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Chaoyang Wang
Zhen Tong
Fang Zeng
Biye Ren
Xinxing Liu

Fluorescence study of chromophore labeled strong polyelectrolyte bound with oppositely charged surfactant

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C. Wang · Z. Tong (✉) · F. Zeng
B. Ren · X. Liu
Research Institute of Materials Science,
South China University of Technology,
Guangzhou 510640, China
E-mail: mcztong@scut.edu.cn
Tel.: +86-20-87112886
Fax: +86-20-87112886

Abstract Four strong polyelectrolyte samples of 2-(acrylamido)-2-methylpropanesulfonic acid (AMPS) and *N*,*N*-dimethylacrylamide (DMAA) were radically copolymerized with a single label of naphthalene or pyrene, with both labels and without label, containing about 40 mol % AMPS. Fluorescence nonradiative energy transfer (NRET) I_{Py}/I_{Np}, anisotropy r, I_1/I_3 and excimer emission I_E/I_M of pyrene labels were observed in dilute aqueous solutions with and without cationic surfactant of cetyltrimethylammonium bromide (CTAB). The overlap concentration was determined as 3 g/L from the appearance of intermolecular excimer. The variation of intra- and intermolecular NRET with total polyelectrolyte concentration showed that the charged chains preferentially interpenetrated each other rather than reduce their coil volume as their concentration beyond the overlap threshold. By binding with CTAB, the polyelectrolyte chain became more coiled as known from the reduced viscosity. The intramolecular NRET was dominant when [CTAB] $\leq 4\times10^{-5}$ M and then the intermolecular NRET occurred at higher CTAB concentrations with hydrophobic aggregation between CTAB tails bound on different polyelectrolyte chains. The CTAB concentration corresponding to the maxima of I_{Py}/I_{Np} just is equal to the AMPS monomer concentration, indicating the formation of 1:1 binding between surfactant and polyelectrolyte in very dilute solutions. Added salt of NaCl up to 0.1 M hardly affected the intramolecular NRET but affected the I_{Py}/I_{Np} value for the intermolecular NRET.

Keywords Polyelectrolyte · Surfactant · Binding · Conformation · Fluorescence · Nonradiative energy transfer

Introduction

Recently, the binding process and solid complex structure of ionic 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 ions onto the charged sites on the polymer chains and propagating aggregation of surfactant molecules to form a micelle-like structure in a highly cooperative manner. 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 alkyl tails and between hydrophobic moieties of the polymer and the surfactant tails. Solid polyelectrolyte–surfactant complexes are easily produced by precipitation from aqueous solution of polyelectrolytes and surfactants [2]. The most attractive finding from the polyelectrolyte–

surfactant complex is its highly ordered structure [3]. Another characteristic factor of the complex is the equivalently stoichiometric composition of the polyelectrolyte to the surfactant in respect of the charge [4].

When considering the polyelectrolyte–surfactant complex, one question is whether the 1:1 stoichiometric complex forms in dilute solution or during the precipitation process. We investigated the binding process of a cationic surfactant cetyltrimethylammonium bromide (CTAB) on a strong polyanion poly(2-(acrylamido)-2-methylpropanesulfonic acid) (PAMPS) with the relative excimer emission intensity I_E/I_M of a cationic pyrene probe 1-pyrenemethylamine hydrochloride [5, 6]. With increasing CTAB concentration, the I_E/I_M first increases, reaches a maximum, and then decreases to zero, where the CTAB concentration is exactly equal to the PAMPS concentration. This fact manifests that the 1:1 stoichiometric binding is formed between CTAB and PAMPS in dilute aqueous solution provided the surfactant concentration is beyond its critical aggregation concentration (CAC), which is about two orders of magnitude lower than the critical micelle concentration (CMC) and is much lower than the precipitation concentration [5].

Another question is about the change in polyelectrolyte chain conformation and aggregation during binding with surfactant in dilute solution, which concerns the formation of the ordered structure in the solid complex. Quasielastic light scattering has been adopted to investigate the conformation and association of polyelectrolytes induced by hydrophobic modification and binding with oppositely charged surfactants [7, 8, 9]. Special care should be taken in interpreting the relaxation data due to the presence of internal and rotational modes besides the translational diffusion [7, 8]. On the other hand, fluorescence techniques are powerful in investigating the polyelectrolyte–surfactant binding [10, 11]. The vibrational fine structure of pyrene probe or label has been also used to detect the conformation change for the polyelectrolyte-surfactant complex [12, 13].

The efficiency of nonradiative energy transfer (NRET) between the two chromophores of energy donor and energy acceptor depends sensitively on their separated distance [14]. Therefore, NRET has been widely used to study the binding interaction and hydrophobic association in polyelectrolyte–surfactant aqueous solutions. Schild and Tirrell [15] found, by the NRET technique, that there was a weak binding between neutral polymer and ionic surfactant derivative of pyrene in aqueous solution. Itaya et al. [16] determined the CAC value of sodium 1-octanesulfonate (Na^+OcS^-) bound to poly(allylammonium) chloride ($PAAH^+Cl^-$) by the energy transfer from 2-naphthalenesulfonate ion (2-NpS$^-$) to 1-pyrenesulfonate ion (1-PyS$^-$). Hayakawa et al. [17] investigated the solubility of the dyes in the surfactant micelle bound on polyelectrolyte by NRET between the dyes. Morishima et al. [7] used NRET of doubly labeled polyelectrolytes with hydrophobic modification to probe the chain conformation change in binding with mixtures of neutral surfactant and ionic surfactants.

Yamamoto et al. labeled the hydrophobically modified strong polyelectrolyte chain with fluorescent donor naphthalene or/and acceptor pyrene, respectively and observed the intramolecular hydrophobic association of doubly labeled polymers with the NRET in dilute solutions [18]. In this work, we are attempting to reveal the conformation change of strong polyelectrolyte with increasing concentration from dilute to semi-dilute range and to observe the occurrence of intermolecular aggregation of strong polyelectrolytes purely induced by hydrophobic association of the bound oppositely charged surfactants. For these purposes, the similar intramolecular and intermolecular NRET techniques and viscometry will be utilized with naphthalene and/or pyrene singly and doubly labeled sulfonate copolymers.

Materials and methods

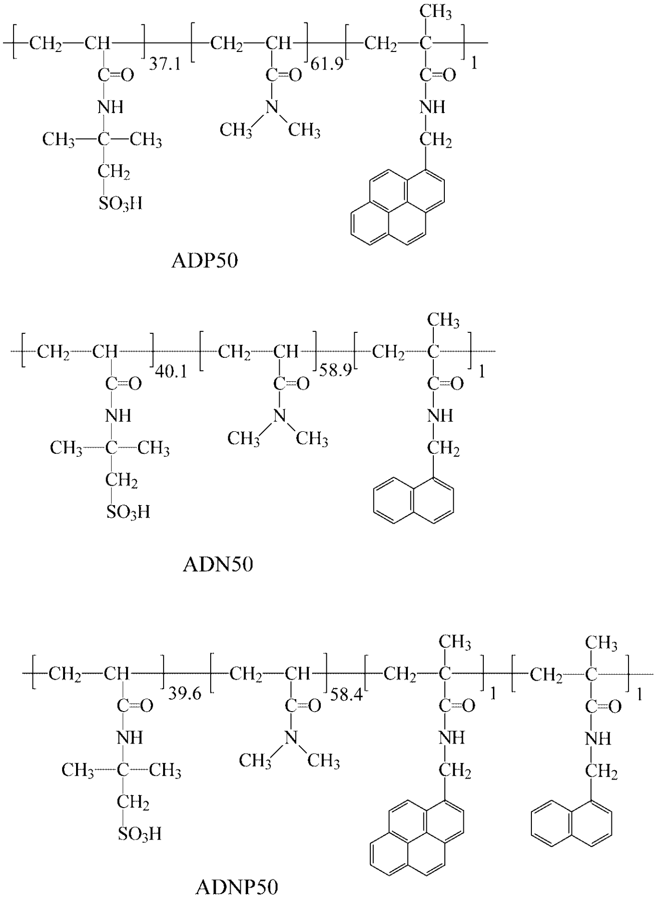
Materials and copolymers

Fluorescence label monomers *N*-(1-naphthylmethyl)methacrylamide (NpMAm) and *N*-(1-pyrenylmethyl)methacrylamide (PyMAm) were synthesized in our laboratory following the procedure of Refs [19] and [20], respectively, and confirmed with ^{1}H-NMR spectra. 2-Acrylamido-2-methylpropanesulphonic acid (AMPS, Fluka) was used without further purification. *N,N*-Dimethylacrylamide (DMAA, Kohjin, Japan) was distilled before used. Cetyltrimethylammonium bromide (CTAB) was recrystallized from ethanol. 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.

Three naphthalene or/and pyrene labeled copolymers of AMPS and DMAA, referred to as ADN50, ADP50, and ADNP50, respectively (Scheme 1), and one copolymer of AMPS and DMAA without fluorescence labels as AD50 were polymerized in dimethylformamide (DMF) solution initiated by 2,2'-azobis(isobutyronitrile) (AIBN). The total monomer concentration was 0.5 M 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 a 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 chromophore content in the samples was verified by UV absorbance. GPC measurement was carried out with a Waters GPC instrument at 40 °C using 0.1 M of Na_2SO_4 aqueous solution as the elution and narrowly distributed PEO as the standard. The results are listed in Table 1.

Measurements

For measuring the fluorescence spectra of naphthalene and/or pyrene labeled polyelectrolyte in aqueous solution with surfactant,


ADP50

ADN50

ADNP50

Scheme 1. Schematic representation of the fluorescence labeled polyelectrolyte samples

concentrated solutions of the copolymer and CTAB were prepared, respectively. Then, the desired amount of concentrated solutions were mixed in a volumetric flask and diluted to test concentrations.

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, then stirred for 1 min prior to measurement. All measurements were performed on air-equilibrated solutions at 25 °C. The excitation wavelength was 290 nm or 340 nm as indicated. The energy transfer efficiency was characterized by the emission intensity ratio $I_{\mathrm{Py}}/I_{\mathrm{Np}}$ for pyrene at 396 nm to naphthalene at 338 nm. I_1/I_3 is the emission intensity ratio for the first peak (375 nm) to the third peak (386 nm) and $I_{\mathrm{E}}/I_{\mathrm{M}}$ is the emission intensity ratio at 490 nm for the excimer to 395 nm for the monomer of pyrene. The fluorescence anisotropy ratio r is defined as:

$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} \quad (1)$$

where $I_{\parallel}$ and $I_{\perp}$ are emission intensities measured parallel and perpendicular to the polarizing direction of excitation, respectively.

For measuring the viscosity of polyelectrolyte–surfactant solutions, concentrated aqueous solutions of ADNP50 and CTAB were prepared and filtered through a sintered glass filter G2, respectively. Then, desired amount of concentrated solutions were mixed in a volumetric flask and diluted to the test concentration. The flow times of solution t and water t_0 were measured at 25(±0.05) °C using a Ubbelohde viscometer and the reduced viscosity η_{sp}/C was evaluated as $\eta_{\mathrm{sp}}/C = (t - t_0)/(t_0 C)$, where C was the polyelectrolyte concentration and kept at 0.0515 g/L for all viscosity measurements.

Results and discussion

Fluorescence spectra of labeled polyelectrolytes with concentration increase

Excimer can be induced by intramolecular or intermolecular aggregation of the chromophore labels depending on the labeled polymer concentration. In very dilute solution, excimer only forms intramolecularly so that $I_{\mathrm{E}}/I_{\mathrm{M}}$ is independent of the polymer concentration. When the concentration of labeled polymer is beyond the overlap concentration, intermolecular excimer appears in addition to the intramolecular excimer. This results in an increase in $I_{\mathrm{E}}/I_{\mathrm{M}}$ with increasing the concentration of labeled polymer, which can be used as an indication of the overlap threshold in the polymer solution.

The variation of $I_{\mathrm{E}}/I_{\mathrm{M}}$ as a function of concentration of singly labeled polyelectrolyte ADP50 in water is shown in Fig. 1. As expected, $I_{\mathrm{E}}/I_{\mathrm{M}}$ does not change at low concentration and then increases obviously when the ADP50 concentration rises up to 3 g/L due to the formation of intermolecular excimer. It indicates that different ADP50 molecular chains begin to interpenetrate each other beyond this concentration. This overlap concentration of ADP50 determined by the labeled pyrene excimer is larger than that of sodium polystyrene sulfonate with molecular weight of 10^5, the latter is 0.245 g/L [21]. The cause is the difference in their molecular weight.

In order to follow the process of the conformation change of polyelectrolyte with increasing concentration,

Table 1. Composition and molecular weight of fluorescence labeled polyelectrolyte samples

sample	$M_{\mathrm{w}}/10^4$	$M_{\mathrm{w}}/M_{\mathrm{n}}$	Elemental analysis (wt%)			F_{AMPS}/mol %	NpMAm/mol%	PyMAm/mol %
			N	C	H			
ADN50	6.0	3.06	9.84	44.20	8.44	40.1	1	0
ADP50	4.7	2.28	10.07	44.75	8.47	37.1	0	1
ADNP50	7.0	2.48	9.88	45.42	9.29	39.6	1	1
AD50	7.1	2.78	–	–	–	–	0	0

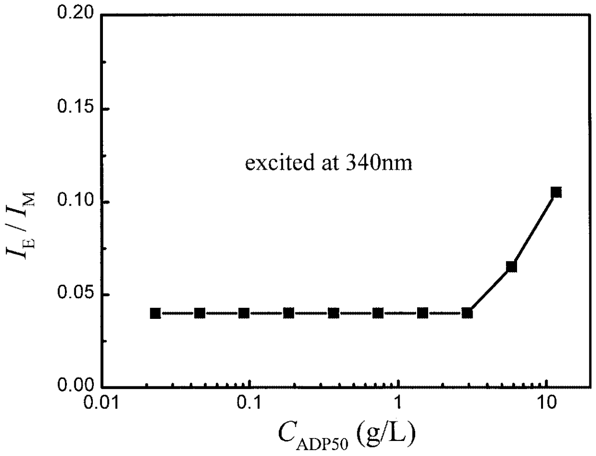


Fig. 1. The variation of I_E/I_M of pyrene labels as a function of concentration of ADP50 in water

we added nonlabeled polyelectrolyte AD50 in the solution of doubly labeled sample ADNP50 or the mixture solution of singly labeled samples ADN50 and ADP50. The concentration of labeled samples was fixed at about 0.05 g/L, much lower than the overlap concentration, where no intermolecular NRET can be observed as indicated by Fig. 1. The NRET efficiency from naphthalene to pyrene at different total concentrations of polyelectrolyte is illustrated in Fig. 2A by I_{Py}/I_{Np}. One can see that the relative intensities of I_{Py}/I_{Np} for both the intramolecular NRET of ADNP50 and the intermolecular NRET of ADP50 and ADN50 are constants when the total polyelectrolyte concentration increases from 0.05 g/L to 10 g/L, crossover the overlap concentration. This fact means that the contacting degree of the labeled polyelectrolyte chains does not increase over the tested polymer concentration range. Therefore, the interpenetration of polyelectrolyte chains would be enhanced as the total concentration is increased beyond the overlap threshold. Otherwise, the spatial volume of polyelectrolyte chains should be reduced, resulting in the increase in I_{Py}/I_{Np}. In other words, the increase in polyelectrolyte concentration causes mutual interpenetration of charged chains rather than contraction of the individual chain molecules.

If the excitation wavelength is at 340 nm, only the emission spectra of pyrene can be observed even there is naphthalene in the solution, because naphthalene cannot be excited at this wavelength. The intensity ratio I_1/I_3 of the first to the third emission of pyrene is known to be sensitive to the local polarity of its microenvironment, which becomes lower in less polar media [22]. Fig. 2B depicts the I_1/I_3 variation with the total concentration of the polyelectrolyte solutions at the constant concentration of doubly labeled ADNP50 or the mixture of singly labeled ADN50 and ADP50. I_1/I_3, like I_{Py}/I_{Np}, is kept constant at 1.53 for ADNP50 and 1.42 for the mixture

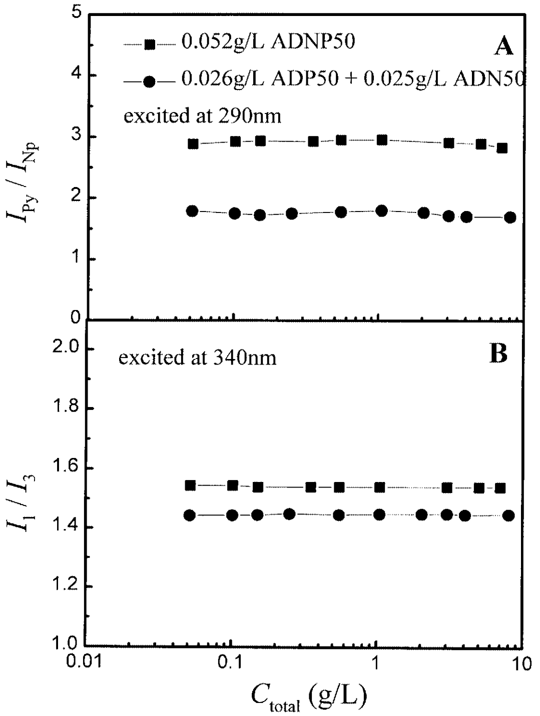


Fig. 2. A The intensity ratio I_{Py}/I_{Np} of pyrene emission to naphthalene emission corresponding to NRET excited at 290 nm; **B** the intensity ratio I_1/I_3 of the first to the third emission peaks of pyrene excited at 340 nm as a function of total concentration of polyelectrolytes in the aqueous solutions containing 0.052 g/L ADNP50 or the mixture of 0.025 g/L of ADN50 and 0.026 g/L of ADP50

solutions over the entire total concentration range of polyelectrolyte. These results suggest that the local polarity surrounding pyrene labels does not change when the concentration of polyelectrolyte solution rises from dilute region to semidilute region. This is also an indication that no molecular chain contraction occurs during the concentration increase.

Owing to the strong electrostatic repulsion, polyelectrolyte chains usually take an extended conformation and exist separately in dilute solution. As the concentration is increased beyond the overlap threshold, the extended chains preferentially interpenetrate each other rather than shrink their spatial volume. This finding appears to be the origin of the results in Figs. 1 and 2.

Fluorescence spectra of labeled polyelectrolytes with CTAB

Ionic surfactant binding on oppositely charged polyelectrolytes and forms micelle-like aggregation due to the electrostatic attraction and hydrophobic interaction. The fluorescence spectra of chromophore labels on polyelectrolytes are adopted to monitor the conformation change during binding. The ratio I_{Py}/I_{Np} corresponding to NRET in 0.052 g/L of doubly labeled ADNP50 (curve *A*) and in the mixture of 0.025 g/L of naphthalene labeled ADN50 and 0.026 g/L of pyrene labeled ADP50 (curve *B*) is plotted in Fig. 3 as a function of CTAB concentration. The I_{Py}/I_{Np} of ADNP50 (curve *A*) increases gradually at low CTAB concentration and then sharply when [CTAB] is beyond 1×10^{-5} M. It reaches a maximum at [CTAB] = 1.5×10^{-4} M and then begins to decrease. According to the result of excimer formation for the cationic pyrene probe bound on AMPS polymer, the CAC value of CTAB with the polyelectrolyte is 10^{-5} M [5]. At CTAB concentrations lower than the CAC, a few CTAB molecules binding on the polyelectrolyte induce a slight change in the polyelectrolyte conformation. Above the CAC, the polyelectrolyte-bound surfactant micelle begins to form and the polyelectrolyte chains become curlier due to neutralizing the charges and increasing the hydrophobicity by binding surfactants. Consequently, intramolecular NRET of doubly labeled ADNP50 is enhanced. It is interesting that the I_{Py}/I_{Np} reaches its maximum at the CTAB concentration of 1.5×10^{-4} M, which equals the molar concentration of sulfonate groups in ADNP50 sample estimated from the F_{AMPS} data in Table 1. Further added CTAB will be dispersed in the solution and isolate the chromophore labels on the polyelectrolyte, causing the decrease in I_{Py}/I_{Np}. This is an evidence for the formation of stoichiometrically equivalent aggregation of polyelectrolyte and surfactant at concentrations much lower than precipitation. We have also found the 1:1 PAMPS-CTAB binding in dilute solution from the disappearance of I_E/I_M of a cationic probe [5].

The curve *B* in the same figure, quite different from the curve *A*, depicts a low constant as [CTAB] ≤ 4×10^{-5} M, which indicates that the NRET from the naphthalene on ADN50 to the pyrene on ADP50 remains at a lower level, implying segregation of polyelectrolyte chains within this [CTAB] range. When [CTAB] > 4×10^{-5} M, an increase in I_{Py}/I_{Np} can be observed, suggesting the occurrence of intermolecular overlap. According to the facts described in the preceding section, the polyelectrolyte concentration of 0.05 g/L is much lower than its overlap concentration. Therefore, this intermolecular overlap is induced by the hydrophobic interaction between the tails of CTAB bound on different polyelectrolyte chains. The I_{Py}/I_{Np} value also gets to the maximal value at [CTAB] = 1.5×10^{-4} M, where the stoichiometrically equivalent aggregation of polyelectrolyte–surfactant is formed. Excess CTAB will be dissolved in solution and isolate the chromophore labels on the polyelectrolyte, resulting in a decrease in I_{Py}/I_{Np}. It should be pointed out that, in ADNP50 solution at higher CTAB concentrations, the intermolecular NRET also contributes to the I_{Py}/I_{Np} increase as the case of curve *B*, but the intramolecular NRET is dominant.

In Fig. 4, I_1/I_3 and the fluorescence anisotropy *r* of pyrene labels on doubly labeled ADNP50 of 0.052 g/L aqueous solution are plotted against the CTAB concentration. The I_1/I_3 value is almost constant at 1.53 as [CTAB] ≤ 1×10^{-5} M, which is the CAC of CTAB. Above the CAC, I_1/I_3 decreases gradually with the increase of [CTAB] and achieves a low value of 1.46 as [CTAB] > 1.5×10^{-4} M. These I_1/I_3 values are comparable with those in Fig. 2B without CTAB. This degree of I_1/I_3 reduction means that the pyrene label does not enter the micelle-like aggregation of surfactant bound on the polyelectrolyte (if it does, I_1/I_3 should be about 1.25 [13]) and this decrease of I_1/I_3 is due to the increasing hydrophobicity of the local environment surrounding

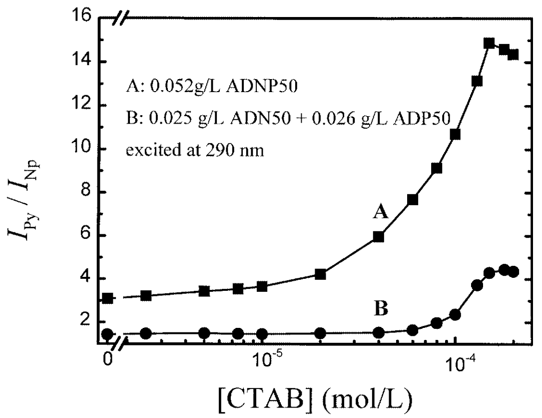


Fig. 3. The ratio I_{Py}/I_{Np} in 0.052 g/L of doubly labeled ADNP50 (curve *A*) and in the mixture of 0.025 g/L of naphthalene labeled ADN50 and 0.026 g/L of pyrene labeled ADP50 (curve *B*) is plotted as a function of CTAB concentration

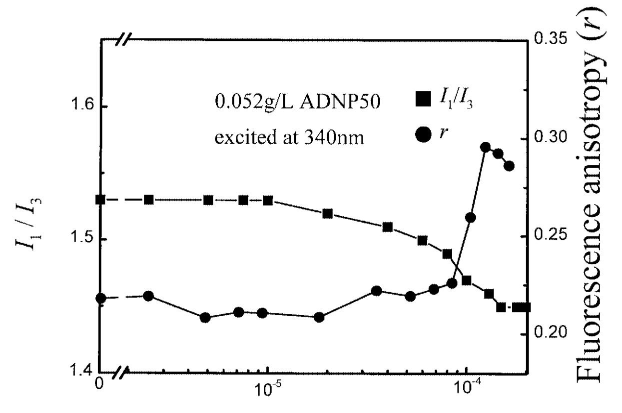


Fig. 4. I_1/I_3 and the fluorescence anisotropy *r* of pyrene labels on doubly labeled ADNP50 of 0.052 g/L aqueous solution are plotted against the CTAB concentration

the polyelectrolyte chains with binding CTAB. Morishima et al. considered that the pyrene label was prevented from penetrating into the hydrophobic core of the micelle with the constraint exerted by the polymer chain [23].

From Fig. 4 we can see a rather abrupt increase in fluorescence anisotropy r at CTAB concentration around 1.0×10^{-4} M and a maximum at [CTAB] = 1.5×10^{-4} M. If the microenvironment viscosity around pyrene increases, the depolarization of the probe will be restricted, inducing an increase in the fluorescence anisotropy r. The I_1/I_3 data suggest that the pyrene label does not enter the surfactant micelle bound on the polyelectrolyte. So that the increase in the fluorescence anisotropy r should be attributed to the intermolecular aggregation of surfactant-bound polyelectrolytes due to the hydrophobic interaction between the CTAB tails.

The conformational change of macromolecules in dilute solutions can be monitored by the reduced viscosity η_{sp}/C [18]. In Fig. 5, the reduced viscosity of 0.0515 g/L of ADNP50 aqueous solution is plotted against the CTAB concentration. With increasing CTAB concentration, the reduced viscosity first decreases gradually and then reaches a constant value at the CTAB concentration of 1×10^{4} M, where 1:1 polyelectrolyte–surfactant binding is formed. As discussed with the curve A in Fig. 3, the binding of ionic surfactant CTAB on the oppositely charged polyelectrolyte in dilute solution neutralizes the charges on the polyelectrolyte and makes the polyelectrolyte chain more hydrophobic, consequently more coiling with a reduced radius of gyration. This is the origin of decrease in the reduced viscosity with binding CTAB. The intermolecular aggregation of CTAB bound polyelectrolyte appears at higher CTAB concentrations as shown by the curve B in Fig. 4, but this phenomenon is not observed from the reduced viscosity (If it was the case, the reduced viscosity would increase). The possible cause seems to be that the association force between the surfactant tails in this aggregation is too weak to bear the flow shearing. Zana and Talmon also reported the decrease in the specific viscosity of poly(disodium maleate-co-hexadecyl vinyl ether) (PS16) aqueous solution with increasing sodium dodecyl sulfate (SDS) concentration [24].

I_{Py}/I_{Np} is plotted against CTAB concentration in Fig. 6 for aqueous solutions with different ADNP50 concentrations. The tendency of all the curves is the same. I_{Py}/I_{Np} increases very slowly at first, then sharply with increasing CTAB concentration, finally reaches maximum and then decreases slowly. Both CTAB concentrations where I_{Py}/I_{Np} begins to increase sharply and where I_{Py}/I_{Np} reaches the maximum increase with the increase of ADNP50 concentration because more surfactant molecules are required to occupy increased ionic sites on the polyelectrolyte. The CTAB concentrations where I_{Py}/I_{Np} reaches its maximum are just equal to the charge concentration of the polyelectrolyte, indicating the formation of 1:1 binding of polyelectrolyte and surfactant.

Effect of Added Salt

Added salt should shield the electrostatic interaction between polyelectrolyte and surfactant, leading to a reduction in the binding force. We investigated the added salt effect on the intramolecular and intermolecular NRET of polyelectrolytes bound with CTAB as shown in Figs. 7 and 8, respectively. It is unexpected that all the curves in Fig. 7 for different concentrations of NaCl overlap that for [NaCl] = 0. This clearly means that added salt has no effect on the intramolecular NRET of labeled polyelectrolyte with surfactant. At the same

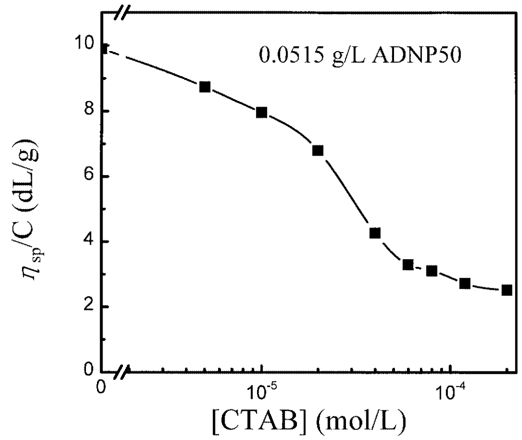


Fig. 5. The reduced viscosity η_{sp}/C of 0.0515 g/L of ADNP50 aqueous solution is plotted against the CTAB concentration

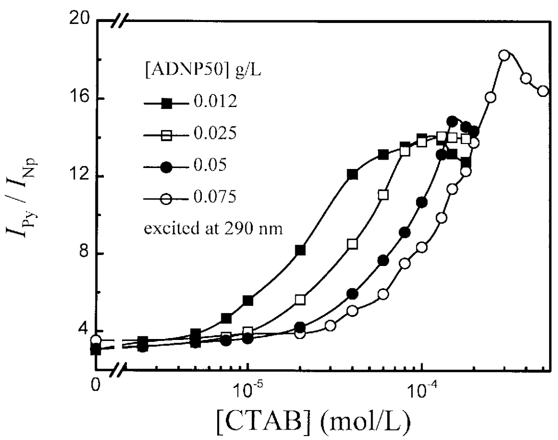


Fig. 6. I_{Py}/I_{Np} is plotted against CTAB concentration for aqueous solutions at different ADNP50 concentrations

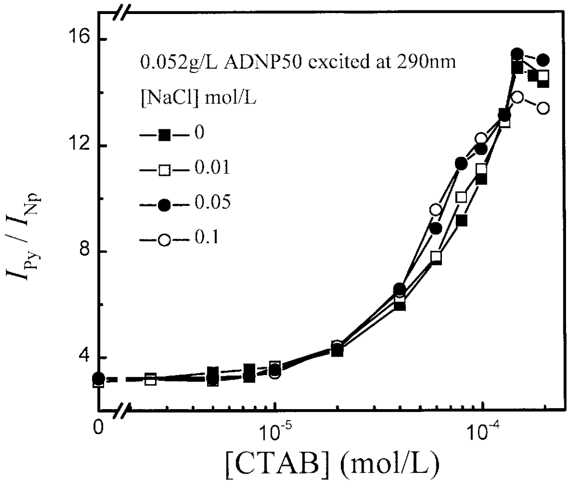


Fig. 7. I_{Py}/I_{Np} of 0.052 g/L of ADNP50 as a function of CTAB concentration at different NaCl concentrations

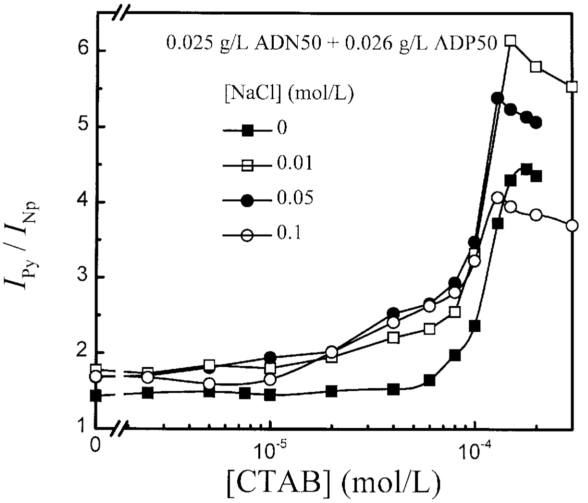


Fig. 8. I_{Py}/I_{Np} of 0.025 g/L of ADN50 and 0.026 g/L of ADP50 mixture as a function of CTAB concentration at different NaCl concentrations

time, NRET in the aqueous solutions of ADN50 and ADP50 mixture with different NaCl concentrations demonstrates that the salt concentration has no effect on the shape of the curves and the CTAB concentration where I_{Py}/I_{Np} reaches the maximum as shown in Fig. 8. We have no appropriate explanation for these unusual phenomena at present.

On the other hand, the maximal value of I_{Py}/I_{Np} changes with the NaCl concentration. A small amount of NaCl (≤ 0.01 M) can enhance the hydrophobic interaction between CTAB tails bound on different polyelectrolyte chains and result in a higher value of the maximum of I_{Py}/I_{Np} due to stronger intermolecular NRET. On the contrary, a large amount of NaCl (> 0.01 M) will weaken the hydrophobic interaction, leading to a lower value of the maximum of I_{Py}/I_{Np}. Yamamoto et al. found that adding NaCl promoted the hydrophobic association for hydrophobically modified PAMPS in aqueous solution [18]. Beyer and Nordmeier reported that at low salt concentration the complexes of poly((dimethylino)ethylene(dimethylimino)methylene-1, 4-phenylenemethylene dichloride) with poly(acrylic acid) and poly(methacrylic acid) formed, and at high salt concentration the complexes redissociated into their single strands and attributed these phenomena to the salting in and salting out effect for hydrophobic aggregation [25]. The present behavior is also originated from the effect of salting in and salting out, because a polyelectrolyte chain changes into a hydrophobic macromolecule after binding with surfactants completely.

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