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Fluorescence and X-ray diffraction studies on binding and complexes of surfactants and dansylated polyelectrolytes with sulfonate groups

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Abstract

Binding of cationic surfactant cetyltrimethylammonium bromide (CTAB) on polyelectrolytes ADDan containing different amounts of sulfonate groups was studied by fluorescence spectrum of dansyl labels in aqueous solution. With increasing concentration of CTAB, there was an abrupt drop in the emission maximum wavelength λ_{em} and a sharp increase in the relative intensity R_F defined as the ratio of emission in the presence of CTAB to that without CTAB. The critical aggregation concentration (cac) determined from the former was about 3×10^{-5} mol/l without obvious dependence on polymer charge density. Solid complex films of polyelectrolyte–surfactant of CTAB or dodecyltrimethylammonium chloride (DTAC) were obtained by precipitation and their fluorescence anisotropy r indicated a high mobility of the dansyl chromophore. The r-value for ADDan–CTAB complexes obviously decreased as the charge density of the polyelectrolyte increased while the r for ADDan–DTAC complexes was slight decline, suggesting the contribution of alkyl tails of the surfactant to local mobility. It was the first time to find that the higher the charge density of the polyelectrolyte, the less polar the micellar aggregation of polyelectrolyte–surfactant complex becomes in dilute aqueous solution, which remains in the solid complex. SAXS of the solid complexes illustrated a long-range ordered lamella structure with the long period d of 3.87 and 3.04 nm for CTAB and DTAC complexes, respectively. © 2001 Published by Elsevier Science Ltd.

Keywords: Polyelectrolyte–surfactant complex; Fluorescence; Micellar aggregation

1. Introduction

Recently, the binding process and complex structure of surfactants with oppositely charged polyelectrolytes have being intensively studied due to the fundamental and application interests [1,2]. The binding process in aqueous solution is considered to be composed of two steps: initial binding of surfactant molecules to the charged sites on the polymer chains and propagating aggregation of surfactant molecules to form micelle-like structure in a highly cooperative manner [3,4]. The driving force is the electrostatic attraction between charged groups on the polyelectrolyte and ionic heads of the surfactant molecules as well as the hydrophobic interaction between the bound surfactant alkane tails and between hydrophobic moieties of the polymer and the surfactant tails. The critical aggregation concentration (cac), at which the binding begins, is about two orders of magnitude lower than the critical micelle concentration (cmc) for the free surfactant, and it is significantly affected by the chemical nature of the polyelectrolyte

and surfactant, e.g. the chemical structure, molecular weight and hydrophobicity of the polymer, alkyl chain length of the surfactant, as well as by the environment, such as ionic strength, pH and concentration [5–9].

Fluorescence techniques are powerful in determining the cac value and aggregation number for polyelectrolyte–surfactant binding [9–15]. For this purpose, the pyrene probe is frequently used due to its special photophysical properties and high efficiency of excimer formation [16,17]. Chu and Thomas [10] reported the cac for decyltrimethylammonium bromide in dilute poly(methacrylic acid) solution estimated by the relative emission intensity of I_1/I_3 for pyrene probes and found micelle-like aggregation consisting of about 100 surfactant molecules for one coiled polymer chain. On the other hand, Chandar et al. [11] adopted the intensity ratio I_e/I_m of excimer to monomer for pyrene labeled on poly(acrylic acid) (PAA) to investigate the aggregation of dodecyltrimethylammonium bromide (DTAB) in PAA solution as a function of pH. Oliveira et al. [18] showed with fluorescence of pyrene probe that the increase in the content of hydrophobic moiety of ethyl methacrylate in the acrylic acid–ethyl methacrylate copolymer favored the surfactant aggregation at low free

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surfactant concentration. However, the pyrene exhibits a tendency to 'organize' hydrophobic domain rather than to 'report' the polarity due to its strong hydrophobicity [19] and correction is necessary for pyrene emission data before quantitative interpretation [11]. In order to avoid this shortcoming, another less hydrophobic chromophore, dansyl group will be a better alternative because its emission maximum wavelength and intensity are very sensitive to the microenvironmental polarity and mobility [20]. However, few papers concern the dansyl fluorescence for the research on binding isotherm for surfactants to polyelectrolyte in dilute solutions.

Solid polyelectrolyte–surfactant complexes can be easily produced by precipitation from aqueous solution with 1:1 stoichiometry with respect of the charges [2]. The most attractive finding from polyelectrolyte–surfactant complexes is the highly ordered structure [21], which varies depending on the charge density and the chemical properties of the polymer and the length and shape of the surfactant. Capability of surfactants to self-assemble into various mesomorphous becomes the organization factor in polyelectrolyte–surfactant complexes and the ordered spatial stack is stabilized by the hydrophobic bonding and electrostatic interaction, the latter is the strongest force in polymeric materials. These ordered structures afford them potential applications from improved mechanical properties to unusual optical, electronic and biological performance.

In the recent years, substantial efforts have been devoted to exploring the relationship of the composition and structure for this kind of complexes, mainly according to X-ray diffraction from nano-scaled space. Osada and co-workers proposed a simple cubic structure for their poly[2-(acrylamido)-2-methylpropanesulfonic acid] gel–N-alkylpyridinium complexes [22] and also a stack model for *x,y*-ionene–surfactants complexes [23]. Antonietti et al. [24–31] have published extensive experimental results of face-centered cubic packing of undulated cylinders for PAA–DTAB complexes, undulated lamella for polystyrenesulfonate (PSS)–alkyltrimethylammonium complexes, and so on. With the cationic or anionic polyelectrolyte gels, Chu and co-workers [32–34] reported upon their highly resolved diffractograms of small-angle X-ray scattering (SAXS) the charge density dependence of the stack structure of the polyelectrolyte–surfactant complexes.

Up to now, it is still an open question where the 1:1 stoichiometric polyelectrolyte–surfactant complex is formed, in aqueous solution or during precipitation process. Because the cac is much lower than cmc, whether the micelle of surfactants aggregated on oppositely charged polyelectrolytes at such low concentration is reserved into the solid complexes is unclear yet. Understanding this process will be significant in the structure design for the polyelectrolyte–surfactant complex since there are different assembled structures for surfactant in polyelectrolyte solutions depending on its concentration, such as sphere, rod, thread and so on.

Recently, we synthesized a dansyl label monomer [35] and prepared a series of dansyl or pyrene labeled strong polyelectrolytes of 2-(acrylamido)-2-methylpropanesulfonic acid (AMPS) and *N,N*-dimethylacrylamide (DMAA) copolymers with different charge densities determined by the AMPS content. The change in electrostatic interaction induced by the different solvation status was investigated on these labeled polyelectrolytes in aqueous solutions and in DMSO/THF mixtures [36–40]. Based on the understanding of the electrostatic interaction and polyelectrolyte behavior, we extended our research to the aggregation behavior in strong polyelectrolyte–surfactant complexes. It has been found by using the excimer emission of a cationic pyrene probe that the 1:1 stoichiometric aggregation already forms in aqueous PAMPS solution without any precipitation provided that the concentration of cetyltrimethylammonium bromide (CTAB) is about 10^{-4} mol/l, higher than its cac but still lower than the cmc [41]. However, this ionic probe is preferentially distributed in water phase as reflected by its high I_1/I_3 value of 2.52 ($I_1/I_3 = 2.50$ in PAMPS solution without CTAB). Consequently, it cannot be used to detect the polarity change in the surfactant aggregation on polyelectrolyte.

In order to determine the coherence of polyelectrolyte–surfactant aggregation in solution and in solid complex, we observed, for the first time, the fluorescence of these dansyl-labeled polyelectrolytes binding with CTAB or dodecyltrimethylammonium chloride (DTAC) in dilute aqueous solution as well as in solid state. Primary observation on the stack structure of our polyelectrolyte–surfactant complexes was also carried out with the wide-angle X-ray diffraction (WAXD) and SAXS.

2. Experimental procedures

2.1. Chemicals

Dansyl chloride (Aldrich) and AMPS (Fluka) were used without further purification. DMAA (Kohjin, Japan) and acryloyl chloride (Aldrich) were distilled before use. CTAB or C16 and DTAC or C12 were recrystallized from ethanol. The silica gel powder for the separation chromatography column was of 200–400 mesh and activated at 300°C for 6 h. Other reagents and solvents were all purchased from commercial sources and purified according to the standard procedure. Highly pure water was obtained by deionization and filtration with a Millipore purification apparatus.

2.2. Preparation of dansylated polyelectrolytes

Radically copolymerizable dansyl monomer *N*-[2-[[[5-(*N,N*-dimethylamino)-1-naphthalenyl]sulfonyl]amino]-ethyl]-2-propenamide (DANSAEP) was synthesized according to the method described previously [35]. Dansyl chloride was reacted with ethylenediamine in THF at 0°C

Table 1

Composition of dansyl-labeled polyelectrolytes ADDan (containing 0.2 mol% of dansyl label monomer DANSAEP)

Sample	AMPS/DMAA (mole ratio in feed)	Elemental analysis (wt%)		F_{AMPS}[a]
		S	N	
ADDan15	15/85	4.46	11.75	0.186
ADDan45	45/55	9.71	9.55	0.440
ADDan75	75/25	13.31	7.83	0.738
ADDan100	100/0	15.41	6.77	0.998

[a] Estimated from the N content.

for 4 h and light-green needle-like crystal of *N*-(2-aminoethyl)-5-(dimethylamino)-naphthalene sulfonamide (DANSA) was obtained after extraction and purification. The DANSA was then combined with acryloyl chloride at room temperature and the products were separated by filtration and chromatography to give final DANSAEP. The DANSA and DANSAEP were confirmed by ^1H and ^{13}C NMR.

The dansyl-labeled polyelectrolytes ADDan with different mole fractions F_{AMPS} of AMPS unit were prepared by free radical copolymerization of AMPS, DMAA and DANSAEP in water at 70°C, using 0.2 mol% of ammonium persulfate as the initiator [36]. The molar ratio of DANSAEP to total monomer was 0.2 mol% and the concentration of total monomer was 0.46 mol/l. The mixture was stirred for 16 h under nitrogen atmosphere and then the product was dialyzed for two weeks against distilled water to thoroughly remove impurities. The dialyzed solution was condensed, freeze-dried and finally dried in vacuum at 60°C to obtain the dansyl-labeled polyelectrolytes (yield about 80%), referred to as ADDan followed by numbers denoting the AMPS mole percentage in feed. The copolymer composition was estimated from the N and S content determined by elemental analysis with a Heraeus CHN–O apparatus and listed in Table 1.
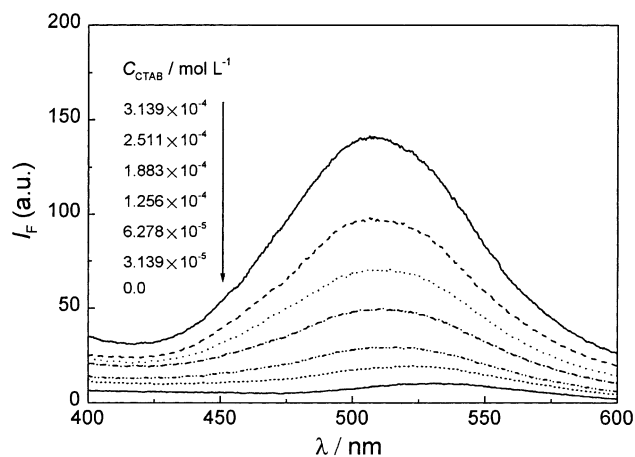

Fig. 1. Fluorescent spectra of ADDan75 in aqueous solution (0.06 wt%) with different concentrations C_{CTAB} of CTAB.

2.3. Preparation of solid complexes

Solid complexes of polyelectrolyte–surfactant were prepared following Antonietti and Conrad's procedure [24]. Dansylated polyelectrolyte sample ADDan (2.5 g) was dissolved in 100 ml of highly purified water and converted into sodium salt with NaOH equivalent to the charges of the polymer. Slight excess of surfactant CTAB or DTAC in water (100 ml) was added dropwise with stirring until no further precipitation appeared. The crude complex was purified by repeat precipitation from methanol solution into water until no halide ion (Br$^-$ or Cl$^-$) could be detected in the water phase with silver nitrate. Solid complex films of ADDan100–C12, ADDan100–C16, ADDan75–C12, ADDan75–C16, ADDan45–C12 and ADDan45–C16 were obtained by dissolving the dried complex (1 g) in chloroform (5 ml), casting it onto a PTFE surface, evaporating the solvent at 60°C in vacuum for a week.

2.4. Measurements

Steady-state fluorescence spectra were measured for polyelectrolyte–surfactant solutions as well as for the complex film with a Hitachi F-4500 fluorescence spectrophotometer at ambient temperature. The excitation wavelength and the slit width were 320 and 5 nm, respectively.

For the spectrum of polyelectrolyte–surfactant solutions, the stock aqueous solution of dansyl-labeled samples ADDan was prepared, and given amount of surfactant CTAB solution was added in the absence or presence of KCl and then diluted to 0.06 wt% of the polyelectrolyte.

DSC and thermogravimetry (TG) were conducted on the complex film with a TA Universal V1.7F apparatus at a heating rate of 10°C/min in N_2 atmosphere. The temperature range for DSC measurements was from 20 to 150°C.

WAXD and SAXS were performed on the solid complex film with a Rigaku D/max-1200 X-ray diffractometer. Ni filtered Cu-Kα radiation of $\lambda = 0.15405$ nm was used in the analysis. The 2θ ranged from 1.00 to 3.50° for SAXS, corresponding to the scattering vector $s = 2\sin\theta/\lambda$ from 0.113 to 0.396 nm^{-1}, where 2θ was the angle between the incident and scattering beams. Step-scan was used in SAXS measurement with the step length of 0.02° and scan rate of 0.04°/min.

3. Results and discussion

3.1. Dansyl fluorescence for binding

Fluorescent spectra of polyelectrolyte sample ADDan75 in CTAB aqueous solutions of different concentrations C_{CTAB} are shown in Fig. 1. It is obvious that the emission intensity increases with the increasing surfactant concentration. Because the dansyl emission at about 510 nm is due to the twisted intramolecular charge transfer (TICT) related to
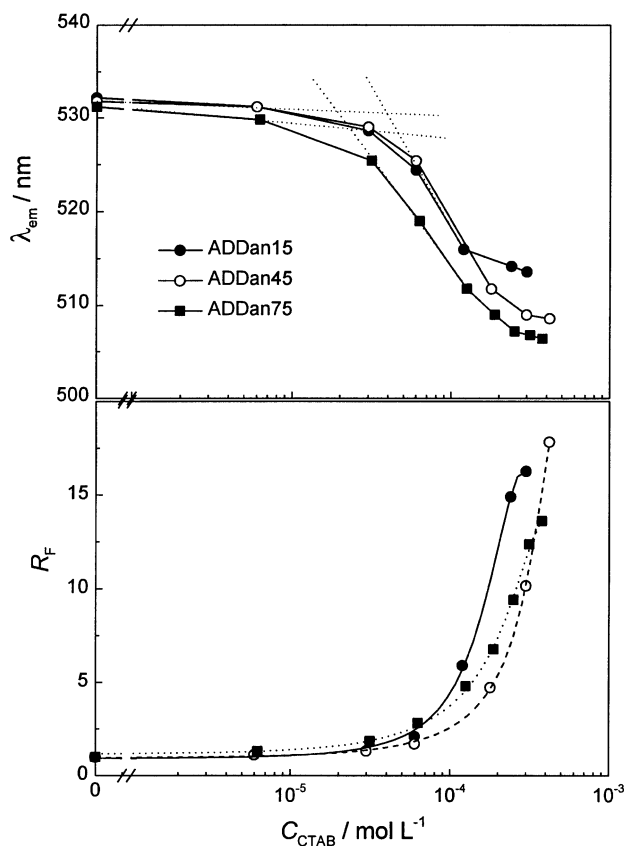
Fig. 2. Emission maximum wavelength λ_{em} (upper panel) and relative intensity R_F (lower panel) for samples ADDan15 (●), ADDan45 (○), and ADDan75 (■) varying with CTAB concentration C_{CTAB}, thin dashed lines indicate the extrapolation for determining cac.

the torsional motion of the dimethylamino group round naphthyl plane [42,43], this intensity increase suggests the enhancement of segment mobility by adding surfactants. The addition of cationic surfactant CTAB decreases the effective charge density of the polymer through binding, which in turn enhances the TICT state as found from the charge density dependence of emission intensity of the same samples without surfactant [37]. One can also find that the emission band shifts to shorter wavelength with an increase in C_{CTAB}. The emission spectra in aqueous CTAB solution of samples ADDan45 and ADDan15 with lower charge density expressed by the mole fraction F_{AMPS} of AMPS in the ADDan samples exhibit the similar features as presented in Fig. 1.

The wavelength blue-shift is expected from the effect of less polar environment formed by adding amphiphilic surfactants as observed from dansyl monomer DANSAEP [36]. Chen and Morawetz [44,45] investigated the association equilibrium and kinetics of dansyl-labeled PAA with poly(ethylene oxide) (PEO) or poly(1-vinyl-2-pyrrolidinone) (PVP). They also found blue-shift of the emission maximum wavelength λ_{em} when PAA formed complex with PEO or PVP, where the microenvironment surrounding the fluorophore became less polar.

The emission maximum wavelength λ_{em} for three polyelectrolyte samples of ADDan15, ADDan45 and ADDan75 is plotted as a function of CTAB concentration C_{CTAB} as shown in the upper panel of Fig. 2. In low C_{CTAB} region, λ_{em} slightly decreases, while there is an abrupt drop in λ_{em} when C_{CTAB} is beyond a certain value. This drop is an indication for the formation of surfactant aggregation since the surfactant aggregation creates less-polar microdomains in the polar bulk solution to wrap the dansyl chromophore attaching to the polyelectrolyte chain, leading to a large decrease in λ_{em}. We have estimated the cac from the intersection point of the tangent lines to each part of the curve as shown by the dashed lines in the upper panel of Fig. 2. The cac value determined is 2.0×10^{-5} mol/l for ADDan75 solution and about 3.5×10^{-5} mol/l for ADDan45 and ADDan15 solutions, 2 orders of magnitude lower than the cmc of about 1×10^{-3} mol/l for CTAB in water without polyelectrolyte. The surfactant aggregation on oppositely charged polyelectrolytes in aqueous solutions is a cooperative process and governed by both the electrostatic interaction and hydrophobic interaction. However, the effect of polymer charge density on the cac is still ambiguous. Kwak and co-workers [7] found no obvious correlation between the charge density and the binding isotherm of cationic surfactants on several anionic polyelectrolytes. To avoid the difference in chemical nature of polymers, Shimizu et al. [8] changed the charge density of maleic acid copolymers by varying pH for binding cationic surfactants, and their results appeared to be markedly influenced by the hydrophobicity of the copolymers. Kiefer et al. [46] used hydrophilic PAA at different neutralization degrees α to determine the binding isotherm of tetradecyltrimethylammonium bromide in the presence of NaBr (0.01 mol/l) and reported a decrease in cac with decreasing α when $\alpha < 0.4$ while a constant cac when $\alpha > 0.4$. Thereby, owing to lack of enough cac data in the presence of ADDan samples, it is inappropriate to go further in discussion about the charge density dependence of the cac.

The final λ_{em} values after the aggregation formation are 513, 510 and 507 nm for ADDan15, ADDan45 and ADDan75, respectively, indicating the microenvironment surrounding the dansyl group becomes less polar with increasing AMPS content in our samples. While little charge density dependence can be recognized from the λ_{em} values on the ordinate for all these polyelectrolyte samples in water without surfactant, which remains at 532 nm. For comparison, λ_{em} for the dansyl monomer is 457 nm in hexane and 505 nm in CTAB micelles in water. At the final stage, most dansyl chromophores are embedded in the domain of aggregated surfactant molecules. More surfactant molecules can be bound to the polyelectrolyte chain with higher charge density, resulting in a less polar microdomain in the aggregation. Using time-resolved fluorescence quench on poly(maleic acid-co-methyl vinyl ether) dilute solution with DTAC, Anthony and Zana [9] revealed that by raising the neutralization degree α the
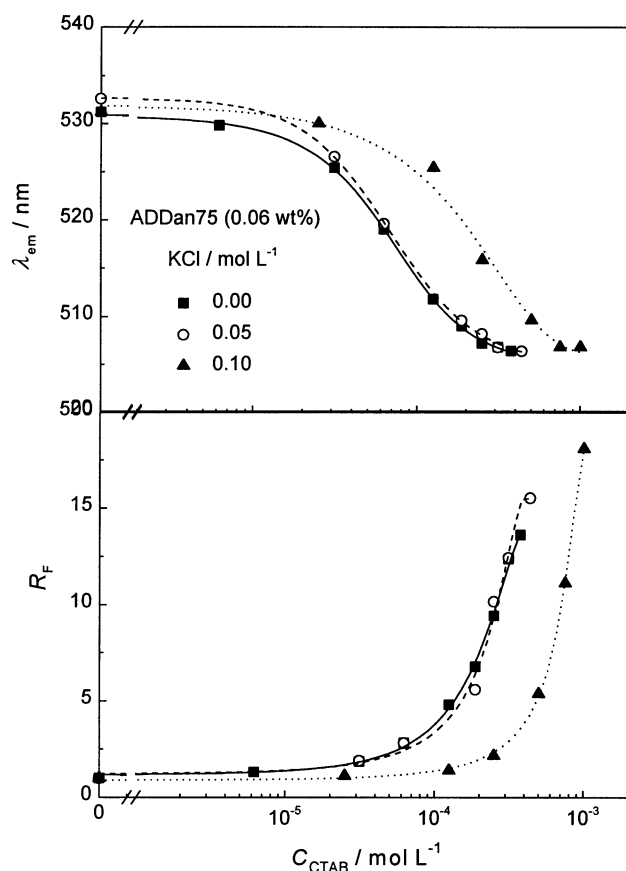
Fig. 3. CTAB concentration dependence of λ_{em} (upper panel) and R_F (lower panel) for ADDan75 in aqueous solution of 0.06 wt% with indicated KCl concentrations.

aggregation number increased and the microviscosity decreased. Similar charge density dependence was also observed from the fluorescence of ADDan–surfactant solid complexes, indicating the causation of solid structure and aggregation in dilute aqueous solution. This will be discussed in the following section.

The lower panel of Fig. 2 presents the surfactant concentration dependence of relative intensity R_F for the emission in the presence of CTAB to that without CTAB. It can be seen that R_F slightly increases below C_{CTAB} of 5×10^{-5} mol/l and sharply increases above this concentration. This C_{CTAB} value is little higher than the cac given above, showing that the abrupt increase of R_F is induced by forming surfactant aggregations to wrap the chromophore, which greatly promotes the formation of TICT state of dansyl groups [37,42,43]. Thus, the surfactant aggregation becomes more perfect at the onset of R_F steeply increasing.

3.2. Salt effect on cac

To investigate the role of electrostatic interaction in the course of CTAB aggregation in dilute polyelectrolyte ADDan75 solutions, the fluorescent spectra were measured with adding salt KCl at various concentrations and the

observed λ_{em} and R_F are given in Fig. 3. The λ_{em} and R_F data at low KCl concentration of 0.05 mol/l almost overlap on those for the solutions without adding salt, indicating no apparent effect of adding salt on the cac value and segment mobility. When the KCl concentration is 0.1 mol/l, both curves of λ_{em} and R_F against C_{CTAB} move towards higher C_{CTAB}, leading to a higher cac value of ca. 10^{-4} mol/l. This can be attributed to the screen effect of salt ions on the electrostatic attraction between surfactants and polyions, but this salt effect is lower than the literature results for carboxyl polyelectrolytes. Benrraou et al. [47] monitored the aggregation of DTAB in NaBr solution of poly(maleic acid-co-methyl vinyl ether) at 2×10^{-4} mol/l of monomer with potentiometry and pyrene probing and found six times of increase in cac as NaBr concentration increased from 10^{-3} to 10^{-2} mol/l. Hansson et al. [14,15] also observed the cac of DTAB raising eight times in PAA–Na solution of 5×10^{-3} mol/l upon addition of 0.01 mol/l NaBr by similar techniques. The real origin for this difference is still unknown but some facts may give some hints for comprehension. The polymer sample used here is a strong polyelectrolyte with the so-called counterion condensation due to its high charge density. Addition of small salt has two effects on the cac value of screening the electrostatic force by reduction of Debye radius and causing the competitive binding on the charged site of polyelectrolyte. As known from the swelling equilibrium of gels with the same monomers AMPS and DMAA in salt solutions [48], the KCl concentration higher than 1 mol/l is required for the sulfonate gel ($F_{AMPS} = 0.608$) to swell like an uncharged hydrogel and the binding strength of potassium cation to the sulfonate group on the polymer is weaker than sodium and proton cation.

3.3. Fluorescence of solid complexes

All of solid complex films of ADDan45, ADDan75 and ADDan100 with C12 (DTAC) or C16 (CTAB) are soft, highly transparent and deformable. The TG chart for these complexes exhibits a weight loss of about 3.4 wt% below 110°C then a constant weight up to 200°C. There is neither visible glass transition nor crystalline melting in the DSC curves for these complexes, except a broad shallow peak around 100°C corresponding to the weight loss. The above facts suggest that the complex is stable below 200°C and contains about 3.4 wt% of water.

The fluorescence spectra of our solid complex films are similar to those shown in Fig. 1 for the aqueous solutions but the λ_{em} shifts to lower values due to the absence of water, the polar solvent. Fig. 4 depicts the emission wavelength λ_{em} of our polyelectrolyte–surfactant films as a function of F_{AMPS} reflecting the charge density. When compared at the same charge density, the polarity of the microdomain around dansyl chromophore becomes less for ADDan–C16 than ADDan–C12, as indicated by λ_{em} values. For the complexes with a given surfactant, λ_{em} decreases with
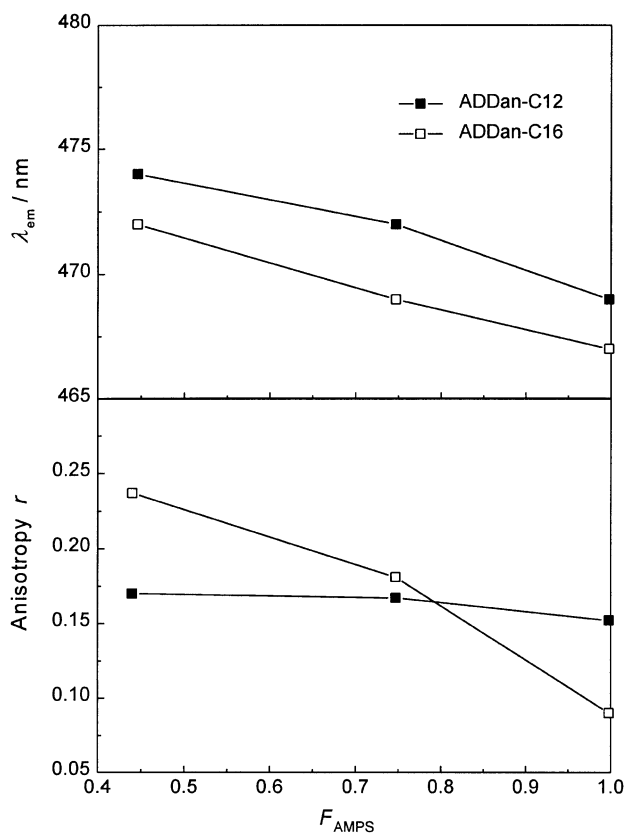
Fig. 4. AMPS mole fraction F_{AMPS} dependence of λ_{em} (upper panel) and fluorescence anisotropy r (lower panel) of ADDan–C12 (■) and ADDan–C16 (□) complex solid films.

Fig. 5. WAXD profiles of ADDan100–C16 (a), ADDan75–C16 (b) and ADDan45–C16 (c) complex solid films.

charge density, showing the same tendency as the final λ_{em} value varying with F_{AMPS} in aqueous solutions after surfactants aggregated as shown in the upper panel of Fig. 2. These observations seem to reveal a new regularity that the surfactant will form micelle-like aggregations of less polar on the oppositely charged polyelectrolyte with higher charge density in dilute solution, which will be retained in the solid complex. This may be attributed to the increase in the aggregation number with the charge density as reported by Anthony and Zana [9] in solution and by Zhou et al. [34] in collapsed gel. The λ_{em} value for the TICT emission of the ADDan solids without surfactants is about 510 nm [36], showing that the polarity surrounding the dansyl labels is greatly reduced by the formation of micelle-like aggregation by surfactant molecules. It is still wondered, however, whether the polarity in the micelle is so sensitive to a little increase in the number of aggregated surfactant molecules.

Fluorescence polarization was detected from the polyelectrolyte ADDan–surfactant C12 or C16 complex films and described by the emission anisotropy r as [49]

$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}}$$

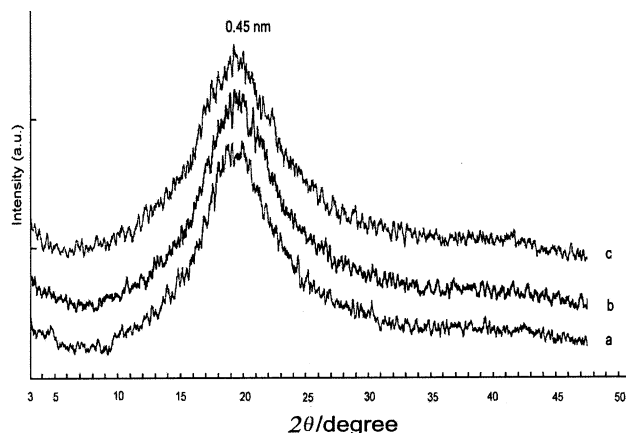where $I_{\parallel}$ and $I_{\perp}$ are fluorescent intensity obtained with the

analyzer parallel and perpendicular to the polarizer, respectively. r is a measure of chromophore mobility and the limiting value of r for dansyl groups is 0.325 in the system without molecule torsion and energy migration [50], The r-values for our complex films are also summarized in Fig. 4. The small r-values for the ADDan–C12 and C16 complexes manifest the high mobility of chromophore segments owing to the embedment of alkyl tails of surfactants. With increasing F_{AMPS}, r for ADDan–C16 complexes quickly decreases while that for ADDan–C12 complexes exhibits only slight incline. The reason for the charge density dependence of r is similar to that for the change in micelle polarity with the charge density as discussed above. The higher rate of r decreasing with F_{AMPS} for ADDan–C16 than that for ADDan–C12 indicates that the longer alkane tail in C16 is more effective than C12 in building hydrophobic aggregation surrounding the chromophore.

3.4. Structure of solid complexes

The WAXD diffractogram indicates that ADDan–C12 and ADDan–C16 samples are locally amorphous unstructured materials as shown in Fig. 5, for examples. The maxima at $2\theta = 19.7°$ ($s = 2.222 \text{ nm}^{-1}$) for all of our complexes correspond to the distance between alkane tails of the surfactant closely packed parallel to each other with the area of 0.203 nm^2 for each tail. Antonietti and Conrad [24] also reported a similar value for PAA–C12 complex and a reasonably larger value of 0.228 nm^2 for the complex with lipid tails [29].

SAXS profiles for ADDan–C16 and ADDan–C12 complexes are illustrated in Fig. 6. Owing to the low S/N ratio, only one narrow peak can be identified from each curve, corresponding to a long-range ordered structure analogous to a smectic phase with the long period d of 3.87 nm for C16 complexes and 3.04 nm for C12 complexes, respectively. According to the interpretation proposed by Antonietti et al. [25,28] we adopt the lamella
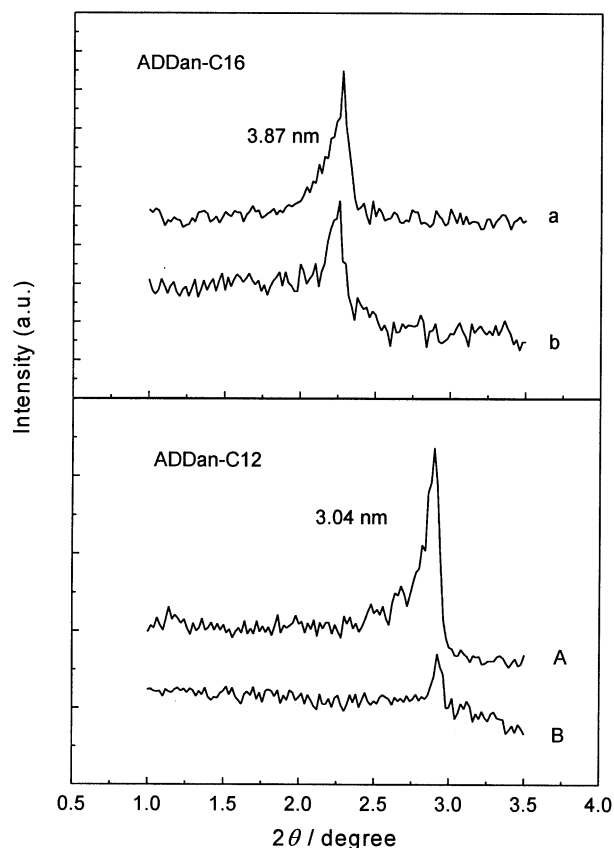
Fig. 6. SAXS profiles of ADDan100–C16 (a in upper panel), ADDan45–C16 (b in upper panel), ADDan100–C12 (A in lower panel) and ADDan45–C12 (B in lower panel) complex solid films.

structure for these polyelectrolyte–surfactant complexes as presented in Fig. 7. The lamella is a combination of layers of polyions and alkane tails and the long period is related to the length and orientation of alkane chains of surfactant. For a completely stretched alkane chain, the increment of one carbon is expected to increase about 0.125 nm in the long period if the chain is perpendicular to the lamella. One can estimate the thickness d_1 of the polyion layer by extrapolating d data at n carbons to n → 0. With the results of Antonitti et al. [51] and Ponomarenko et al. [52], $d_1 = 1.40$ nm is used for our complexes. Consequently, the thickness d_2 for the alkane tail layer is 2.47 nm for C16 complexes and 1.64 nm for C12 complexes, respectively. These values are
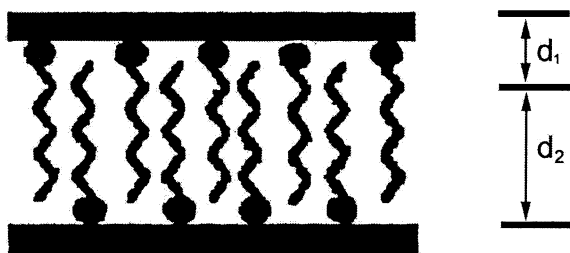

Fig. 7. Schematic representation of the lamella structure proposed for polyelectrolyte ADDan–surfactant complex solid films.

larger than those calculated from the carbon number of the corresponding alkanes, indicating the interpenetrating finger parking of the surfactant tails.

4. Concluding remarks

Dansyl label is an effective probe for studying the interaction of ionic surfactants CTAB and DTAC binding with oppositely charged polyelectrolyte P(AMPS-co-DMAA) in both states of solution and solid. The magnitude of cac is about 10^{-5} mol/l without obvious charge density dependence. The structure of solid P(AMPS-co-DMAA)–CTAB or –DTAC complexes can be reasonably interpreted by lamella stack with long period of 3.87 nm for CTAB complexes and 3.04 nm for DTAC complexes with assuming the alkyl tails of the surfactant perpendicular to the polymer chain. The most important finding of present work is that the surfactant will form the micelle-like aggregation of less polar and higher mobile on the oppositely charged polyelectrolyte with higher charge density in dilute aqueous solution, which can be retained in the solid complex.

Acknowledgements

References

[1] Wei Y-C, Hudson SM. JMS, Rev Macromol Chem Phys 1995;C35:15.
[2] Ober CK, Wegner G. Adv Mater 1997;9:17.
[3] Okuzaki H, Osada Y. Macromolecules 1994;27:502.
[4] Okuzaki H, Eguchi Y, Osada Y. Chem Mater 1994;6:1651.
[5] Hayakawa K, Kwak JCT. J Phys Chem 1982;86:3866.
[6] Hayakawa K, Kwak JCT. J Phys Chem 1983;87:506.
[7] Hayakawa K, Santerre J, Kwak JCT. Macromolecules 1983;16:1642.
[8] Shimizu T, Seki M, Kwak JCT. Colloids Surf 1986;20:289.
[9] Anthony O, Zana R. Langmuir 1996;12:1967.
[10] Chu D-Y, Thomas JK. J Am Chem Soc 1986;108:6270.
[11] Chandar P, Somasundaran P, Turro NJ. Macromolecules 1988;21:950.
[12] Almgren M, Hansson P, Mukhtar E, van Stam J. Langmuir 1992;8:2405.
[13] Hansson P, Almgren M. Langmuir 1994;10:2115.
[14] Hansson P, Almgren M. J Phys Chem 1995;99:16684.
[15] Hansson P, Almgren M. J Phys Chem 1995;99:16694.
[16] Morishima Y. Prog Polym Sci 1990;15:949.
[17] Winnik FM. Chem Rev 1993;93:587.
[18] Oliveira VAD, Tiera MJ, Neumann MG. Langmuir 1996;12:607.
[19] Magny B, Iliopoulos I, Zana R, Audebert R. Langmuir 1994;10:3180.
[20] Li Y-H, Chan L-M, Tyer L, Moody RTC, Himel M, Hercules DM. J Am Chem Soc 1975;97:3118.
[21] Chu B, Yeh F, Sokolov EL, Starodoubtsev SG, Khokhlov AR. Macromolecules 1995;28:8847.
[22] Okuzaki H, Osada Y. Macromolecules 1995;28:380.

[23] Chen L, Yu S, Kagami Y, Gong J, Osada Y. Macromolecules 1998;31:787.
[24] Antonietti M, Conrad J. Angew Chem Int Ed Engl 1994;33:1869.
[25] Antonietti M, Burger C, Effing J. Adv Mater 1995;7:751.
[26] Antonietti M, Kaul A, Thünemann A. Langmuir 1995;11:2633.
[27] Antonietti M, Henke S, Thünemann A. Adv Mater 1996;8:41.
[28] Antonietti M, Maskos M. Macromolecules 1996;29:4199.
[29] Antonietti M, Wenzel A, Thünemann A. Langmuir 1996;12:2111.
[30] Antonietti M, Radloff D, Wiesner U, Spiess HW. Macromol Chem Phys 1996;197:2713.
[31] Antonietti M, Neese M, Blum G, Kremer F. Langmuir 1996;12:4436.
[32] Yeh F, Sokolov EL, Khokhlov AR, Chu B. J Am Chem Soc 1996;118:6615.
[33] Sokolov EL, Yeh F, Khokhlov AR, Chu B. Langmuir 1996;12:6229.
[34] Zhou S, Burger C, Yeh F, Chu B. Macromolecules 1998;31:8157.
[35] Ren B, Gao F, Tong Z, Yan Y. Chem Phys Lett 1999;307:55.
[36] Tong Z, Ren B, Gao F. Polymer 2001;42:143.
[37] Ren B, Tong Z, Gao F, Liu X, Zeng F. Polymer 2001;42:2001.
[38] Gao F, Yan Y, Ren B, Tong Z. Chem J Chinese Univ 2000;21:976 (in Chinese).
[39] Gao F, Ren B, Yan Y, Tong Z. Acta Physico-Chim Sin 2000;16:450 (in Chinese).
[40] Sun Q, Wang C, Tong Z, Yan Y, Gao F, Liu X, Zeng F (in preparation).
[41] Wang C, Sun Q, Tong Z, Liu X, Zeng F, Wu S. Colloid Polym Sci (in press).
[42] Rotkiewicz K, Grellmann K, Grabowski ZR. Chem Phys Lett 1973;19:315.
[43] Rettig W. Angew Chem Int Ed Engl 1986;25:971.
[44] Chen H-L, Morawetz H. Macromolecules 1982;15:1445.
[45] Chen H-L, Morawetz H. Eur Polym J 1983;19:923.
[46] Kiefer JJ, Somasundaran P, Ananthapadmanabhan KP. Langmuir 1993;9:1187.
[47] Benrraou M, Zana R, Varoqui R, Pefferkorn E. J Phys Chem 1992;96:1468.
[48] Liu X, Tong Z, Hu O. Macromolecules 1995;28:3813.
[49] Monnerie L. The fluorescence polarization technique as a tool to investigate chain orientation and relaxation in bulk polymers. In: Winnik MA, editor. Photophysical and photochemical tools in polymer science. Dordrecht: Reidel, 1986.
[50] Hu Y, Horie K, Ushiki H, Tsunomori F, Yamashita T. Macromolecules 1992;25:7324.
[51] Antonitti M, Conrad J, Thünemann A. Macromolecules 1994;27:6007.
[52] Ponomarenko EA, Waddon AJ, Bakeev KN, Tirrell DA, MacKnight WJ. Macromolecules 1996;29:4340.