cations in the micelle like aggregation bind on the AMPS site of PAMPS in equimolar quantities when $Y > 0.1$ (Fig. 4c).

Fig. 4a–c Schematic representation for the aggregation between polyelectrolyte and mixed CTAB/$C_{12}E_8$ surfactants



Observation by NRET of labeled polyelectrolytes

Fluorescence NRET from an energy donor to an energy acceptor covalently attached to the same polymer chain or different polymer chains provides information about changes in chain conformation and aggregation [38, 39, 40, 41, 42]. Naphthalene and pyrene are often used as the donor and the acceptor, respectively, because of their large spectral overlap and because naphthalene can be selectively excited at 290 nm.

I_{Py}/I_{Np} is shown as a function of c_{Surf} in Figs. 5 and 6 for solutions of doubly labeled sample ADNP50 and for solutions of mixtures of naphthalene-labeled ADN50 and pyrene-labeled ADP50, respectively. The NRET for doubly labeled ADNP50 mainly reflects the intramolecular aggregation and the NRET for ADN50 and ADP50 mixtures is completely induced by the intermolecular approach. With increasing c_{Surf} for the surfactant mixtures of $Y \geq 0.25$, I_{Py}/I_{Np} in Figs. 5 and 6

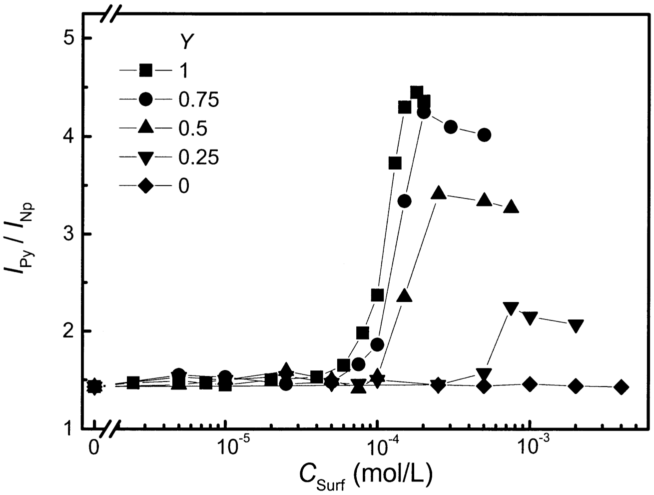


Fig. 6 I_{Py}/I_{Np} due to NRET as a function of c_{Surf} in the mixture of naphthalene-labeled ADN50 at 7.03×10^{-5} mol AMPS/l and pyrene-labeled ADP50 at 6.93×10^{-5} mol AMPS/l

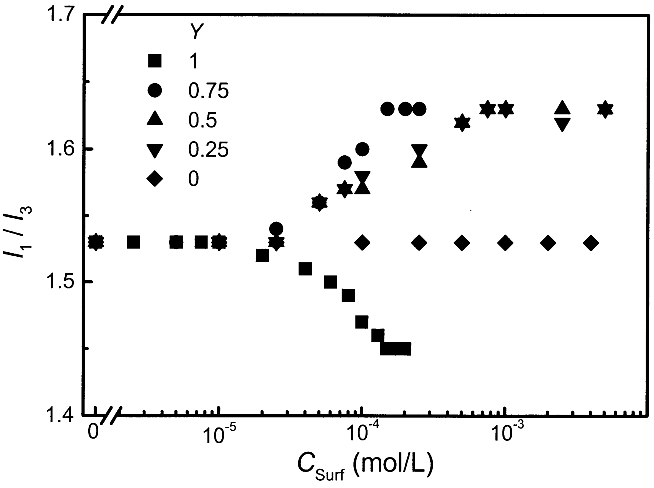


Fig. 7 I_1/I_3 of pyrene labels of doubly labeled ADNP50 at 1.45×10^{-4} mol AMPS/l in aqueous solution against c_{Surf}

is unchanged at lower c_{Surf} then increases rapidly to reach a maximum, and finally decreases. Binding of surfactant on polyelectrolyte makes the chain more hydrophobic and more coiled in favor of both the intramolecular and intermolecular NRET, increasing I_{Py}/I_{Np}. At the I_{Py}/I_{Np} maximum, the CTAB concentration in the micellelike aggregation of mixed surfactant just equals the AMPS concentration in the labeled polyelectrolytes, except the curve for $Y=0.25$ in Fig. 5, indicating the maximum binding capacity of the polyelectrolytes to the mixed surfactants. The excess surfactants remain in the solution separating the surfactant-bound chains, inducing the decrease in I_{Py}/I_{Np}.

On the other hand, the maximum value of I_{Py}/I_{Np} in each figure decreases with decreasing Y in the surfactant mixtures. As discussed in the previous paragraph, the maximum corresponds to the equimolar binding of cationic surfactant CTAB on the charged site AMPS in the copolymer. Because the charge density and the concentration of the polyelectrolyte are fixed, the total amount of surfactant aggregated on the polyelectrolyte is higher for the surfactant mixture with lower Y since more neutral surfactant $C_{12}E_8$ is accompanied into the aggregation with CTAB. This consequently results in the surfactant-bound chains being more expanded and separated more from each other, reducing the NRET. This is further evidence for the formation of surfactant mixture–bound polyelectrolyte complexes at high surfactant concentration when Y is beyond a certain critical.

If excited at 340 nm, only pyrene emission can be observed because naphthalene cannot be excited at this wavelength. The intensity ratio I_1/I_3 of the first to the third emission peak of pyrene is known to be sensitive to the microenvironmental polarity, which becomes lower in less-polar media [43, 44]. I_1/I_3 of the pyrene-labeled sample ADNP50 in aqueous solution is plotted in Fig. 7 against c_{Surf} for various Y. The I_1/I_3 value is constant at 1.53 as $c_{Surf} \le 1\times10^{-5}$ mol/l, then decreases with increasing c_{Surf} for CTAB ($Y=1$) and achieves a low value of 1.46 when $c_{Surf} \ge 1.5\times10^{-4}$ mol/l. This degree of I_1/I_3 reduction in the solution suggests that the pyrene label is not encapsulated in the micelle like aggregation of mixed surfactant on polyelectrolyte (if it were the case, I_1/I_3 should be about 1.25 [18]) and the decrease of I_1/I_3 is due to the increasing hydrophobicity of the local environment surrounding the polyelectrolyte chains with bound surfactants. However, the I_1/I_3 value increases as $c_{Surf} > 1\times10^{-5}$ and achieves a high value of 1.63 in the presence of $C_{12}E_8$ ($Y=0.1$–0.75). Morishima et al. [13] concluded that the increase in I_1/I_3 was due to the incorporation of the pyrene label into the ethylene oxide palisade layer in the $C_{12}E_6$/CTAC mixed micelle when the complexes were formed in mixtures of poly(ethylene glycol) and pyrene-labeled polyelectrolyte at various compositions.

The neutral surfactant $C_{12}E_8$ ($Y=0$) cannot bind on the polyelectrolytes, so it has no effect on either the intramolecular or the intermolecular NRET as seen from Figs. 5 and 6, and has no effect on the I_1/I_3 value as seen from Fig. 7.

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